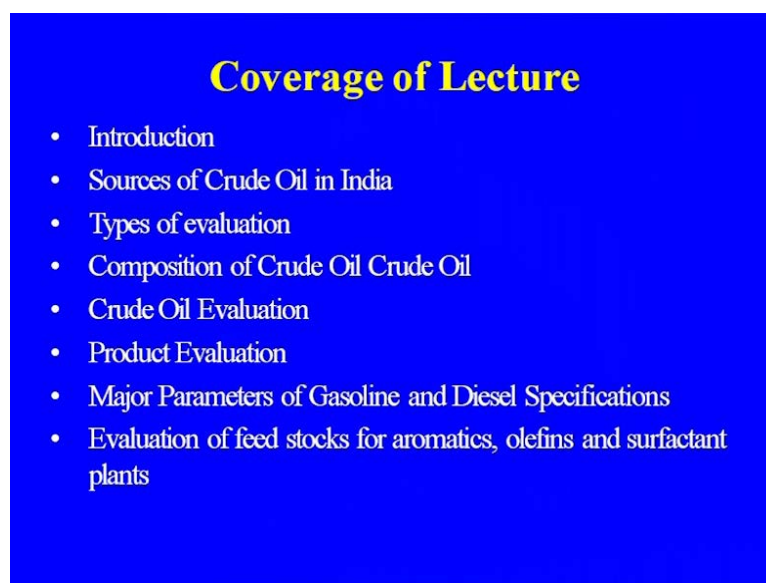


**Chemical Technology**  
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**Module - 6**  
**Petroleum Refinery**  
**Lecture - 2**  
**Evaluation of Crude Oil Petroleum Products and Apetrochemicals**

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**Coverage of Lecture**

- Introduction
- Sources of Crude Oil in India
- Types of evaluation
- Composition of Crude Oil Crude Oil
- Crude Oil Evaluation
- Product Evaluation
- Major Parameters of Gasoline and Diesel Specifications
- Evaluation of feed stocks for aromatics, olefins and surfactant plants

We are discussing module 6 of the chemical technology course organic and in module 1, in lecture 1 we discussed about the various development that has taken place in the petroleum refinery. What is the crude oil quality? How it is varying availability of the crude oil? And then the changing's injuring the refinery and what are the various developments and what, what will be the concept of the future refinery? And if you see the there has been lot of variation while refining the crude oil quality from the sweet to sour crude and so the evaluation of the crude oil that is very important part in case of the petroleum refinery.

And for the beating the information about the various products which will be getting; what will be the quality of the product. So, evaluation of the crude oil petroleum products and because these raw materials we as using in the petro chemical complexes especially kerosene or the naphtha for catalytic forming or the naphtha for the cracking.

So, requirement is different all we will be discussing the importance of the evaluation of the crude oil in this area.

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## Introduction

- Crude oil is complex mixture of various types of hydrocarbon containing traces of impurities like sulphur compounds, metals, nitrogenous compound, naphthenic acid. Crude oil quality varies in composition and properties.
- Crude oil is becoming more and more heavier and sour
- Crude oil characteristic have large impact on the processing of crude oil.

The coverage will be the introduction sources of the crude oil in India, types of the evaluation, Composition of the crude oil, crude oil evaluation then the product evaluation. Major parameter of the gasoline and diesel specification because as I discuss in the lecture 1 there has been continuous change in the requirement of the gasoline and diesel specification then evaluation of the feedstock for aromatics olefins and the surfactant plant l a b, where we are using the kerosene as a raw material.

Now the let us discuss the why the importance of the crude oil evaluation is there. Crude oil is complex mixture of various type of the hydrocarbon although it is you can see the c and s but, containing a large number of the hydrocarbons and it is reported it may be around 1000 hydrocarbons that may be present and along with these traces of the impurities like sulfur compound, metal, nitrogenous compound and naphthenic acid. All these impurities are also present.

So crude oil quality as I discuss in the lecture 1 also that is varying in composition and properties from 1 well to even 1 well to another. Well from one region to another region, from one country to another country. So, this is the changes as we are using the crude oil both the indigenous and the imported in other part of the world, also they are using the indigenous and the imported crude. So, the evaluation of the crude oil that is becoming

and that is more important just to have the exact idea and knowing the blending composition of the crude oil. So, crude oil is becoming more and more heavier and sour as I told you and so, the quality of the crude oil, evaluation of the quality of the crude oil, base of the crude oil that is very important. Crude oil characteristic have large impact on the processing of the crude oil because whatever the products we will be getting the quality of the products, we will be getting from the refinery that will be totally dependent on the quality of the crude oil which is being processed.

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### **Introduction**

- There are basically four type of crudes available around the world.
- Light sweet (30-400 API, sulphur <0.5)
- Light sour( 30-400API, sulphur<1.5)  
Heavy sour(15-300 API 1.5 , sulphur< 3.1%)
- Extra heavy(<150 API & sulphur >3% )
- Source:Ganesh et al. 2011

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### **Introduction**

- As both imported and indigenous crude from various oil field is being processed, blending of crude is very common practice in the refineries.
- Crude oil evaluation is very important
- With advancement of technologies the requirement and scope of evaluation is also changing

These are the basically four type of the crudes available around the world that is the light sweet. This is the API sulfur content is low lighter sour means the sulfur content is slightly higher than the light sweet. But still it is on higher sour 1 point 5 and the API is around same. Then the heavy this is 15 to 300 API 1 point 5 because you see the API as I told you a API is just reverse of the density . So, more API means lighter and the higher API means low API means it is heavier.

So, sulfur content 3percent extra heavy, where it can be as high as 3 percent of the sulfur as both imported and indigenous crude from various oil fields is being processed. Blending of the crude is very common practice in the refineries all the refineries. Now even the refineries which we are totally depend upon the Assam good they are using the imported crude, because number of refinery even Assam that has come. So, how to meet that requirement and the increase in the capacity so they are using the indigenous and the imported crude?

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### **Sources of Crude Oil in India**

Indigenous and imported crude oils are being process in India for production of gasoline, diesel, kerosene and lube oil, wax and feed stock for petrochemical industry like naphtha, kerosene etc.

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## Sources of Crude Oil in India

Sources of Indigenous Crude: Assam ; Bombay high and satellite fields, North Gujarat & Ankhleshwar, KG basin-Rava, Cauvery basin, Rajasthan crude

Sources of Imported Crude: Arab mix, Lavan blend, Upper Zakum, Iran mix; Dubai, Kuwait crude, Suez mix, Zeit Bay, Quaiboe, Miri light, Bonny light

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## Types of Evaluation

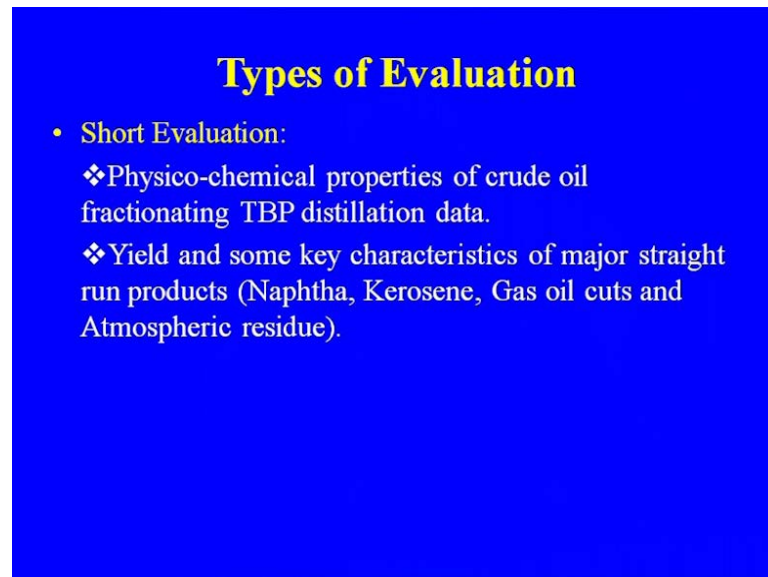
Preliminary Assay:

- ❖ Properties of crude oil.
- ❖ Distillation data generated through a semi fractionating or fractionating distillation.

So, crude oil evaluation is very important with the advancement of the technology the requirement and the scope of the evaluation is also changing. Because, now more sophisticated energetic instruments are available and you can have the better idea of the quality of the crude. As I told you the indigenous and imported crude oils that is being processed in India for production of the gasoline, diesel, kerosene and lube oil wax and feed stock for petrochemical industry like naphtha and kerosene sources of the indigenous crude. I discuss earlier also in lecture 1 these are the various sources from where VO especially the Assam and Bombay high crude in north Gujarat, Ankhleshwar

Rava and the now the Rajasthan crude. But, only problem in case of the Rajasthan crude is heavier, more sulfur content. These are the sources of the imported crude Arab mix Lavan blend upper Zakum Iran mix Dubai, Kuwait and Sue Zeit. These are all from the various sources we are getting the crude oil then, the types of the evaluation.

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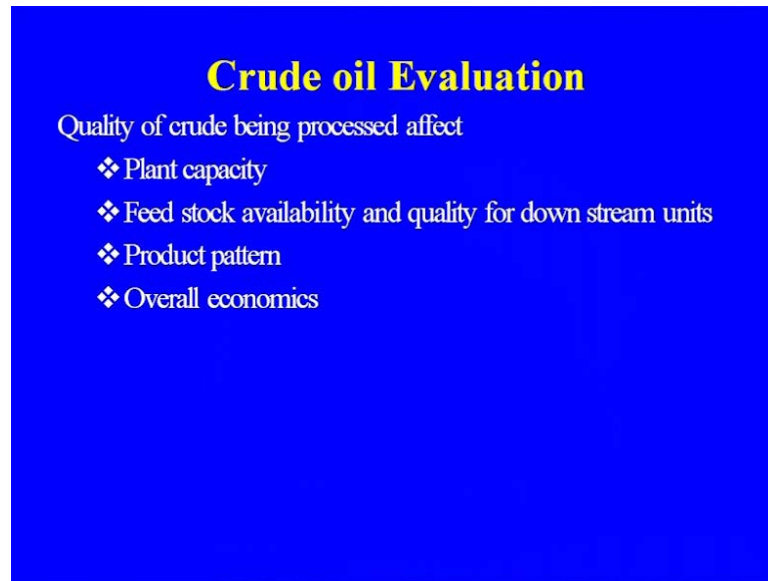
**Types of Evaluation**

- **Short Evaluation:**
  - ❖ Physico-chemical properties of crude oil fractionating TBP distillation data.
  - ❖ Yield and some key characteristics of major straight run products (Naphtha, Kerosene, Gas oil cuts and Atmospheric residue).

The preliminary assay is the properties of the crude oil distillation. Data is generated through a semi fractionating or the fractionating distillation. We are having these STM distillations and your TBP distillation. So, various type of the distillation equipments are available for evaluating the quality of the crude oil short evaluation that is around routine basis we are doing the physico-chemical properties of the crude oil fractionating TBP distillation data to boiling point distillation data.

Yield and some key characteristics of the major straight run products naphtha, kerosene, gas oil cuts and atmospheric residue. So, detailed evaluation of physico-chemical properties. Already we discussed these are the things that is required, and what is the impact? Why we are doing the crude oil impact quality of the crude oil being processed affect the plant capacity? Because out of the output of the product whether we are getting more lighter or more heavier product that will totally depend upon the quality of the crude oil or the product which we are getting that will contain high sulfur or the low sulfur. How much actually desulfurization that is needed everything that will depend upon the quality of the crude.

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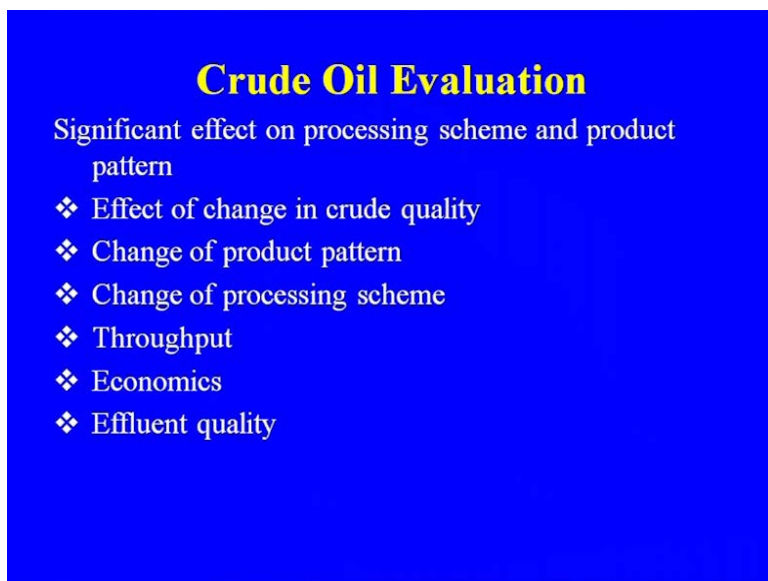


**Crude oil Evaluation**

Quality of crude being processed affect

- ❖ Plant capacity
- ❖ Feed stock availability and quality for down stream units
- ❖ Product pattern
- ❖ Overall economics

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**Crude Oil Evaluation**

Significant effect on processing scheme and product pattern

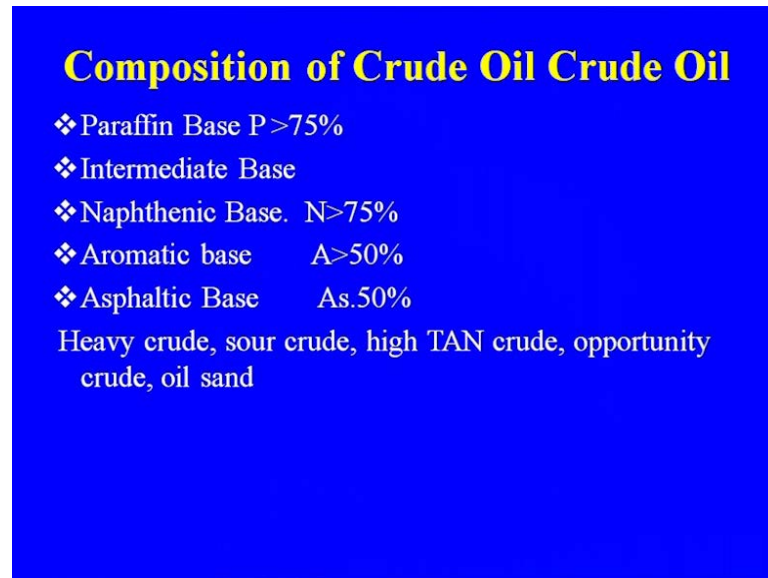
- ❖ Effect of change in crude quality
- ❖ Change of product pattern
- ❖ Change of processing scheme
- ❖ Throughput
- ❖ Economics
- ❖ Effluent quality

So, the plant capacity feed stock availability and the quality for downstream units product pattern and overall economics of because, as I told you now the entire refinery they are going just to meet the sulfur extender of the SO<sub>2</sub> extender for the fuel. And so to meet that stringent condition definitely more hydro desulfurization that will be needed significant effect on processing scheme and the product pattern effect of change in the crude quality change of the product pattern that we are getting from the refinery that is because of the variation in the crude oil quality change of the processes scheme will have to go for the some of the more treatment pre treatment units through output economics



and the effluent quality because this is also very important because if you are having more sour gases chances of the contamination of the waste product that is more and more as i told you the may lecture one that the composition of the crude oil.

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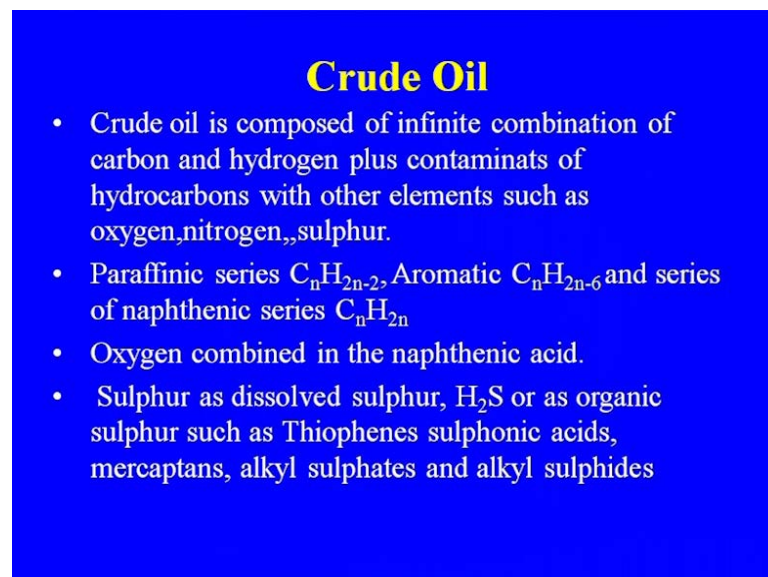


**Composition of Crude Oil**

- ❖ Paraffin Base P > 75%
- ❖ Intermediate Base
- ❖ Naphthenic Base. N > 75%
- ❖ Aromatic base A > 50%
- ❖ Asphaltic Base As. 50%

Heavy crude, sour crude, high TAN crude, opportunity crude, oil sand

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**Crude Oil**

- Crude oil is composed of infinite combination of carbon and hydrogen plus contaminants of hydrocarbons with other elements such as oxygen, nitrogen, sulphur.
- Paraffinic series  $C_nH_{2n-2}$ , Aromatic  $C_nH_{2n-6}$  and series of naphthenic series  $C_nH_{2n}$
- Oxygen combined in the naphthenic acid.
- Sulphur as dissolved sulphur,  $H_2S$  or as organic sulphur such as Thiophenes sulphonic acids, mercaptans, alkyl sulphates and alkyl sulphides

We are having the various type of the crude oil that may be paraffinic base as the paraffin's are on a very higher side intermediate base the in between paraffin and the naphthenic base. Naphthenic base, where naphthenic are more than 75 aromatic base more aromatic will be there asphaltic base means the more heavier product there and the



quality heavy crude sour crude high TAN crude opportunity crude. Now, we are also calling the heavy crude the opportunity crude how to process this that is also posing big challenge to the refinery and the last which is the new development is the oil sand. Again here in Canada lot of the oil sand is that is available and how to use this oil sand that is one of the big challenge and already they have been started. As I told you the in case of the shell gas and the oil, oil sand already they have started using crude oil is compose of infinite combination of the carbon hydrogen plus contaminants of the hydrocarbons with other element which are very important. Already I discuss we are having the various ways say paraffinic aromatic intermediate or it may be naphthenic series. Oxygen is combined in the form of the naphthenic acid that is present sulfur as dissolved sulfur H<sub>2</sub>S or organic sulfur.

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- **Density and API Gravity:** Weight to volume and vice versa calculation, checking consistency of crude oil, control of refinery operation and give rough estimation of crude oil. API gravity of lighter crude oil may be of the order of 45 whereas in heavier asphaltenes API is 10-12.
  - Density = Mass/volume
  - API gravity =  $\frac{141.5}{\text{Spec. Grav. At } 15.6/15.6\text{ }^{\circ}\text{C}} - 131.5$

Such as thiophenes, sulphonic acid, mereaptans, alkyl sulphates and various form of the but, thiophene that is one of the very important because it is very difficult to remove in the process. Now, let us discuss in detail about the some of your laboratory testing which you are doing. First part that comes the evaluation of the base of the crude oil because knowing the quality of the base oils whether it is heavier or the lighter. We can adjust all the processing as can so the first thing that is the earlier method that was because some of the correlation that has been given which has been used for just to have knowledge of the base whether it is the naphthenic or the paraffinic or the aromatic. So, first thing that was actually the crude method even by seeing the density or the API gravity you can say

that whether the crude is sour heavier or the lighter. So, this is the weight to volume and the vice versa calculation that was the as I told API is reverse of the density.

That was just to control the checking of the consistence of the crude oil control of the refinery operation and give rough estimation of the crude oil quality. So, API gravity of the lighter crude oil may be of the order of 45 whereas, in the heavier it may be around 10 to 12. So, API will be lesser, density will be high. So, this is the how we density and API gravity that can be use for the characterization of the crude oil and the same time viscosity also that is one of the highly viscous, slow viscous. So, we can have any rough idea of the crude oil quality.

Now let us come to the base of the crude oil because this is the one of the important first step in the characterization of the crude oil, that is the whether it is paraffinic intermediate or naphthenic. Because the further requirement of the octane number or as a petroleum feed stock for the various uses whether naphtha you are going for the petro chemical or you are going for the aromatic production or your kerosene extraction of the kerosene that has to be efficiently more effective. Because aromatics that may present even the kerosene if you are using for the as the elimination. So more smoking with requirement that will depend upon the base that you can have the.

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### **Base of the Crude Oil**

For characterisation of the crude oil base paraffinic/ intermediate/ Naphthenic and for measure of the aromaticity various parameters used are

- ❖ Characterisation factor,
- ❖ Bureau of Mines Correlation Index (BMCI)
- ❖ Viscosity Gravity correlation (VGC)

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**Base of the Crude Oil**

- **Characterisation Factor**  
 $K = 3\sqrt{T_B} / G$  (G= sp. gr. at 15.6/15.6 °C)  
 $T_B$  = Mean avg. Boiling point in Rankine; paraffinic base,  $K \geq 12.1$  Intermediate base,  $K = 11.5-12.1$   
Naphthenic,  $K = 11.5$   
Aromatics,  $K = 9.8-12.0$

$$\frac{10G - 1.0752 \log(V - 38)}{10 - \log(V - 38)}$$

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**Base of the Crude Oil**

- **BMCI (Bureau of Mines Correlation Index)**  
 $BMCI = 48640/K + 473.7$  g-456.8  
 $K$  = avg. boiling point in °K,  $g$  = sp. gr. at 15.6/15.6 °C  
*BMCI value:*  
Paraffinic  $\leq 15$ ;  
Intermediate = 15-50; Naphthenic  $\geq 50$

So, some of the parameters which I may be suggested one is the very important parameter that we are using in the petroleum refinery also in the petro chemical industry the characterization factor bureau of mines correlation index and viscosity gravity correlation. This is the characterization factor that is the 2 boiling point mean average boiling point and the divided by density ranking you can have the paraffinic base if the characterization factor is greater than 12 intermediate base between 11 point 5 to 12 point 1 naphthenic base around 11 point 5 aromatics 9 point 8 to 11. So, this is how you can characterize the base of the oil whether it is more paraffinic or the naphthenic.

Another correlation that we are using in the your knowing the base of the crude oil that is the bureau of mines, correlation index and this is the how the with the boiling point and the density that has been correlated and based on this we can find out the what is the actually the whether it is the paraffinic base inter mediate base or naphthenic base.

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**Base of the Crude Oil**

- Viscosity Gravity correlation (VGC)

$$VGC = \frac{10G - 1.0752 \log(V - 38)}{10 - \log(V - 38)}$$

G is specific gravity and V is Saybolt universal viscosity

Paraffinic base: 0.80-0.83, Intermediate base: 0.83-0.88,  
Naphthenic base: 0.88-0.95

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**True boiling Point(TBP Assay)**

- It is done for generating distillation data and for study of variations of some key properties throughout the distillation range.
- TBP distillation is carried out at high reflux ratio to obtain effective fractionation

Depending upon these values you can just have a rough idea of the base of the crude oil. So, this is the about the there is also one lecture is viscosity correlation constant this is the base of the crude oil which I was telling the viscosity of the crude viscosity gravity

correlation and based on this factor where the viscosity term is there and the that is say bolt universal velocity. That is one way of the measuring the velocity various type of the your instruments are available for measuring the viscosity say bolt viscosity and based on this you can have here the parameter is the viscosity and based on the viscosity and the density this correlation that can be used for knowing the base of the crude oil. There is the one another important distillation earlier it was the esteemed distillation. Now the through boiling point distillation for that has become very important. It is done for generating distillation data and for study of the variation of the some of the key property through the distillation range.

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- Reid vapor pressure and light end analysis: Indicates the relative percentage of gaseous and lighter hydrocarbons.

TVB distillation is carried out at high reflux ratio to obtain the effective fractionation another actually the measurement for the quality of the crude oil reid vapor that is also for the product also the reid vapor pressure and light end analysis indicates the relative percentage of gaseous and lighter hydro carbon. Because again the quality of the crude oil more gaseous part will be there or more lighter part will be there that you can get an idea with the help of the reid vapor pressure and the lightened analysis cloud point and the pour point for the estimating the relative amount of wax present in the crude oil cloud. Point gives the rough idea about which the oil can be safely handled. One of the problem you see the in case of the that is in case of the wax and even in case of the oil also it is getting solidified during the winter season viscosity.

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- **Cloud Point and Pour Point:** For estimating the relative amount of wax present in the crude oil. Cloud point gives rough idea above which the oil can be safely handled.
- **Viscosity:** Viscosity indicates the relative mobility of various crude oils. Temperature has a marked effect on viscosity.

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- **Aniline point:** Aniline point indicates the lowest temperature at which the oil is completely mixed with an equal volume of aniline.
- **High aniline point** indicates that the fuel is **Paraffinic** and hence has a **high diesel index** and very good ignition quality.

Viscosity indicates the relative mobility of the various crude temperatures has a marked effect on the viscosity because it is a normally in many of the pressure bed. They are using fuel oil they are facing trouble during the winter season. Because of the low temperature aniline point indicates the lowest temperature at which the oil is completely mixed with an equal volume of aniline high. Aniline points indicate that the fuel is paraffinic and hence has a high diesel index and very good ignition quality or vice versa. Asphaltenes carbon residue and asphalt content because these are all being very important knowing the carbon residue which is left after burning, because that creates

problem in engine that creates problem and kerosene that is being used or other usage. So, carbon residue asphaltenes indicate the presence of heavier hydrocarbons in the crude carbon residue is the measure of the thermal coke forming property.

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- **Asphaltenes, carbon residue and asphalt content:** Carbon residue and asphaltenes indicate the presence of heavier hydrocarbons in the crude. Carbon residue is the measure of thermal coke forming property.
- It is determined by Conradson carbon residue and Rams Bottom carbon residue method.

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- **Flash and Fire point:** Flash point is the lowest temperature at which application of test flame causes the vapour and air mixture above the sample to ignite. Fire point is the lowest temperature at which the oil ignites and continues to burn.
- Pensky Martens open/closed cup is used.

Because this is one of the problem we are facing in the refinery because we are using large number of the furnaces, where we are heating the and even in case of your naphtha cracker where coke formation is there which is reducing the efficiency of the furnaces. So, it is determined by these are the some of the major conradson carbon residue and the



rams bottom carbon residue method both the methods that is being used and based on that you can find out the what is the residue from that particular carbon residue from particular type of the your crude flash. Fire point is the lowest temperature the flash and fire point these are very important because we are handling the gasoline diesel or the other petroleum products. So, the flash and fire point that is very important from the safety point of view also and at the same time from the quality of the product as well so flash point is the lowest temperature at which application of the test flame causes the vapor. Air mixture above the sample to ignite fire point is the lowest temperature at which the oil ignites and continues to burn so this is the 2 types of methods Penskys martens, open closed cup is being used for flash point

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- **Acidity:** It is an indication of corrosive properties of products.
- **Colour:** Indication of the thoroughness of the refining process.
- **Copper corrosion test:** This test serves as a measure of possible difficulties with copper, brass, bronze part of the fuel system.

Acidity because you see the corrosion problem that is a serious problem in case of the refinery especially, the distillation column that will be discussing because the presence of the naphthenic acid. So, it is an indication of but, the products also if you are having higher acidity then the chances of the corrosion will be there. And so that is that has to be avoided so it is an indication of the corrosive properties of the product color indication of the thoroughness of the refining process. Normally we are darker side we are getting and so the you can imagine but, in case of the refinery at the same color in different type of the product diesel kerosene or the gasoline we are adding that you do not confuse with that color then the copper corrosion test. As I told you the corrosion problem may be one

of the major problems while using the crude oil in the process or the product which we are getting from the crude oil distillation.

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- **Smoke Point:** It is indication of smoking tendency of fuel. It is used for evaluating the ability of kerosene to burn without producing smoke. It is the maximum flame height in mm at which the fuel will burn without smoking.
- **Smoke volatility Index( SKI) = Smoke point + 0.42 x recovery at 204 °C**

Because depending upon the your desalting process or the pre treatment process which are have been the corrosiveness of the crude oil being processed that will change. So, this test serves as a measure of the possible difficulty with the copper brass bronze part of the fuel system that we are using smoke point that is very important from the for the kerosene. So, it is indication of the smoking tendency of the as it is thumb ruled if the more aromatic more tendency of the smoking level it is a it is used for evaluating the ability of the kerosene to burn without producing smoke because smoke less flames will be there. It is the maximum flame height in milli-meter at which the fuel will burn without smoking. So, this is the another term that we are using for the smoke volatility index in the refinery and from this smoke point you can find out the smoke volatile index, diesel index that is one of the very important characteristic of the diesel

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- **Water, salt and sediments:** These cause irregular behavior in the distillation and cause blocking and fouling of heat exchanger and result in corrosion
- Water content is determined by Dean & Starck. Sediment and water is determined by centrifuging a mixture of crude oil and toluene. Salt content is determined by titrating the water extract with  $\text{KCNS}/\text{AgNO}_3$ .

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- **Colour:** Indication of the thoroughness of the refining process.
- **Antiknock quality (octane number):** Octane number(ON) is the percentage of iso-octane in the reference fuel which match the knocking tendency of the fuel under test. RPM: ResON: 600 MotorON:900
- Research octane number (RON) and Motor octane number (MON) are two methods used.
- Anti knock index (AKI)=  $(\text{RON} + \text{MON})/2$

So, from the aniline point you can calculate the diesel index, water salt and sediments these cause the irregular behavior in the distillation and cause the blocking and fouling of the heat exchanger and results in the corrosion. So, the water salt and sediment determination is developed also very important part of the crude oil corrosion water content is determined dean and stack methods sediment. Water is determined by centrifuging a mixture of the crude oil and toluene salt content is determined by titrating the water extract with KCN s and the  $\text{AgNO}_3$  color indication of the thoroughness. Already we discussed another property from the fuel point of view it is very important

that is the octane number of the product. As I told you the octane number requirement of the octane number that is changing so octane number is the percentage of the iso-octane in the reference fuel which matches the knocking tendency of the fuel. Under test r p m because we are having the two types of octane number one is the research octane number. Another motor octane number RON or the MON. So, this would be the speed of the test machine and as you see the in case of the research octane number the speed is lower than the motor octane number.

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Parameters	Significance
Cetane number	Cetane number is the percentage of octane (100) which must be mixed with hexamethyl Nonane (16) to give the same ignition performance as the fuel in question.
Stability test	It is used for the evaluation of storage stability and resistance to oxidation.

Research octane number and the normally we are taking the average of the two and this is what we call is the anti knock index RON plus MON research. Octane number plus motor octane number divided by 2 gum again it is the indication of the gum at the time of the test and amount of the deposition. During the service time sometimes the engines are creating problem and you must have face even in case of the ignition in the scooter and that is especially the carbon deposits are there. But, gums that is determination that is very important frass breaking point this is the temperature below which the bitumen tends to break rather than flow. This is also characteristic of the bitumen that we are cetane number. Already we discuss cetane number is the percentage of cetane just like the in case of the octane number it was the octane cetane which must be mixed with the hexamethyl nonane to heptane that is the hexamethyl octane to give the same ignition performance as the fuel in the question.

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Parameters	Significance
Acidity	It is an indication of corrosive properties of products.
Weathering test for LPG	This test shows the volatility of the LPG

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**Product Evaluation**

- Major parameters for gasoline included in Bharat or Euro norms are
  - ❖ Lead phase out
  - ❖ Lower RVP
  - ❖ Lower benzene & aromatics
  - ❖ Lower olefin content
  - ❖ Limited Oxygen content
  - ❖ Lower Sulfur content

Stability test it is used for the evaluation of the storage stability and resistance to oxidation acidity. Already we discuss about the acidity what is the importance of the acidity weathering test for the l p g this test show the volatility of the l p g. Now let us come to the product evaluation what is the parameters major parameter for gasoline included in the Bharat norms or euro norm or the lead phase out. Lead free gasoline lowers RVP less benzene and aromatics. That is, now the figure which I told you while discussing this tender that is 1 percent lower olefin content, limited oxygen content and lower sulfur content. These are the some of the requirement for the gasoline similarly,

the some of the properties which are being used I am going in detail because again it will be part of the petroleum refinery course and if we start discussing all those parameters that will take two three lectures and methods if we discuss.

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### **Product Evaluation**

Other parameters of importance are RON, MON, Lead, Gum, Oxidation stability, density, VL Index, Final boiling poin(FBP)

In case of reformulated gasoline aromatics, Olefins , Oxygen, Antiknock index, Vapor lock Index

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### **Major Parameters of Diesel Specifications**

Major parameters for diesel included in Bharat or Euro norms are

- ❖ Low sulfur
- ❖ Low aromatics
- ❖ High cetane number
- ❖ Lower density
- ❖ Lower distillation end point

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## Major Parameters of Diesel Specifications

Other parameters for diesel are Density, Viscosity, Cetane Number Distillation Range, Sulphur, Carbon Residues, Oxidation Stability, Flash Point, Acid Value, Ash and Water Contents

So, the various parameters which we are using for the gasoline characteristics, that is RONMON lead gum oxidation stability density FBP final boiling point. In case of the reformulated gasoline, aromatics, olefins, oxygen, antiknock index and vapor lock index. That is whichever in v l i that vapor lock index all those parameters that we are determined in case of your gasoline. Similarly, in case of the diesel also because the as I told you our environmental standards are becoming more and more stringent. same thing happened in case of the diesel also diesel specification as per the Bharat or euro norm that should have the low sulfur and low aromatics, high cetane number high and lower density and lower distillation end point.

These are the some of the major actually the requirement but, as I discuss in case of the gasoline in some of the parameters which are to be evaluated for diesel or the density viscosity cetane number distillation range sulfur carbon residue oxidation stability, flash point, acid value ash and water contents. So, these are the some of the parameters which are being used for the valuation of the products.



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<b>Evaluation of Feed Stocks for Aromatics, Olefins and Surfactant Plants</b>	
Aromatics	Naphtha, Pyrolysis gasoline, LPG
Olefins	Ethane, Propane, Naphtha, Gas oil
Surfactant Plants	Kerosene for paraffins, benzene

Now let us discuss about the, that was part of the fuel the requirement of the gasoline requirement of the diesel requirement of the kerosene. Kerosene the smoke point and that was the important parameter and the in case of the your gasoline high octane number in case of the diesel high cetane number that was the requirement and some other properties like acidity or the fire point, pour point or it may be sediments corrosiveness all those parameters. Similarly, in case of some of the raw material just like naphtha kerosene we are using in the petroleum petro chemical complexities for the production of the aromatics olefins and the surfactant.

So, evaluation of the quality of the product of these feed stock that is very important so for aromatics what we are using naphtha that we are getting from the actually the naphtha which is having the higher octane number, or even in case of the aromatic the low octane number naphtha where we are because there are two operation. In case of the two objectives we are performing in case of the catalytic reforming.

Whether it is for the production of the aromatics or it is production of the gasoline. So, the aromatics production here also the same catalytic reforming process, we are using and so the naphtha that we are using pyrolysis gasoline which we are getting from the cracker plant especially the naphtha cracker LPG because from LPG to aromatics the process technology available. Then the olefins ethane propane naphtha gas oil these are the raw material which are using for the production of the olefin because the quality. If

you see the quality of these feedstock that will affect the product quality from a during the aromatic production or the production of the olefins or the for the surfactant where the kerosene for paraffin. What we are using we are separating the particular carbon number of the kerosene so evaluation. Why the evaluation dealt and the benzene of course that we are using from the catalytic and this aromatic complex. What we are doing? We are converting the paraffin to olefin and then alkylating we are getting the linear alky benzene for making of the surfactant or detergent.

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### **Evaluation of Feed Stocks For Aromatics, Olefins and Surfactant Plants**

- Input cost of feed constituents is a major portion of the variable cost of production in petrochemical plants.
- Major feed input naphtha/kerosene from the refinery.
- Feed quality monitoring and improvement efforts are therefore very important aspects having significant impact on the economics of the operation cost.
- The precursors and undesirable constituents in feed including catalyst and adsorbents poisons should be known, analyzed and monitored continuously.

Already we discussed about the LAB plant so what the requirements for evaluation of the feedstock parametry are. Why we need the evaluation input cost of the feed constitute the major portion of the variable cost of the production in the petrochemical because, this is the reason why the depending up on the cost of naphtha cost of the natural gas the cost of the whole downstream processing or the that will be affected cost of the ethylene propylene or the other products which we are getting from the cracker plant. The aromatic that will be directly related to the variation in the property of the plant so major feed input naphtha kerosene from the refinery that we are using their in case.

So, the evaluation that is very important feed quality monitoring and improvement efforts are therefore, very important aspect having significant impact on the economics of the operation which I told you. Because all the product which we are getting from further processing of the aromatic this naphtha that will be effected if the lower aromatic

content is there or if it is more aromatics from the cracker point of view as we prefer more paraffinic. Similarly, if the aromatics are there that is going to affect the quality of the kerosene.

But there in case of the LAB what we need in case of the petro chemical that will be the your carbon number. So, the precursors and undesirable constituent in the feed including the catalyst and adsorbents poisons should be known. Because this is the naphtha kerosene we already discuss about the while discussing parax process, why we are doing the pre treatment? Similarly, in case of the refinery operation we are using a large number of the catalyst whether it is the catalytic reforming or FCC or hydro cracking all the processes that is the pre treatment that is being done.

But if these impurities even in case of the aromatic production or even when you are going for the steam reforming of the naphtha for production of the hydrogen what we are doing, we are doing the pre treatment. Because, the requirement of the catalyst the catalyst poison that has to be removed just like sulfur or nitrogen nitrogenous compound. So, they will poison the catalyst and so that is very important.

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### **Desired Components in Feed for Olefins Productions**

- **Naphthenes:** Naphthene yield olefins of higher carbon number. Butane yield increases appreciable with naphthenic feed. Naphthenes also enhance production of aromatics.
- **Aromatics:** The aromatics is feed are highly refractory and they pass through the furnace unreacted.
- **Sulphur:** The sulphur in feed suppress steam reforming reaction catalyzed by nickel present in radiant coil. Optimum level of sulphur- 1 ppm.

Desired component for the your let us discuss about the olefin production. Here what we are doing, we are cracking up the naphtha and from the naphtha you are getting the both natural gas means ethane propane or the naphtha that we are using for production of the olefin. And naphtha is around 50 to 54 percent of the cracker plant is still based on the

naphtha as a feed stock. So, quality of the naphtha again that will be totally affected by the type of the crude which we are processing. So, naphthenic yields if you are using the more naphthenic olefins of higher carbon number. Because now in the cracker what we are interested, we are interested more in ethylene and the propylene than other C4, C5 gases. So, butane butane means C4 gases yield will increase if you are having the more naphthenic appreciable with the naphthenic acid that is contain and the naphthenic as also enhance the production of the aromatic.

So, the aromatic means more paralysis gasoline that will be there from the naphthenic if the more naphthenic aromatics the aromatics feed are highly refractory and they pass through the furnace un reacted. So, this is the problem in case of the when we are having the more aromatic and the why we are preferring the paraffinic sulfur the sulfur in the feed suppress the stream reforming reaction catalyzed by the nickel present in the radiant coil. So, this is the also the problem we are facing in the sulfur even in case of the catalytic reforming which we are using for the production of the your aromatics. There also the sulfur that has to be removed. Here also the hydrogen that we are using here in case of the olefin plant. In the cracker plant that is also very important one of the very important parameter hydrogen to hydro carbon ratio. So, if this is the more sulfur is there so that may be present in the your hydrogen

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### **Desired components in Feed for Olefins Productions**

- **Physical Properties:** Density, distillation range are useful and give a rough assessment of feed quality.
- **Ethylene:** The following components in feed give ethylene in decreasing order:
- Ethane, Butane to Decane, 3 and 2 Methyl hexane, 2 methyl Pentane/ 2,2 Dimethyl Butane, Isopentane.

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### **Desired Components in Feed for Olefins Productions**

- Propylene: The following components in feed give propylene in decreasing order:
- Isobutane, n-butane, n-propane, 3 methyl pentane, 2,3 dimethyl butane, 2 methyl hexane, n-pentane, 3 methyl hexane, iso pentane.
- Butadiene: The following components of feed give butadiene in decreasing order:
- Cyclo hexane, methyl cyclo pentane.

Some of the physical property desired for the which you are determining that is the density distillation range they are useful to give a rough assessment of the feed quality ethylene the following components will give the ethylene in the decreasing order. Because if you see the compare the cost of the cracker plant the total cost that is lower in case of the ethane propane. And if you are going for the cracker so lowest is if you take one for the ethylene ethane. Then it will be higher in case of the if you are using the naphtha so the ethane cracking or the propane cracking more lighter more ethylene or the propane production will be there if you are having the naphtha or even if you are going for the gas oil cracking more heavier fraction will be there. Production of the more paraffin gasoline will be there. Propylene again depending upon the content of the naphtha or the gas the propylene yield also varies because our interest is in ethylene and propylene from the naphtha cracker oil.

So, this is the how the iso-butane to iso-pentane the yield of the propylene that will be affected. Similarly, butadiene the following component of the feed gives the butadiene in the decreasing order. Butadiene also because especially in case of the cracker plant naphtha cracker we are getting a very valuable byproduct butadiene and which is although the other actually the routes are there for making butadiene. But, the naphtha cracker olefin plants we are generating large amount of the butadiene. And this is the reason why some of the means they are having the cracker plant they are having the poly butadiene plant and refinery they are going to have the styrene butadiene plant SBR

manufacture the butadiene that will be made available from the cracker plant. Let us come to the aromatic plant the aromatics are either process in refinery in catalytic reforming. What will happen is some of the refineries they are producing the aromatics also along with reformat which is going to the gasoline pool.

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### Aromatic Plant

- Aromatics are either processed in Refinery in Catalytic reforming are processed separately in petrochemical complex for manufacture of p-xylene required for DMT/PTA plant.
- Naphtha cut  $C_6$  to  $C_9$
- Paraffin, Naphthenes, Aromatics 110 to 140 °C
- Dehydrogenation of  $C_8$  Naphthene yield  $C_8$  aromatics. Most desirable component
- 90% of  $C_8$  naphthalene in feed gets converted to  $C_8$  aromatics

Or it may be separately processed for production of the aromatic in the aromatic plant that is just like the by the LAB we are making. Whereas, you are making the terra ethylic acid so in all those some of the petrochemical complexes they are also having. In case of the terra ethylic or the DMT what we need we need the paraxylene from there the paraxylene come that is coming from the aromatic plants? So the importance of the aromatic is because of that. And apart from that we are also using the various product of the aromatics means benzene for making the cyclo-hexane. Another application is also there so naphtha cut normally 6 to 9.

Again that will depend upon the whether you are interested for aromatic whether you are interested for benzene if you are having the paraxyene plant. The higher cut of the naphtha that will be required means the boiling point plus if you are interested for both benzene, ethylene, xylene. Then 90 plus are the around 90 plus because, the boiling point of the benzene is 90. So, paraffins, naphthenes aromatics this is the actually boiling point which I was telling dehydrogenation of the c 8 naphthenic acids. Most desirable component that is there in case of the when you are going for the catalytic reforming



dehydrogenation that is one of the very important reaction which it is powerful for improving the octane number so 90 percent of the c 8 naphthene feed gets converted to c 8, aromatics c 8 paraffin..

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### **Aromatic Plant**

- **C<sub>8</sub> Paraffin's:** Dehydro cyclisation of C<sub>8</sub> paraffin's yield aromatics difficult to 20% C<sub>8</sub> paraffins gets converted to C<sub>8</sub> aromatics.
- **C<sub>8</sub> Aromatics:** Pass as refractory and directly contribute to C<sub>8</sub> aromatic production.
- **C<sub>8</sub> Aromatic Precursors:** It is useful to monitor aromatic precursors=  $0.2x C_8 P + 0.9 x C_8 N + 1.0 C_8 A$

Because the in case of the catalytic reforming for production of the aromatics series of reaction that is taking place just to have the higher aromatic content and definitely that will improve the octane number. Also, de hydro cyclisation reaction c 8 aromatics pass as refractory and directly contribute to c 8 aromatics c eight aromatic precursor. It is useful to monitor the aromatic precursors also surfactant as I told you we are using huge amount of the kerosene for making of that linear alkyl benzene. Because that was because we started with the non-linear component which was less biodegradable then there was lead of the environment to have the biodegradable rate of the detergent for that the linear benzene that played very important. Because benzene and the paraffin for making the olefin that was available from the refinery



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## Surfactants

- Linear alkyl benzene is one of important feed stock for production of surfactant.
- LAB requires paraffins for production of olefins of carbon range  $C_{10-12}$  to have more biodegradable detergent.
- Benzene is required for alkylation of olefin to produce LAB.
- Feed stock for paraffins are Kerosene feed 150-265 °C cut from refinery containing mainly  $nC_7$  to  $NC_{18}$  components.

So the LAB requires the production of the olefins or carbon range C10 to C12 to have more biodegradable detergent. Benzene is required for alkylation of the olefin to produce LAB. So, the benzene again it is coming from the aromatic plant and this was the reason you see the Nirma that that is using the raw material or even in case of the Gujarat research fertilizer complex at Vadodara, they are using the benzene for making the cyclo-exchange there which they are using for the making of the same thing is in case of the Nirma. Because in case of the Indian oil corporation that Vadodara unit they are making rate of the benzene. So, feed stock for the paraffins are the kerosene because we are taking a particular fraction of the kerosene for extracting the paraffins from the kerosene and so that is going to for the making of the olefin. So, that the particular cut is there. Again we are fractionating so that we are getting a required carbon number atom and to have the more biodegradable nature of the surfactant.

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### **Desirable for Surfactants**

- LAB requires olefin and benzene.
- At present trend is for manufacture of biodegradable low molecular weight LAB,
- nC12 improve the flammability of LAB product [Dave & Khurana 1996].
- Some of the undesirable components in the feed which are sensitive to mox molecular sieves are contaminants like water, sulphur, nitrogen, oxygen, chlorides, metallic poisons.

So, desirables require LAB require olefin and benzenes. As I told you for alkylation of the benzene, so at present trend is to manufacture the biodegradable low molecular weight LAB. So, if you are having the lower carbon number means around n C12 so improve the flammability of the LAB products. Some of the undesirable components in the feed which are sensitive to the mox sieves are contaminants like water sulfur, nitrogen, oxygen, chlorides and metallic. And this is the region in case of the LAB plant also we are doing the pre treatment of the feed is going to the mox process. So, these where the some of the requirement which I discuss earlier about what are the requirement of the feed stock for the petro chemical industry and the evaluation of the some of the parameters which are important in case of the even the phase product. If you are making the LAB some of the requirements are there that is not we will be discussing separately while discussing the petro chemical.

So, in the refinery so the evaluation of the feed stock that is very important to get an idea of about what are the what will be composition of the product in stream particle quality of the product. We are going to get and the whole economy of the plant that will depend and with the availability of the some of the analytical equipment. Now, the evaluation that has been be possible to more actually the in the estimation that has been possible and the accurate method of the knowledge of the various products that will.

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### **Analytical Development**

- Gas Liquid chromatography(GLC), Mass Spectroscopy (MS), Nuclear Magnetic resonance, X ray Fluorescence(XRF)
- High and Ultra Performance chromatography (HPLC and UPLC)
- Atomic absorption spectroscopy(AAS)
- FTIR

So, what was the analytical instrument now available for the evolution apart from the routine instrument which we are using that is the gas liquid GLC gas liquid chromatography masses spectroscopy or GSM, GMS, nuclear magnetic response, NMR x ray, fluorescence, high and ultra performance chromatography that is available now atomic absorption spectroscopy for determining the middle content FTIR. So, all these instruments are available, and which, and the use of this instrument they have facilitated the evaluation of the crude oil and the evaluation of the paraffin's, the evaluation of the naphthenic acid and other product. So, this is the all about the crude oil evaluation, and what is the impact of the crude oil on the further processing of the substantive stage of operation?

And one important aspect that is the first major operation that we are doing in the refinery that is the crude oil distillation where we are distilling the crude oil to different fraction which is finding application either as a fuel or as a petro chemical feed stock. So lecture 2 will, lecture three will be about the crude oil distillation.