Technologies for Clean and Renewable
Energy Production

Prof. Prasenjit Mondal
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture-12
Characteristics of Crude Oil and
Petroleum Products

Hi friends, now we will discuss on the topic characteristics of crude oil and petroleum products. In the last class, we have discussed on petroleum, we have seen that what petroleum is? How it is produced? And how did how it is different from crude oil? And we have also seen some types of this and some issues for its utilisation. In this class we will discuss on the characteristics of petroleum both crude as well as its different products.

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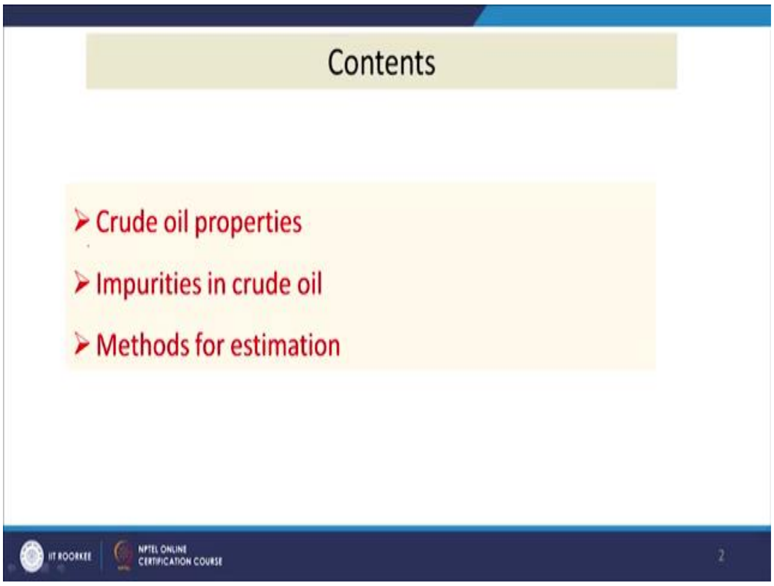

So, content is, crude oil properties, then impurities in crude oil and methods for estimation, how we will estimate that we will also cover in this class. Now we will see the properties of petroleum, so, petroleum has some properties which are interesting for us as we are dealing with its utilisations as energy feedstock. Like coal it also has some properties. But unlike coal, this petroleum is mostly use to produce transportation fuel.

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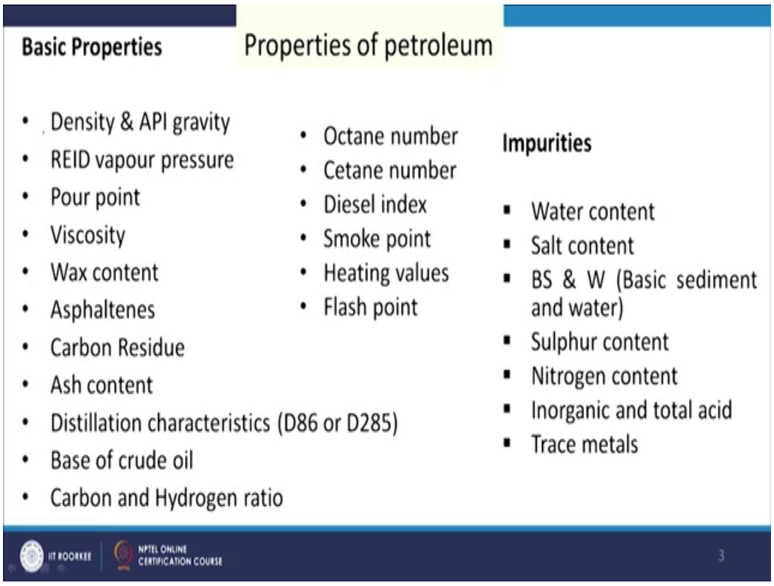

So, the properties which are most important are density and API gravity, REID vapour pressure, Pour point, viscosity, flash point, cloud point, wax content, asphaltenes contents, carbon residue, ash content, distillation characteristics, distillation characteristics is important for this, because, if for a pure compound we get a specific boiling point. But petroleum is a mixture of compounds; large numbers of organic compounds, hydrocarbons are present in it.

So, each will be having different boiling points. So, when it is going for distillation so, then different components will be vaporised at different temperature. So, we will not get a specific temperature for this petroleum crude as a boiling point so, we will be having some initial boiling point and one will be end boiling point for a particular part or particular sample.

Then we have base of crude oil, that is also one important parameters and then carbon and hydrogen ratio and octane number, cetane number, diesel index, smoke point and flash point are also related with the application point of view for some petroleum crude, petroleum products like for example smoke point is used for kerosene. Octane number is used for gasoline and cetane number is used for diesel. And over all heating values is very, very important as we are dealing with the energy from the feedstock and different types of impurities are also present.

The one is water content, then salt content, then basic sediment and water, sulphur, nitrogen, inorganic acid and trace metals. So these are the different properties of the crude oil. And we will discuss the importance of these and how to measure these properties.

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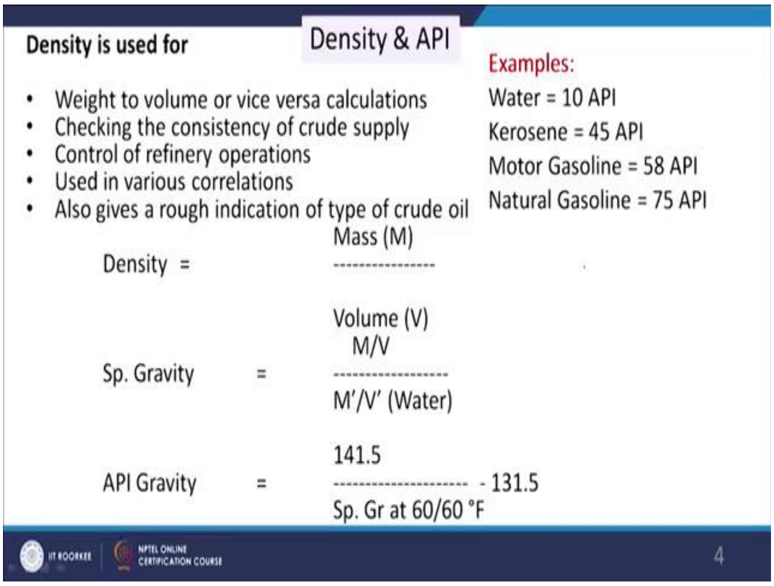

First we will see density and degree API or API gravity. As you know density is nothing but mass by volume (Density = M/V) of any substance and specific gravity is also used M by V divided by M dash by V dash (Specific gravity = (M/V)/(M'/V')) that means with respect to water, so, it is the density of any material and density of water at 4 degrees centigrade that is specific gravity. So, similar way API gravity has been defined by American Petroleum Institute that is API Gravity = (141.5/specific gravity at 60 degree Fahrenheit) -131.5. So, this is the definition of API gravity as for American Petroleum Institute.

And this is used to clearly understand the difference between fractions of petroleum crude. For one example, if say, if we consider the water then specific gravity, API gravity will be 141.5 – 131.5, almost 10. But if it is lower; it is lighter than water then specific gravity will be less, so, this minus this will be more than 10. So, for kerosene, we get 45 API, for moter gasoline, we can get 58 API and for natural gasoline we can get 75 API. So, higher the API, lighter the fractions of the product we are considering.

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Density & API gravity

Density and API gravity of some crude samples

Crude	API	Density	Total Distillate upto 370 °C
Sobashan	33.99	0.8549	43.0
N. Gujarat	33.85	0.8553	44.0
Geliki	31.50	0.8675	54.5
Nahorkatiya	31.30	0.8688	60.9
Kuwait IF IR. Oman	31.10	0.8698	47.0
Kalol	36.55	0.8414	47.0
Rumaila	35.90	0.8448	55.7
Ratna	35.20	0.8484	51.0
Rostam	35.00	0.8495	59.7
Basrah	34.40	0.8527	52.5
Narimanam	47.08	0.7920	79.6
Ankleshwar	46.85	0.7930	78.2
Jotana	41.80	0.8161	52.0
Bombay High	39.35	0.8278	65.4
Heera	36.62	0.8412	60.6

Now, we will see some example of density and API and total distillate upto 370 degrees centigrade. So, these are the source of different crude, so, if we see the maximum API is here, say 47.08. So here we see maximum distillate. So, more the API lighter, more will be the lighter that is why more the value of, here of the distillate product operate at 370 degree centigrade.

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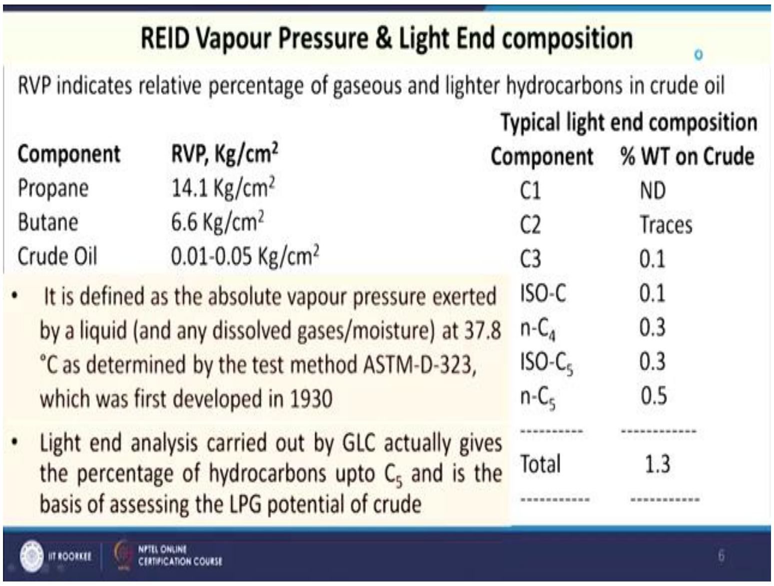

REID Vapour Pressure & Light End composition

RVP indicates relative percentage of gaseous and lighter hydrocarbons in crude oil

Component	RVP, Kg/cm^2
Propane	14.1 Kg/cm^2
Butane	6.6 Kg/cm^2
Crude Oil	0.01-0.05 Kg/cm^2

- It is defined as the absolute vapour pressure exerted by a liquid (and any dissolved gases/moisture) at 37.8 °C as determined by the test method ASTM-D-323, which was first developed in 1930
- Light end analysis carried out by GLC actually gives the percentage of hydrocarbons upto C_5 and is the basis of assessing the LPG potential of crude

Typical light end composition

Component	% WT on Crude
C1	ND
C2	Traces
C3	0.1
ISO-C	0.1
n-C_4	0.3
ISO-C_5	0.3
n-C_5	0.5
Total	1.3

And another properties REID vapour pressure, so REID vapour pressure that is the indicative or what are the extent of volatiles present in the crude. So, it is determined under specific a condition that is 37.8 degrees centigrade and as for ASTM-D-323 this method it is measured. So, more the vapour pressure more will be the lighter fractions in the crude. If we take some example, say in petroleum crude we get C_2 to C_8 or more than that. So, C1 is very less in this case, so, C_2, C_3, C_4, C_5, n-C_5 these fractions produces the LPG.

So, how much LPG we can get from that crude that we indicated by the REID vapour pressure. So, these vapour pressure if we consider for propane it is 14.1 kg per centimetre square, butane it is 6.6 kg per centimetre square whereas for crude oil it is 0.01 to 0.05 kg per centimetre square. Another property is pour point and ash content. So, pour point indicates the solubility of this that means, it is that temperature at which the fuel ceases its flow.

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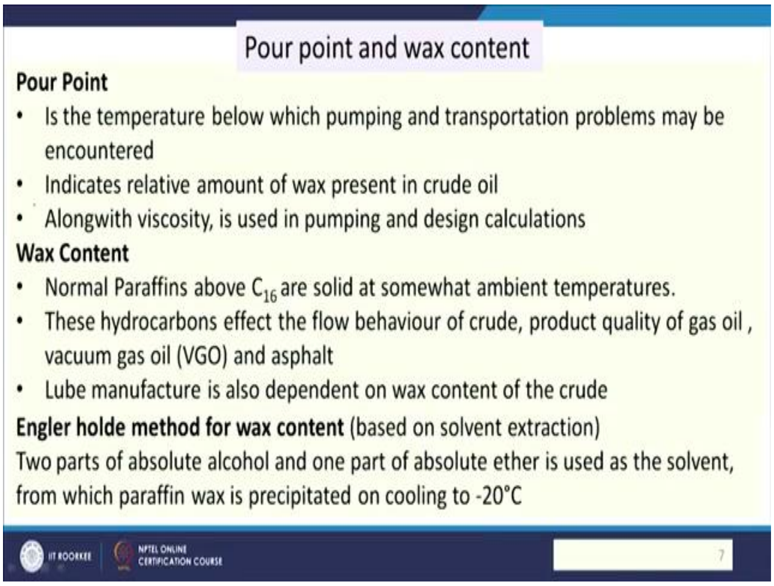

So, it is related with the wax content also, more wax, more easy to get, to cease the flow of it and it alongside the viscosity this is also used for pumping design and then wax content as you know that paraffins of having carbon more than 16 is solid. So, this solidified paraffins are considered as the wax in it and this is determined by Engler holde method and under this method is based on the solvent extraction method.

So, as shown here, the two solvents that is absolute ether and absolute alcohol solvent system is used. And then paraffin wax is precipitated at -20 degree centigrade. So, this is a method of determination of the wax. Now, we will see asphaltenes, carbon residue and ash content. They are also important parameter of the crude oil, asphaltenes basically is related with the residual part, more the asphaltene we will be having more vacuum residue.

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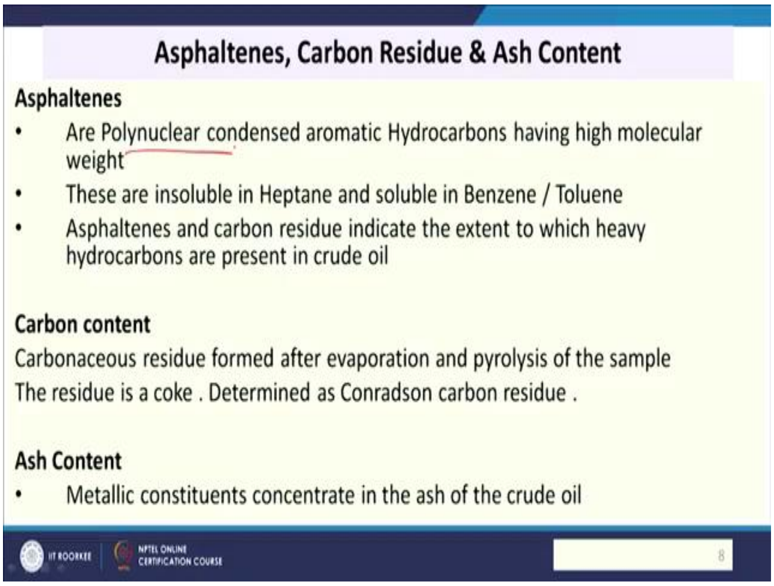

And this is nothing but the poly nuclear condensed aromatic compounds and its solubility is also different in different solvents, and we can take advantage of it for its determination where it is insoluble in heptane and soluble in benzene/toluene solvent. Next is your carbon residue, so, carbon residue it is a carbonaceous material. So, it is if we evaporate it and finalise it at specific conditions, then it will be remaining some residue so that residue is called carbon residue.

And conradson method is used and ash content we can measure from the proximate analysis and just like coal here also ash content is related to mineral matters present in it. Metals which are present that also contribute to ash and you can convert the ash into dry basis and wet basis also as provided here.

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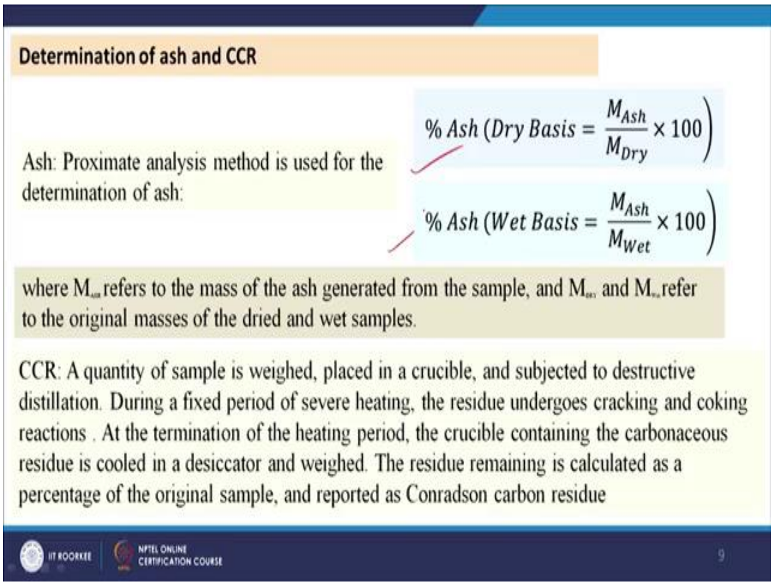

And Conradson carbon residue we can determine under specific condition we will take the weight certain amount of material, we place it in a crucible and subject to destructive distillation during a fixed period by some severe heating, after that we will collect the residue and how much is left that is considered as Conradson carbon ratio and is expressed in terms of percentage with the original sample.

Salt content is also one parameter of the crude oil. So, when the crude oil is taken out from the underground, then it forms it contains different type of material including water and salt.

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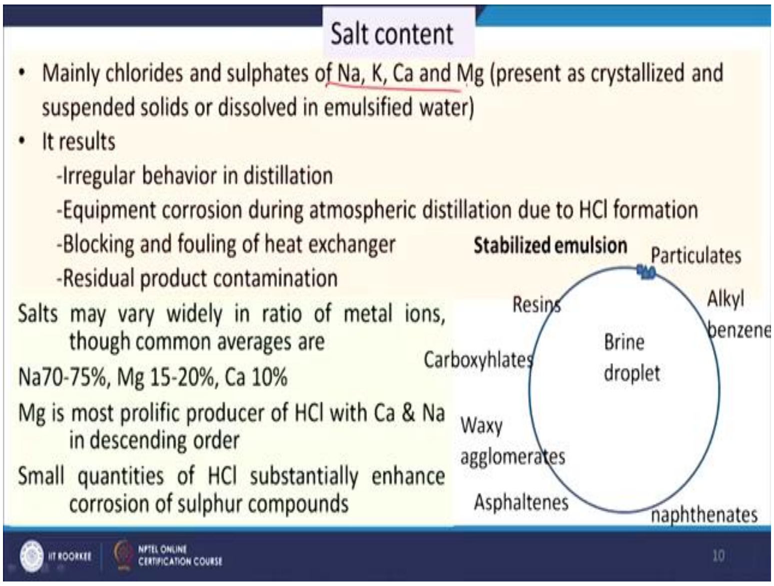

These salts are basically sodium, potassium, calcium and magnisium chloride and the salt can be present as crystallised solid or maybe dissolved in water, which water can form an emulsion with the organic phase in the oil in the crude oil. As shown here so one Brine droplets, salt in water Brine droplet, so this droplet size is maintained by the formation of a layer and resins, asphaltenes, waxy agglomerates, carboxyhlates and naphthenates or alkyl benezene all those things helps to get the stability of this brine droplet.

And some brines may also b, some salts may also be available in terms of particulates, so or solid particles. So, this is a salt and this salt if present in crude that will create lot of problem and above certain limit it is not desirable in the refinery, it will create pollution, it will give the irregular behaviour in distillation, it will be fouling the heat exchanger and it will also cause equipment corrosion.

So, these are the disadvantage of the salt and if we think about different type of salts, mostly sodium is used at 70 to 75% typically, magnesium at 15 to 20%, calcium is around 10% and magnesium salt mostly gives a HCL so, that is corrosive in nature.

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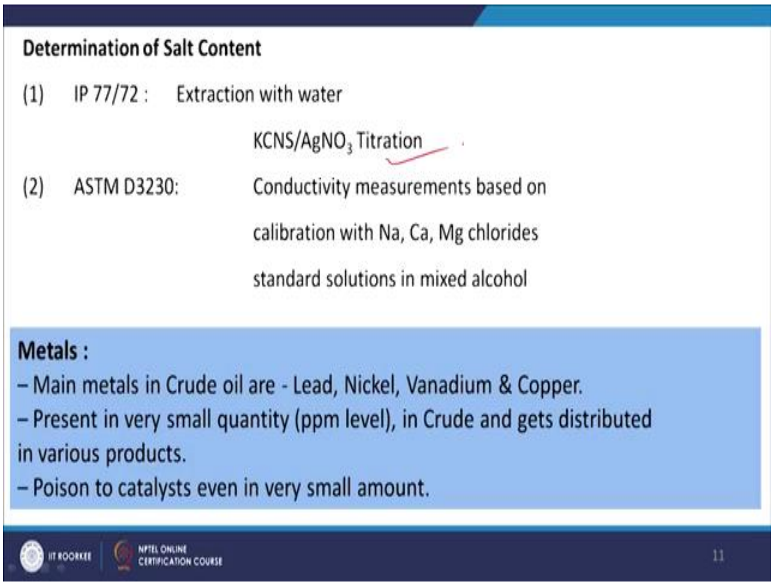

Then for the determination of this salt, some methods are available, that is here, silver nitrate and KCNS method by titration or by conductivity measurement based on the standard sodium calcium and magnesium chlorides and standard solutions in mixed alcohol. So, these are methods which are used for its determination. Then metals which are available metals, which are available in crude oils, are mainly lead, nickel, vanadium and copper.

So, it will also contribute on ash when it will be burn then soot will be formed and particulates will be formed and it poisons the catalyst. So, the lesser the metals more we will get the quality of the crude or of the derived product from it.

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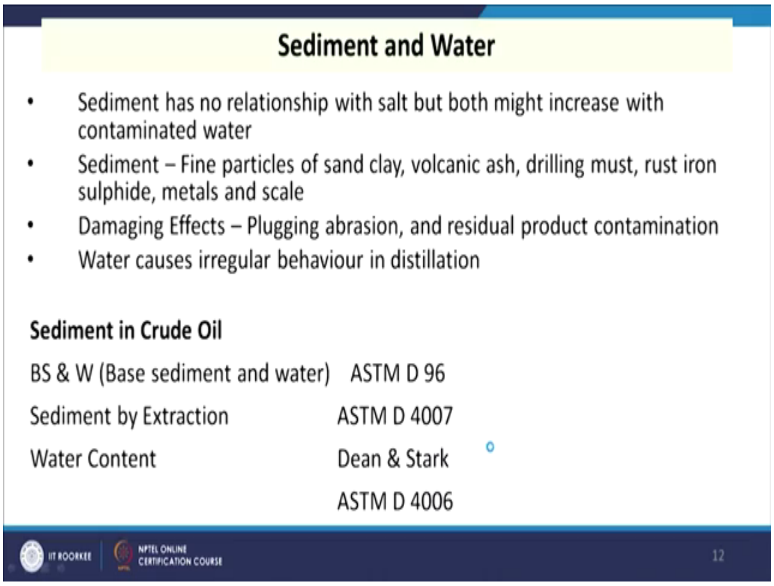

Now, this can be measured by using atomic absorption spectroscopy and another property sediment and water. So, as I told that, when crude oil is taking out, then it contains salt, different types of sediments which are basically sand clay, volcanic ash, drilling must, rust iron and sulphide and metals and different types of scales. So, these contributes the sediment and water is already available in the crude oil.

So, the presence of these affects the process of refining and it damages that is the plugging abrasion and residual product contamination. So, these are the important effect of these contaminants on the crude oil. And water causes irregular behaviour in the distillation and for the measurement of this there are a number of methods that is Base sediment and water measurement is ASTM D 96, Sediment by extraction is ASTM D 4007 and Water content Dean and Stark or ASTM D 4006 methods.

Now we will be discussing some property of the refined products that is your octane number. Octane number is the property of the gasoline and it is related with the knocking property of it. Now what is the resistance of a motor fuel to knock, this indicates.

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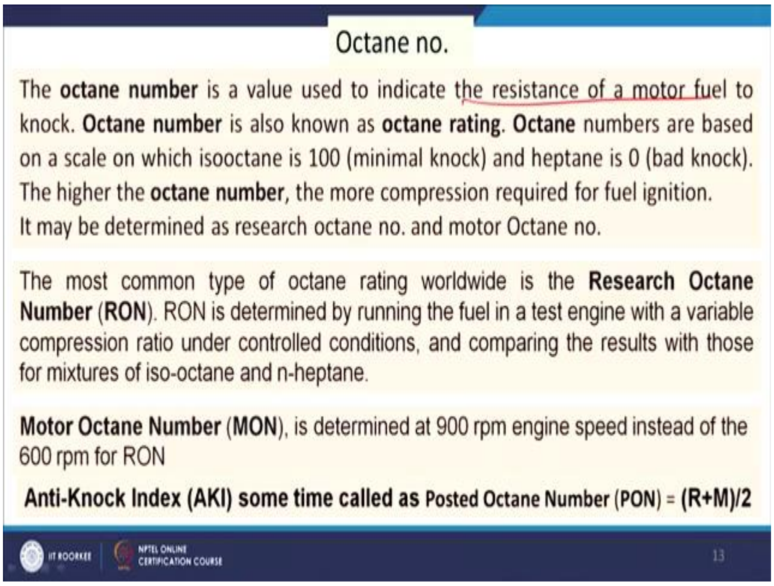

So, more the octane number more the quality of the gasoline and this is also called octane rating and octane number are based on a scale on which the isoocatane is 100 and heptane is 0. So if we have a fuel, which burns in the similar way, which are having the similar knocking property with a blend of isooctane and heptanes in that blend, what is the percentage of isooctane that will be the octane number of this fuel.

And for the determination of octane number, some standard machine is used in laboratory. So, in that case, what number octane number we get that is called research octane number and it is determined by running the fuel in a test engine with a variable compression ratio under control condition and the comparing the results with those for mixture of isooctane and n-heptane as it to what is the percentage of isooctane in this mixture, that will be the having the similar knocking barrier that will be the octane number.

So, that is called your research octane number and when the vehicle will be on road with actual loading, then it will be consuming some amount of more energy so motor octane number is also used in this case higher RPM is used a whereas that is equal to 900 RPM, but for RON it is 600 RPM. Another property that is Anti knock index is also used in some country to get the knocking behaviour of the gasoline.

And this is defined by R+M by 2, research octane number plus motor octane number divided by 2 then we come to cetane number. So, cetane number is the property of diesel.

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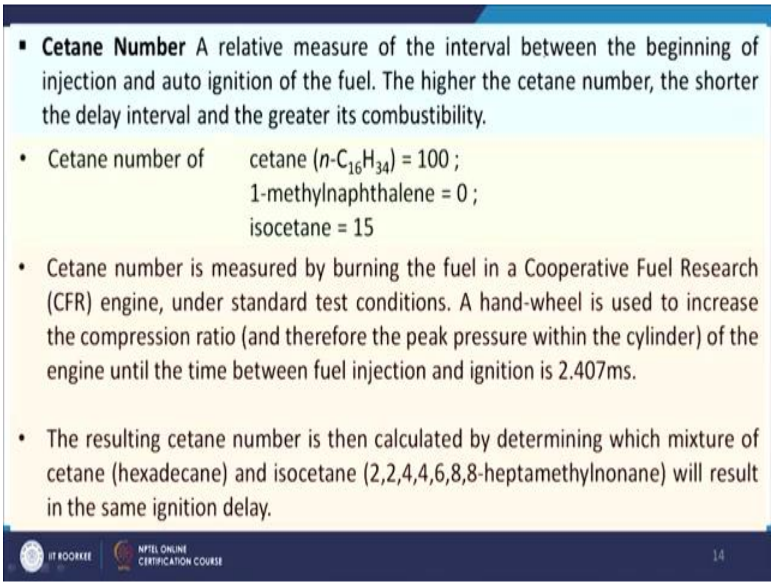

So, it is a relative measure of the interval between the beginning of injection and auto ignition. So, how much time it is late that is the indication of the cetane number and again like octane number there are two compounds here the cetane which is having 100 and 100 number and then for one methylnaphthalene it is zero. And isocetane is also 15 so 0 and 100 will be blending with different ratio and used in the specified machine and you will get the delay period and then that will be and the percentage of cetane will be the cetane number.

So, catane number is measured by burning the fuel in a cooperative fuel research engine under standard test conditions a wheel is their, hand wheel is used to increase the compression ratio and then this compression ratio is increased until the time between the fuel injections and ignition is 2.407 millisecond. So, then this cetane and 1-methylnaphthalene mixture is also used in the similar way on the same compression ratio, then time requirement is considered and then for the composition which is having the same time, in that mixture, the percentage of cetane will be the cetane number.

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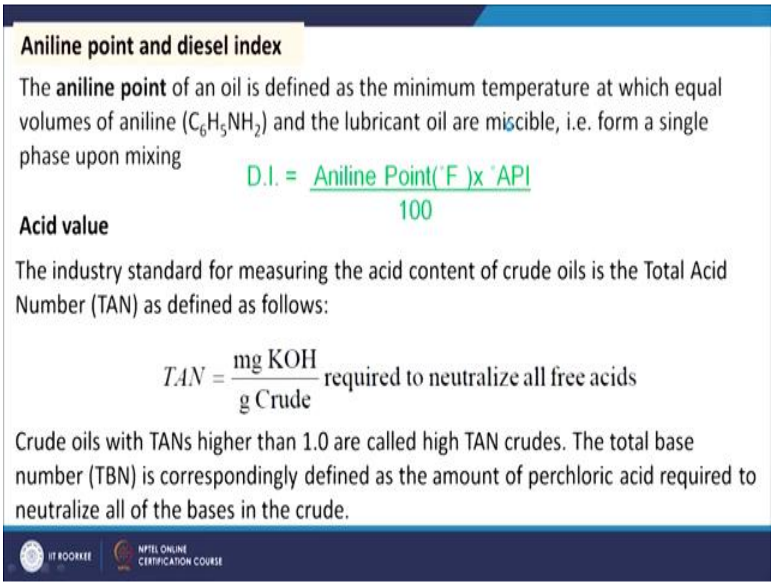

And another Aniline point and diesel index; So, for diesel cetane number is measured for other fuels like say lubricating oil etcetera for these diesel index is measured and diesel index is defined as aniline point in degree Fahrenheit into API gravity divided by 100. So aniline point is measured first then diesel index is measured. So, what is aniline point? It is a temperature at which equal volume of aniline and the lubricant oil will be mixed.

See if we get that temperature we will put it here. If we have the degree API of the fuel, then we will multiply it by it and divide by 100 will get the diesel index. So, next is acid value. So, crude also have some acids organic and inorganic acids may be available in it and total acid content we can measure by its titration with base solution. And it is defined as total acid number TAN that is equal to mgKOH required to neutralise all the free acids per one gram of crude.

So, this is our total acid number. Similarly, total base number is also determined by the titration using perchloric acid.

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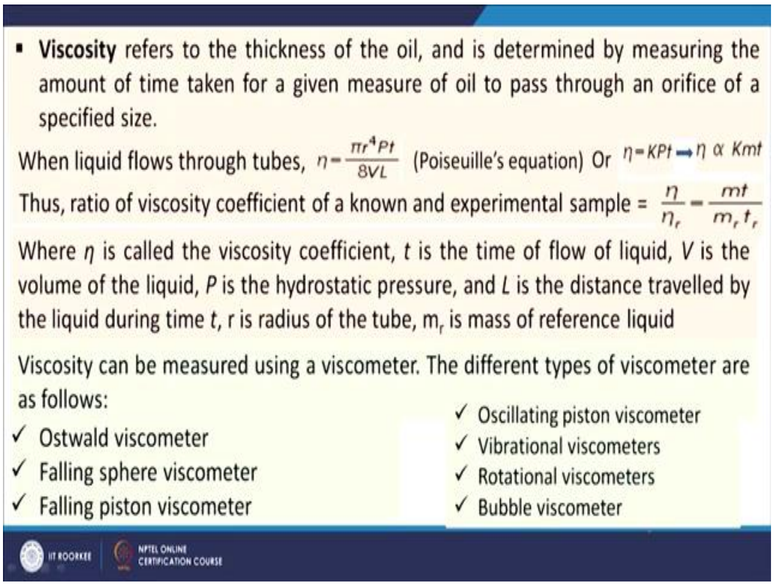

Viscosity is another property of the crude oil, which is very important for its transportation and for pumping purpose. As you know, the viscosity indicates the resistance and so, in one form layer flows on the other layer that is the fluid one fluid layer is flowing on the another layer that experienced resistance and that is related to the viscosity. So, it also represents the thickness of the oil and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size.

So, for the determination of viscosity, what happens for a simple arrangement we can make, we can pass the fluid through orifice and know what time it is taking we can measure it because this is a flow through a porous channel we can consider and in this case, we can use the Poiseuilles's equation that is $\eta = \pi r^4 Pt/8VL$ and we get η is viscosity coefficient.

And P is the hydraulic pressure and t is the time of falling and V is the volume of liquid collected an L is the distance travelled by the liquid during time t and r is the radius of the tube. So, in this formula, we can see the π, radius of that tube is fixed, V volume how much liquid you are collecting, that can also be targeted and fixed and then L is the length of the distance travelled by the fluid. So that L is also fixed for the system.

So we can get η = kPt. This P is nothing but related to P, the hydrostatic pressure it is proportional to Kmt we can get, because P proportional to m. Now, if we have 2 fuels one is standard known viscosity and another viscosity is not known, we are getting what is the time to fall certain distance through the orifice for both oil samples.

Then we will get the viscosity coefficient ratio by this $mt/m_r t_r$ where m_r is the reference mass of the reference fuel and t is the time required to travel the same distance by the reference oil and this is for our which I want to determine t the time required by the oil which we are interested to get the viscosity and mass is the mass of that oil for which we are interested to get the viscosity. So, now we can get the value of viscosity coefficient.

So this viscosity can be measured by different ways. As mentioned here, viscometer are there Ostwald viscometer, Falling sphere viscometer, falling piston viscometer, oscillating piston viscometer, vibrational viscometer, rotational viscometer, bubble viscometer.

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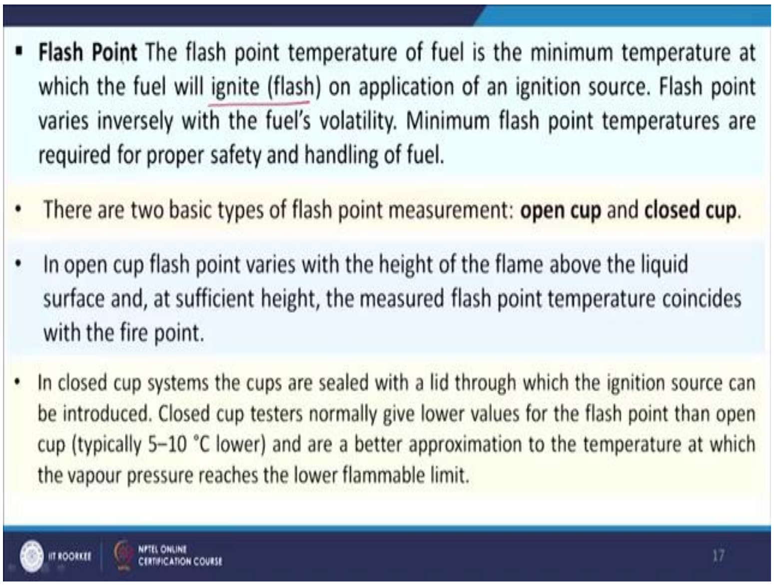

Another property is flash point. So, if we heat any fuel, it will produce vapours. So, if we can bring one matchsticks for ignition, immediately the temperature will come at which sufficient vapour will form and flash will take place at the first time. So, that temperature is called Flash point if we apply more heat and temperature will increase and more vapours will form and fire will take place and that time that temperature has a minimum temperature at which fire takes place that is called fire point.

So, Flash point and fire Point are the properties of the liquid fuels which are produced through refining of the petroleum crude and it is determined in an Open Cup system and closed cup system. In Open Cup system, the flash point varied with the height of the flame above the liquid surface and at sufficient time the measured flash point temperature coincides with the fire Point, but in case of closed cup, there is a lid and we get the; we bring the ignition source for a moment and we get the flash.

So, it has been shown that the value of flash point in case of closed cup is normally lower than that obtain through Open Cup and it is typically 5 to 10 degrees centigrade lower. Then asphalt properties, asphalt, which are present in the crude oil that will be available in the residue, vacuum residue and this is made of some polymeric compounds and it is aromatic rings are present in it as we discussed and it may be directly used.

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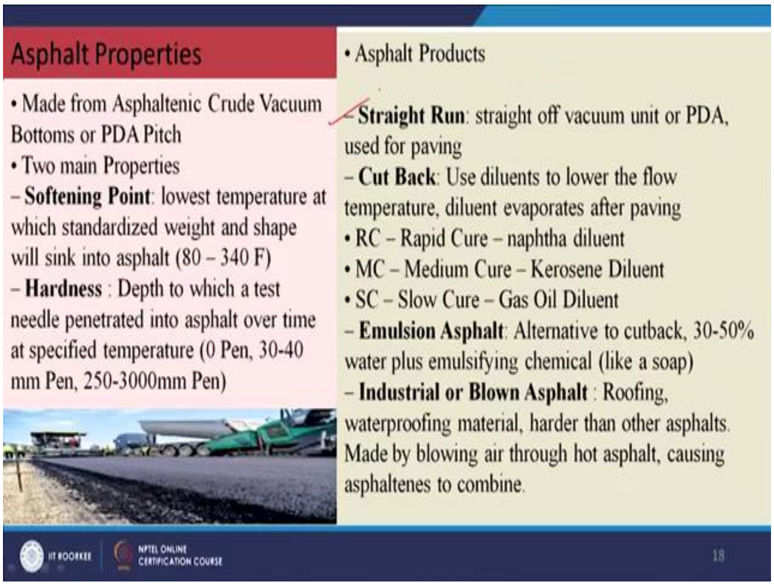

That is the straight run that means starting off vacuum unit or PDA propane deasphalting. So, vacuum residue we are getting that is directly we are using or we are separating the lighter part from it by propane deasphalting and using the asphalt. So, that asphalt is called straight run asphalt. So, Cut Back; so cut back we are using some solvent here. So rapid cut, a rapid cure RC that may be Naphtha diluent, when we use naphtha then that is called rapid cure.

We can use kerosene with asphaltene that is called medium cure and slow cure when gas oil is used. Apart from these emulsion asphalt is also available when the water is added with these 30 to 50% water plus emulsified chemicals then gives the emulsion asphalt and then industrial or blown asphalt another type of asphalt is also available, which is formed by the air blowing in hot asphalt and these asphalts that is industrial or blown asphalt these have some applications as your waterproofing material and it is harder than the asphalt.

So, it has some properties that is softening point and hardness these properties are measured to assess its quality, the softening point is a lowest temperature at which standardised weight and shape will sink into asphalt that is around say 80 to 340 Fahrenheit and hardness it is the depth to which a test needle penetrates into asphalt over a time at specified temperature as a certain condition is maintained and how many what is the depth penetrating needle is going inside that is the hardness related to hardness. Zero pen, 30 to 40 pen millimetre and 250 to 3000 millimetre pen is reported.

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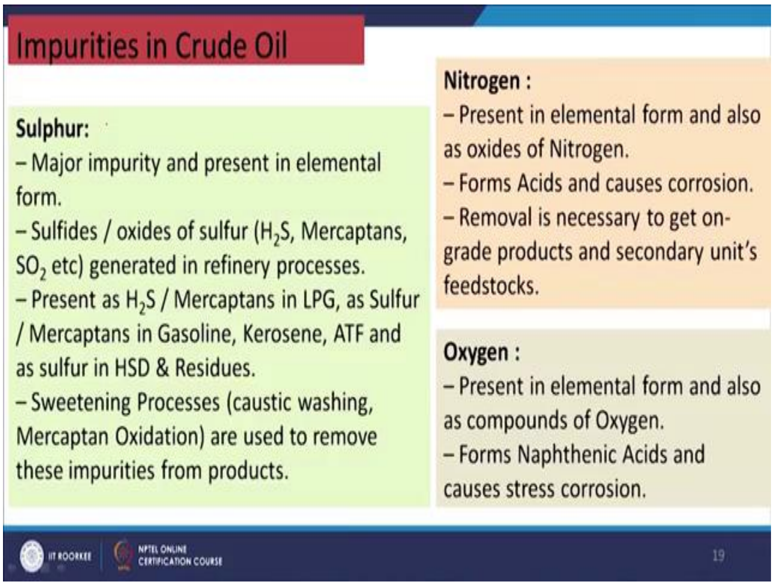

So, there are some impurities in the crude oil also like say sulphur, nitrogen and oxygen. So, the sulphur is present in elemental form or in case of sulphide or oxide form. Some organic sulphur is also present and those are called Mercaptans. So, different products have different types of sulphur as for example present H2S and Mercaptans in LPG, sulphur Mercaptans in gasoline kerosene ATFs.

And to remove the sulphur we can use some sweetening process that is caustic washing, mercaptan oxidation etc. And nitrogen present in elemental form and also as oxides of nitrogen and it forms acids and causes corrosion. So, removal is necessary to get on grade products and secondary units feedstock. And oxygen present in the elemental form and also as compounds of oxygen, it forms naphthenic acid and causes stress corrosion.

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Sulphur content range
Location wise

Low	Medium	High
Bony Lt., Nig. – 0.12	Olemeca – 0.8	Eocene, Wafra – 4.55
Challis, Aust – 0.07	Walia – 0.7	Kirkuk – 2.0
Aching, Chaina – 0.08	Syrian Lt. – 0.74	Jodhpur Ind. – 3.0
Siabarian, Russ. - 0.4		Quatar Export – 1.15
Brent, North Sea – 0.24	ABU Dhabi – 0.78	Ras Gharib – 2.41
Odavari Basin – 0.08	Oman – 0.79	Dubai – 2.0
Tapis, Malas. – 0.023		Isthamus – 1.4
Seberg, Oman – 0.32		Myril, Vanu. – 2.2
Bekapai, Indo. – 0.08		Belaym Egt. – 2.2
Mumbai High – 0.17		Arabian Hy. – 2.85
N – Gujarat – 0.17		Basrah Hy. – 3.5
S – Gujarat – 0.04		Basrah Lt. – 1.95
Assam Mix – 0.24		Zakum – 1.88
Narimanam – 0.08		Kuwait – 2.6

Low Sulphur	Upto 0.5 % Wt
Medium	0.5 – 0.8 % Wt
High	> 0.8 % Wt

Sulphur content is may vary, it may be low sulphur up to 0.5% it may be medium 0.5 to 0.8% or maybe high greater than 0.8% these are some example of different crude different crude oils and different sulphur content. So, you get medium and high as well as low. So, crude oil and their sulphur content.

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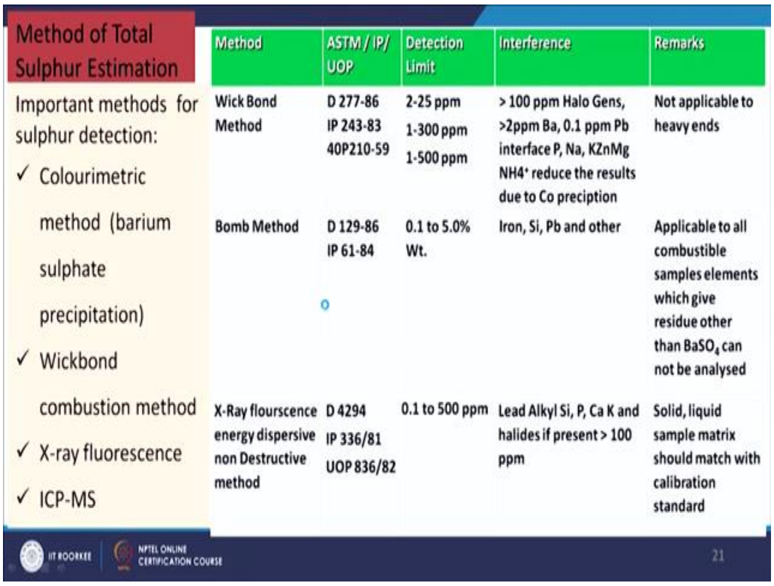

Method of Total Sulphur Estimation

Important methods for sulphur detection:
- ✓ Colourimetric method (barium sulphate precipitation)
- ✓ Wickbond combustion method
- ✓ X-ray fluorescence
- ✓ ICP-MS

Method	ASTM / IP/ UOP	Detection Limit	Interference	Remarks
Wick Bond Method	D 277-86 IP 243-83 40P210-59	2-25 ppm 1-300 ppm 1-500 ppm	> 100 ppm Halo Gens, >2ppm Ba, 0.1 ppm Pb interface P, Na, KZnMg NH4⁺ reduce the results due to Co preciption	Not applicable to heavy ends
Bomb Method	D 129-86 IP 61-84	0.1 to 5.0% Wt.	Iron, Si, Pb and other	Applicable to all combustible samples elements which give residue other than $BaSO_4$ can not be analysed
X-Ray flourscence energy dispersive non Destructive method	D 4294 IP 336/81 UOP 836/82	0.1 to 500 ppm	Lead Alkyl Si, P, Ca K and halides if present > 100 ppm	Solid, liquid sample matrix should match with calibration standard

Method of sulphur determination there are a number of methods. So, some important are colourimetric method or barium sulphate method it is also known as and Wickbond method and the combustion method this is and then X-ray fluorescence method and ICP-MS. So, these are the different methods I have mentioned here. These are the number, test number and these are detection limit and here are some interference which can compounds are elements which can interfere on the detection.

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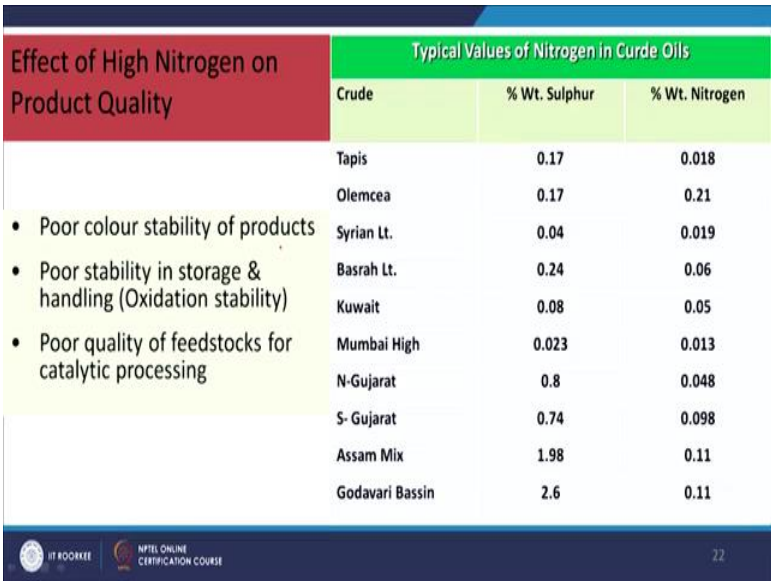

Effect of High Nitrogen on Product Quality

- Poor colour stability of products
- Poor stability in storage & handling (Oxidation stability)
- Poor quality of feedstocks for catalytic processing

Typical Values of Nitrogen in Curde Oils

Crude	% Wt. Sulphur	% Wt. Nitrogen
Tapis	0.17	0.018
Olemcea	0.17	0.21
Syrian Lt.	0.04	0.019
Basrah Lt.	0.24	0.06
Kuwait	0.08	0.05
Mumbai High	0.023	0.013
N-Gujarat	0.8	0.048
S- Gujarat	0.74	0.098
Assam Mix	1.98	0.11
Godavari Bassin	2.6	0.11

So, for the nitrogen, so, it is poor colour stability of production, nitrogen gives poor colour stability of products; it is poor stability in storage and handling also and poor quality of feedstocks for catalytic processing. So, removal of nitrogen is important and required. So, now, we see the different crude and presence of nitrogen and sulphur in it. And nitrogen can be determined by some methods.

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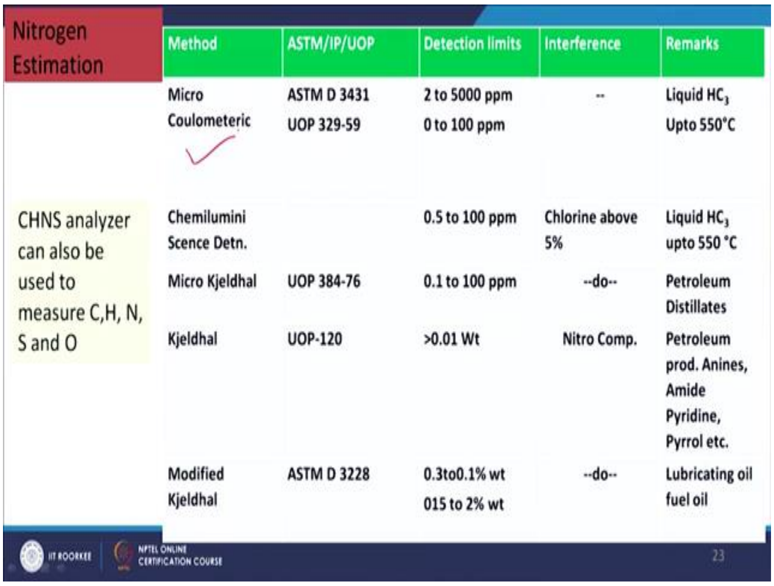

Nitrogen Estimation

CHNS analyzer can also be used to measure C,H, N, S and O

Method	ASTM/IP/UOP	Detection limits	Interference	Remarks
Micro Coulometeric	ASTM D 3431 UOP 329-59	2 to 5000 ppm 0 to 100 ppm	--	Liquid HC_3 Upto 550°C
Chemilumini Scence Detn.		0.5 to 100 ppm	Chlorine above 5%	Liquid HC_3 upto 550 °C
Micro Kjeldhal	UOP 384-76	0.1 to 100 ppm	--do--	Petroleum Distillates
Kjeldhal	UOP-120	>0.01 Wt	Nitro Comp.	Petroleum prod. Anines, Amide Pyridine, Pyrrol etc.
Modified Kjeldhal	ASTM D 3228	0.3to0.1% wt 015 to 2% wt	--do--	Lubricating oil fuel oil

There is micro coulometric, chemillumini scence, micro kjedhal and modified kjedhal. So, these are the methods through which nitrogen is determined and different products are used for this purpose and detection limits are also given. Apart from this CHNS or elemental analysis can be done to measure the carbon, hydrogen, sulphur, nitrogen and oxygen of the crude oil sample. Upto this in this class on the characteristics of crude oils and petroleum products, thank you very much for your patience.