Mechanical Characterization of Bituminous Materials

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Lecture No 19
Chemical composition of bitumen Part-03

So we will now continue with the fractionation of bitumen. In the earlier lectures we have seen about the introduction related to the chemical composition of bitumen, where is information related to chemical composition used, what are the different scales in which it can be characterized, we saw the elemental level and the molecular level. So in this lecture we will be discussing about the fractionation techniques which are used to classify bitumen.

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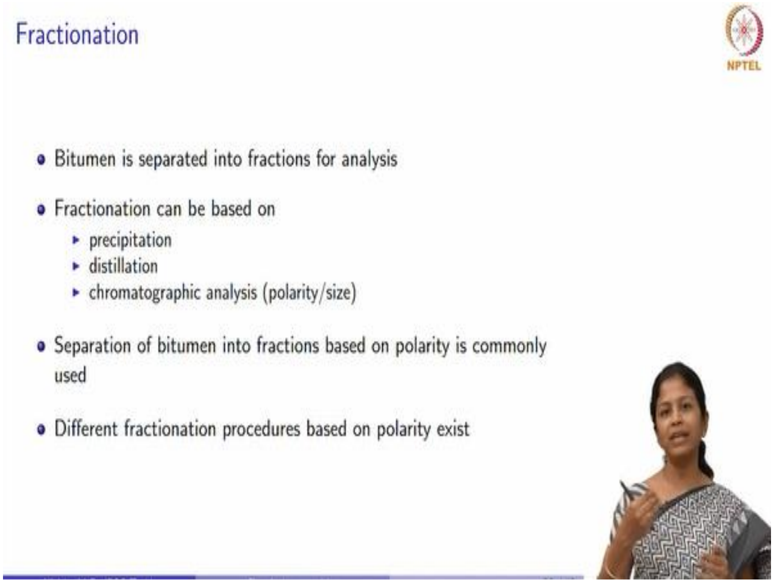

Fractionation

- Bitumen is separated into fractions for analysis
- Fractionation can be based on
  - precipitation
  - distillation
  - chromatographic analysis (polarity/size)
- Separation of bitumen into fractions based on polarity is commonly used
- Different fractionation procedures based on polarity exist

So what are these fractionations? Bitumen is now separated into different fractions, the separation can be based on precipitation or distillation or chromatographic analysis. So we identify some property of this material and separate molecules which have identical property. In the previous lecture we saw that, we were separating molecules based on their molecular size and then we calculated the molecular weight.

Here we are going to separate fractions based on their polarity. So what do we mean by polarity? How reactive they are? How affinitive they are to a particular solvent. So that is the parameter which is used here to separate fractions and this separation of fractions based on polarity is very commonly used and these solubility based techniques are relevant even today.

There are different fractionation procedures which exist today and we will look at each of them.

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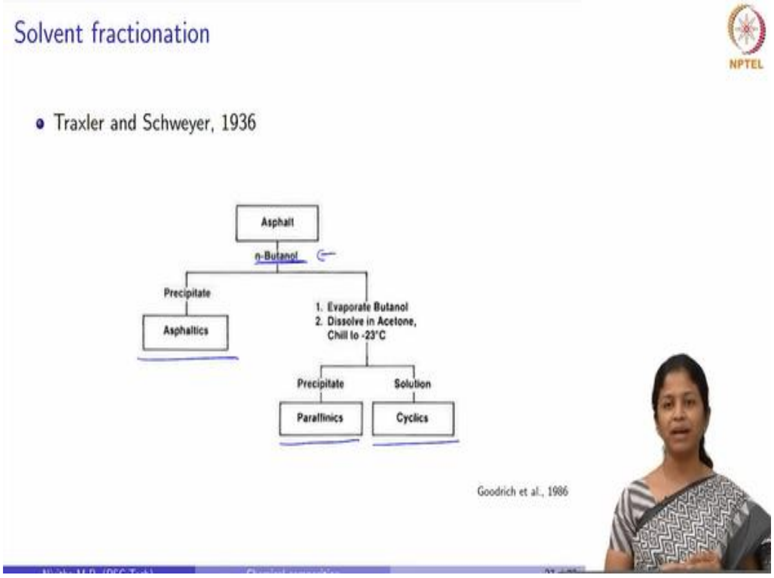

Solvent fractionation

- Traxler and Schweyer, 1936

Asphalt

n-Butanol

Precipitate

Asphaltics

1. Evaporate Butanol
2. Dissolve in Acetone, Chill to -23°C

Precipitate

Paraffinics

Solution

Cyclics

Goodrich et al., 1986

The first fractionation procedure is by Traxler and Schweyer in the year 1936. So what is this fractionation procedure is. You take bitumen. We dissolve it in some particular solvent and then we allow it to precipitate. Whatever is the precipitate that we are getting here is called as asphaltics. So you would have heard the term asphaltenes right? So that is the next version of this term asphaltics. Initially this asphaltene fraction was referred as asphaltics.

Further it was coined as asphaltenes and that terminology is used even now. So the insoluble fraction when it is mixed with the solvent is called as asphaltics and whatever is the remaining part in the solution, in that the butanol is evaporated, here we have to see that n butanol is used as a solvent. So this solvent is evaporated and then the remaining material is dissolved in acetone after dissolving it in acetone it is chilled to -23 degree Celsius. After chilling it to -23 degree celsius whatever is precipitated is called as paraffinics.

So these paraffinics crystallize and hence they kind of precipitate when it is chilled to sub-zero temperatures. The remaining thing in the form of solution are called as cyclics. So we have a procedure where we dissolve bitumen in a solvent; n- butanol is a solvent which is used here and then whatever is precipitated initially we call it as asphaltics and in the solution we evaporate the solvent, mix it with acetone and then we chill it to -23 degree celsius.

So whatever is precipitated in that case is called as paraffinics and the remaining are called cyclics. So we have three fractions based on this procedure. So this was the initial procedure which was given by Traxler and Schweyer in the year 1936.

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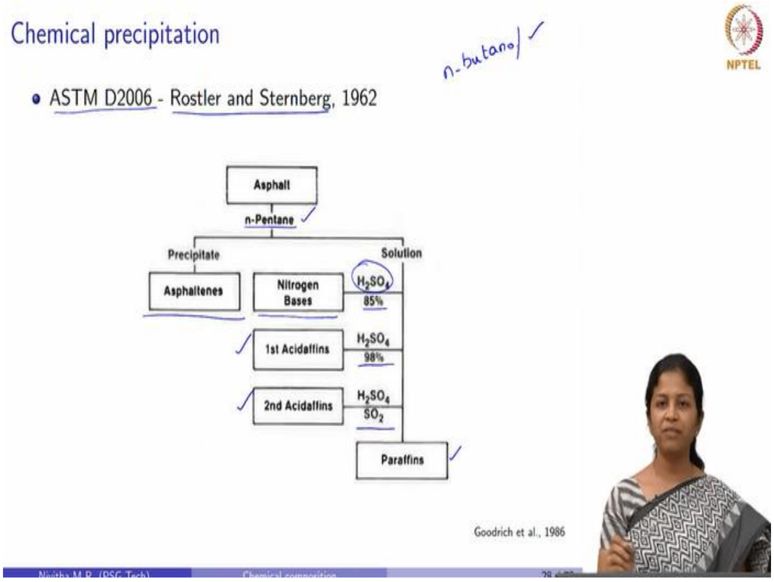

Chemical precipitation

n-butanol ✓

- ASTM D2006 - Rostler and Sternberg, 1962

Asphalt

n-Pentane ✓

Precipitate

Solution

Asphaltenes

Nitrogen Bases

H_2SO_4 85%

✓ 1st Acidaffins

H_2SO_4 98%

✓ 2nd Acidaffins

H_2SO_4 SO_2

Paraffins ✓

Goodrich et al., 1986

The next procedure which is based on chemical precipitation was given by Rostler and Sternberg in the year 1962. So this was part of this particular standard ASTM D2006. So here also we do identical kind of procedure. We take bitumen we dissolve it in a particular solvent. So here we can see n-pentane is used as a solvent. In the previous case, n-butane was used as a solvent. Here we are using and pentane as a solvent and after mixing bitumen in the solvent whatever is precipitated is called as asphaltenes.

The remaining part in the solution form is added with H_2SO_4 sulphuric acid at a concentration of 85%. So after precipitating asphaltenes the solution is added with sulphuric acid at a concentration of 85 %. So in that case whatever is precipitated is called as nitrogen bases. Whatever is not precipitated again in the solution form is added with again sulphuric acid but at a higher concentration 98 %.

So then what is precipitated is called as first acidaffins. After that whatever is still remaining in the solution form is added with sulphuric acid and sulphur dioxide and whatever is precipitated in this case is called as second acidaffins. So after doing all these things whatever still remains in the solution form are called as paraffins, right? So we have five fractions based on this particular procedure.

Asphaltenes again the precipitate. But whatever is in the solution form is classified differently. We have nitrogen bases, first acidaffins, second acidaffins and paraffins. We need to note that the asphaltics what we got in the previous case is not similar to the asphaltenes, what we have seen here. It is just not with the name alone but it depends upon the dissolving capacity of the solvent. In the previous case we used n-butanol as the solvent but in this case we are using n-pentane as the solvent.

So as the number of carbon atoms increase, the solvent becomes more strong in nature. Say n-pentane is more strong in nature compared to n-butanol. So this n-pentane can dissolve more number of insoluble fractions compared to n-butanol. So the amount of asphaltenes fraction that we are getting here and its properties are different in this procedure compared to the previous procedure.

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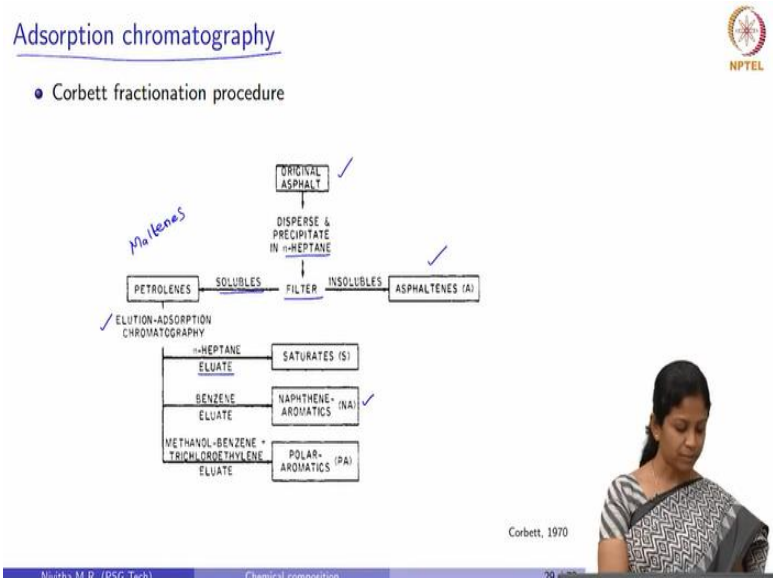

Adsorption chromatography

- Corbett fractionation procedure

Corbett, 1970

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Next we have another procedure which was proposed by Corbett, it is called as Corbett fractionation procedure. It is based on an adsorption chromatographic technique. I will tell you what this technique is; we will be seeing in detail about this particular technique. But for now let us look into this Corbett fractionation procedure. So here we have this original asphalt the bitumen which is dissolved in n-heptane, so we are using n-heptane as a solvent here.

So we can see that as the procedures come down we are using stronger solvents here. Whatever is the insoluble again it is called as asphaltenes similar to the previous cases. When you dissolve it in a solvent the insoluble fraction which immediately kind of settles down are called as asphaltenes. So these asphaltenes are higher molecular weight compounds and they try to easily separate out from the remaining fraction of bitumen.

So the insoluble fraction is called as asphaltenes; the soluble fraction is called as petrolenes. It is also called as maltenes, These petrolenes can also be called as maltenes. So generally people divide the composition of bitumen into asphaltenes and maltenes or asphaltenes and petrolenes. Now this petrolene fraction is subjected to an elution adsorption chromatography.

Again we will see what this is; just hold on it for a while. So then n-heptane is first used as an eluate. So we have seen that we have initially dissolving it in n-heptane, so we are using the same solvent, mixing it with the solution and whatever is coming out are called as saturates. So initial eluate is the n-heptane and then we are using benzene as an eluate. So whatever is coming out is called as naphthene aromatics.

Then we are using methanol benzene plus trichloroethylene as a solvent and then whatever is eluting is called as polar aromatics. So here we are having three different fractions saturates, naphthene aromatics and polar aromatics. So initially n-heptane is used as a solvent and whatever is removed it is called as saturates. Then benzene is used as a solvent and whatever is removed is called as naphthene aromatics.

Finally a higher concentration solution methanol, benzene and trichloroethylene is used right? So this is the original fractionation procedure which was proposed by Corbett.

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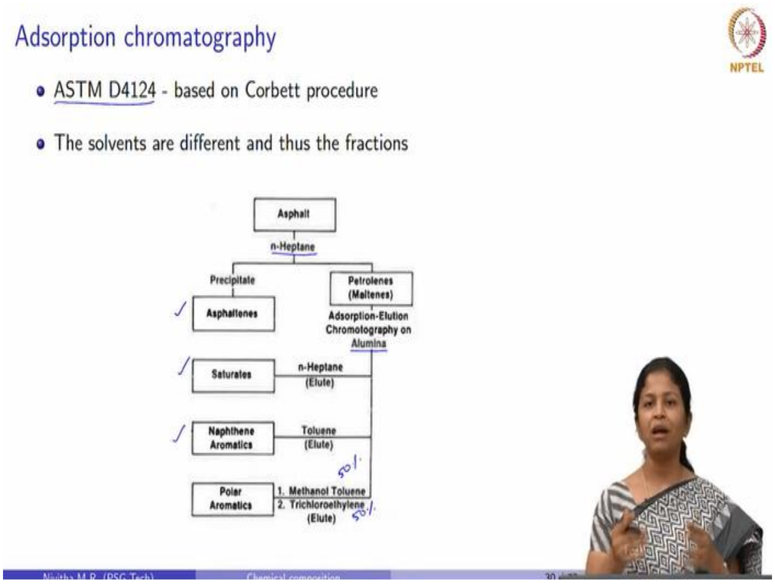

Adsorption chromatography

- ASTM D4124 - based on Corbett procedure
- The solvents are different and thus the fractions

This was later revised into an ASTM standard so we have this standard ASTM D4124; this is based on the Corbett procedure. So here again it is kind of identical; we have asphalt, we are using n-heptane as a solvent, we are dissolving in it.

Whatever is precipitated is called as asphaltenes and whatever is in the solution form we call it is called as petrolenes or here they have defined it as maltenes. It is in subjected to adsorption elution chromatography on alumina. So here alumina is used as a chromatographic column. So they have specified the material also. So in the first cut n-heptane is used as a solvent and whatever we get initially is saturates.

Then toluene is used as a solvent whatever we get is naphthene aromatics finally methanol toluene and trichloroethylene is used as a solvent. So here they have specified methanol toluene is 50% and trichloroethylene is 50%. So in the previous case we see they have used benzene as a solvent here. So due to the hazardous nature of benzene, benzene is restricted from using in laboratory and that was replaced by toluene.

So that is the major difference between the original Corbett procedure and the procedure which is given in ASTM D4124. There is something which is very important when you read ASTM D4124. They say that there is nothing called as a repeatability for this kind of procedure because we know that bitumen is heterogeneous but it kind of forms a homogeneous material right?

So because of that if we take a sample and then do this procedure on one material, we will get some results. If you are repeating the same procedure on an another sample it is not necessary that we need to get exactly the same numbers. There will be some variability because this procedure is not a particular standardized procedure; it works on adsorption chromatography.

So when we see how this adsorption chromatography works then we will understand why we will not get repeatable results for two kind of specimens of the same material.

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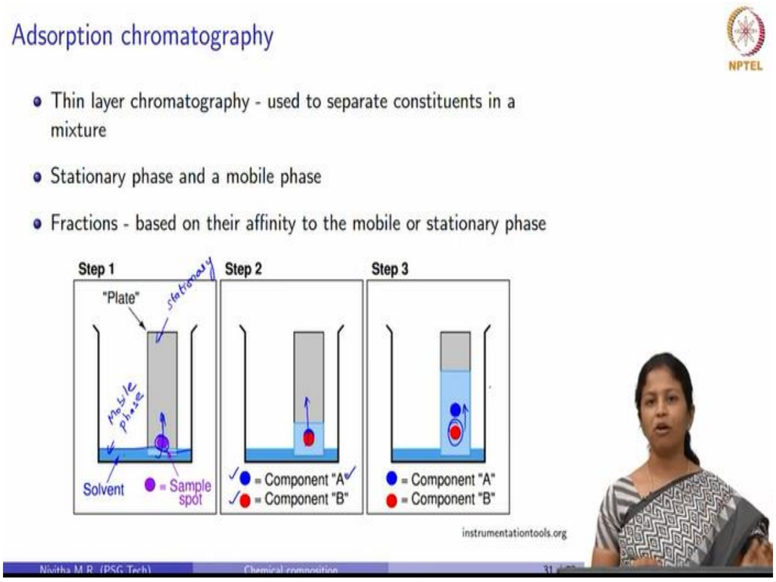

Adsorption chromatography

- Thin layer chromatography - used to separate constituents in a mixture
- Stationary phase and a mobile phase
- Fractions - based on their affinity to the mobile or stationary phase

So this is how an adsorption chromatography works; it is also called as a thin layer chromatography. So what is this thin layer chromatography? It is used to separate constituents in a mixture right? So we have a mixture of we said that we have a mixture of four different materials; let us just stick on to the Corbett procedure now, we have four fractions here; what are they? asphaltenes, naphthene aromatics, polar aromatics and saturates.

So we have four fractions, now we need to separate these four fractions right? So for that we use an adsorption chromatography. So here we have two phases; a stationary phase and a mobile phase. So this column which is present here is a stationary phase and we also have a mobile phase which is this solvent here right? The solvents are separated based on their affinity towards the solvent phase or the mobile phase.

So that is the basic principle which is used in this particular procedure to separate fractions. So what happens here is, the solvent is placed as a spot here so we have the stationary phase so at the bottom of the stationary phase we have this solvent which is placed as a spot. Now I'm sorry we have this sample which is placed as a spot and then we have a solvent which is filled here the blue colour one what we see here right that is the solvent.

Now this solvent tries to rise up this chromatographic column because of capillary action. So when this tries to move up this chromatographic column it dissolves this sample and it tries to carry this sample along as it moves up the chromatographic column. Now, how is mixture separated in this case? So we said that the different components of this mixture can have different affinities towards the stationary phase and towards the mobile phase.

Now, if this one component of this mixture has more affinity towards the solvent phase it will try to move along with the solvent up the chromatographic column. Whereas another component can have relatively lesser affinity towards the solvent and more affinity towards the stationary phase, so in that case it will rise up only slowly in the chromatographic column. So you can see here it has two components this sample spot which is in purple colour has two components here, one is component A and the other one is component B.

So we can see that they start rising at different rates in the chromatographic column. So this one in blue colour has more affinity towards the solvent which is the mobile phase whereas the one in red colour has more affinity towards the stationary phase which is the alumina column which is used here. So depending upon the relative affinity of the different components they rise up the chromatographic column at different rates and by this process we will be able to separate out different fractions.

So here in this third image, step three you can see it clearly, the one in blue colour has risen up whereas the other one is still remaining at a lower level. So this will be eluted out of the chromatographic column initially but this will happen at a later time. So at time interval we will be getting components at different time interval so by this manner we can separate out the fractions.

So this is the principle which is used in the Corbett procedure to separate out all the four fractions or the three fractions in fact because the asphaltene fraction is initially precipitated out separately so only to separate the saturates, naphthene aromatics and polar aromatics, we are using this adsorption chromatography.

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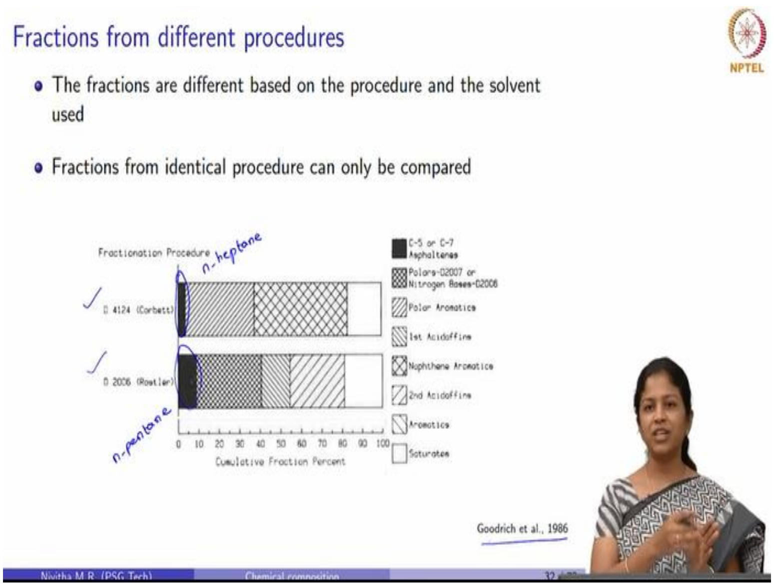

Fractions from different procedures

- The fractions are different based on the procedure and the solvent used
- Fractions from identical procedure can only be compared

Goodrich et al., 1986

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Now we have asphaltenes in all these three procedures we have asphaltenes from the Traxler and Schweyer process, we have asphaltenes from the Rostler and Sternberg process; we also have asphaltenes from the Corbett process or the ASTM D4124 procedure. Now can I compare all the four asphaltenes? I said initially right? We cannot make such comparison because it depends upon the strength of the solvent to dissolve the components in bitumen.

So we said n-heptane is related has higher strength to dissolve the components so the amount of asphaltene fraction here will be very less compared to the use of n-pentane. So the amount of asphaltenes we get in the case of n-butanol as a solvent will be high compared to the percentages of asphaltenes we get when you use n-heptane as a solvent. So this study by Goodrich et al. compares the different fractions from two different procedures.

So we see that the first one is ASTM D4124 based on the Corbett procedure and the second one is D2006 based on the Rostler procedure. You can see how the again the fractions are different right? In Rostler we defined five fractions; in Corbett we have four fractions; so again the fractions are going to be different. Let us just compare the asphaltenes fraction alone. Like I mentioned earlier the amount of asphaltene fraction in the Corbett procedure is relatively lower compared to that what we get from the Rostler procedure.

So this is because here we use n-heptane as the solvent whereas here n-pentane is used as the solvent. So depending upon that we will get different fractions. So the ultimate point which we are trying to convey here is different fractionation procedures use different solvents and the procedures are completely different. So all of these fractions are completely solubility based, so how much this particular fraction can dissolve in a particular solvent.

So if I change the solvent, the affinity is going to change so my proportions will be completely different. So only when I use a particular solvent based on a particular procedure then we will be able to compare these fractions of two different materials. So if I use the standard Corbett procedure given in ASTM D4124 using n-heptane as a solvent and all the other solvents which were described earlier, then I can compare the four fractions from two different materials.

If I change the solvent or any of the steps which is given in the procedure, then I will not be able to compare across these different fractions obtained for two different samples. So this we need to keep in mind when we are looking into these fractions for different samples. It is very convenient to represent the chemical composition of bitumen using these fractions. Even now, people prefer this as a very convenient method to represent the change in chemical composition of two different samples, but when we do that we need to make sure on what procedure these fractions were evaluated.

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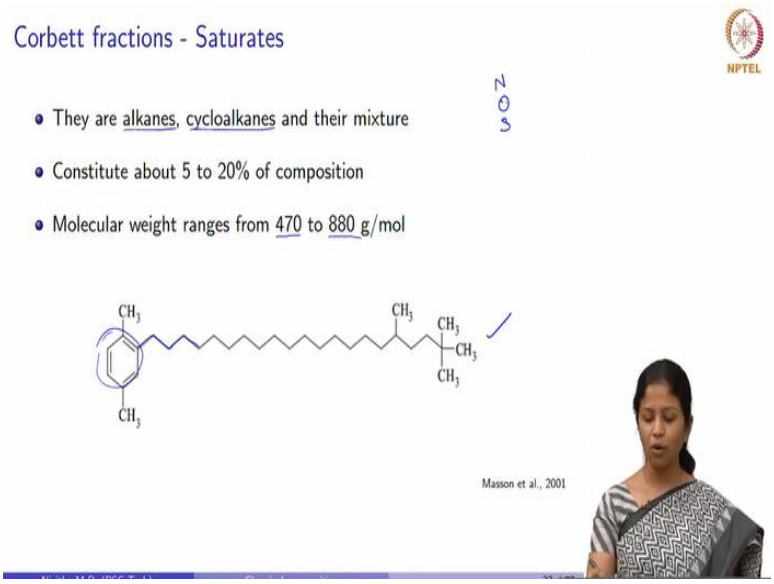

Corbett fractions - Saturates

- They are alkanes, cycloalkanes and their mixture
- Constitute about 5 to 20% of composition
- Molecular weight ranges from 470 to 880 g/mol

Masson et al., 2001

Next we will define what are these four fractions? because the Corbett procedure is what is commonly used and we said we have four fractions. Let us just see at the molecular level what these four fractions are composed of. Let us begin with saturates; they are composed of alkanes right? By this time we know what these alkanes are; they are linear long-chain compounds;

we also have cycloalkanes. So we said again rate they form into cyclic structures but without an inner ring core and also their mixture right? Again this is a hypothetical structure which was given by Masson et al. We can see they are composed of mostly linear long-chain but they also have some amount of aromatic content which is present here. They constitute about 5 to 20% of the composition of bitumen and the molecular weight here ranges from 470 to 880 gram per mole.

This is again a range; it can vary from one end to another depending upon the type of bitumen we use. So this is the first fraction; saturates which are only linear compounds; we can see there are no hetero atoms here, no carbon, no nitrogen, no oxygen; so none of these again no sulphur none sorry no nitrogen, no oxygen, no sulphur none of these elements are present in this particular fraction.

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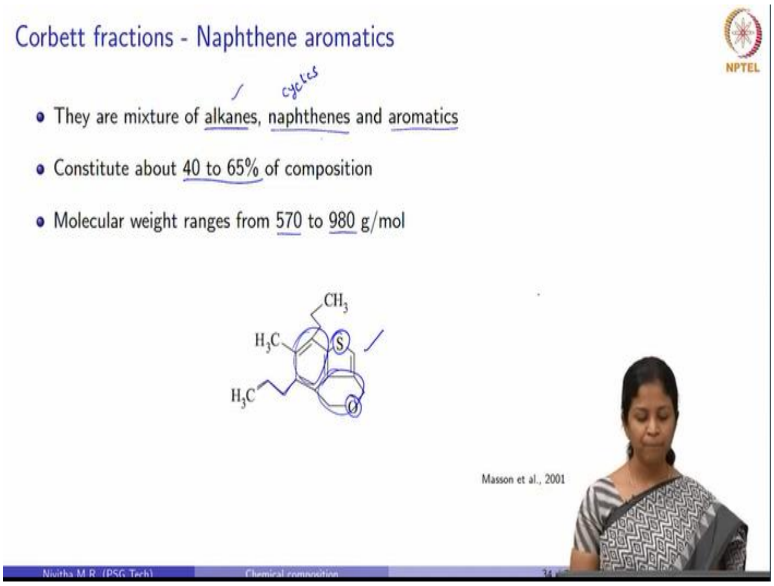

Corbett fractions - Naphthene aromatics

cyclics

- They are mixture of alkanes, naphthenes and aromatics
- Constitute about 40 to 65% of composition
- Molecular weight ranges from 570 to 980 g/mol

Masson et al., 2001

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Next we move on to the next fraction which is naphthene aromatics. These naphthene aromatics are a mixture of alkanes, naphthenes and aromatics. Again these naphthenes are nothing but cyclics right? So they also are composed of alkanes, naphthenes and aromatics but they have more proportion of alkanes compared to these two fractions and they constitute about 40 to 65% of the composition in bitumen and the molecular weight here ranges from 570 to 980 gram per mole.

So you can see this again hypothetical structure of a naphthene aromatic, we can see it is composed of some alkanes it also has some amount of naphthenes it also has aromatics it has some amount of hetero atoms also. You can see oxygen and sulphur present here very small percentages compared to the other two fractions, polar aromatics and asphaltenes. So this is the composition of naphthene aromatics.

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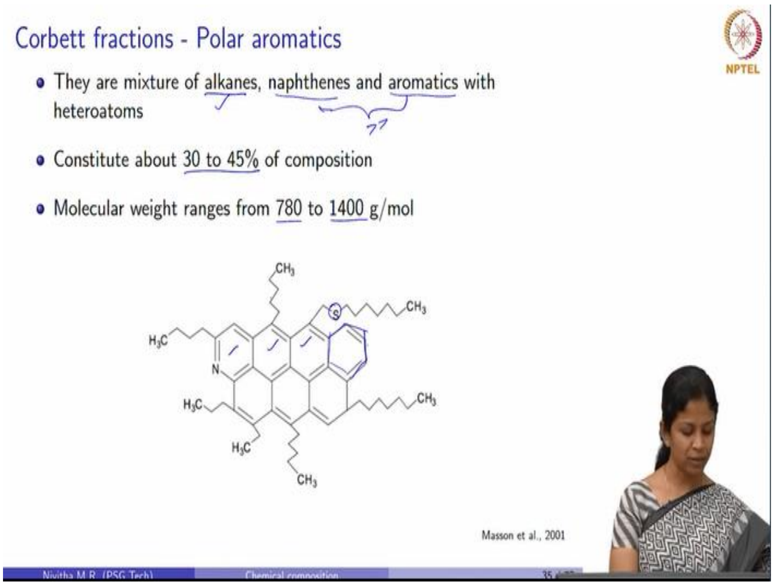

Corbett fractions - Polar aromatics

- They are mixture of alkanes, naphthenes and aromatics with heteroatoms
- Constitute about 30 to 45% of composition
- Molecular weight ranges from 780 to 1400 g/mol

Masson et al., 2001

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These polar aromatics are again a mixture of alkanes, naphthenes and aromatics. Similar to the previous case. In the previous case also we defined only these three; so here also it is composed of these three compounds but then the naphthene and aromatics are present in higher percentages. So this is present in higher percentage compared to alkenes and they constitute about 30 to 45 % of the composition.

Again here, the molecular weight ranges from 780 to 1400 gram per mole. If you look at this structure we can see they have more amount of aromatics which is present here all these rings which we can see here right? They have more amount of aromatics, they also have alkanes, they also have hetero atoms and you can see the molecules tend to get bigger right? So these are the polar aromatics fraction.

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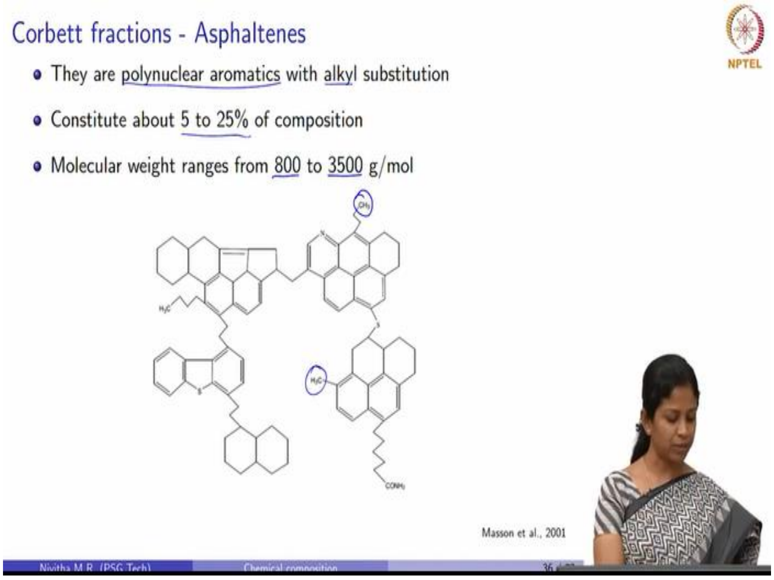

Corbett fractions - Asphaltenes

- They are polynuclear aromatics with alkyl substitution
- Constitute about 5 to 25% of composition
- Molecular weight ranges from 800 to 3500 g/mol

Masson et al., 2001

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And finally the asphaltene fraction, so these asphaltenes are polynuclear aromatics with alkyl substitution. So it is like they are a very big molecule not with a single nucleus but they have many nucleus, so that is what is called as a poly nuclear aromatic with alkyl substitution. So they have some alkyl chains which are present here and they constitute about 5 to 25% of composition.

When you look at you know different crudes or chemical composition techniques on bitumen people usually tend to separate out asphaltenes and study asphaltenes in detail because these are the higher molecular weight compounds and people believe that they tend to influence the physical properties more compared to the other three fractions. That is one reason; the other reason is these asphaltenes can be easily separated out because we dissolve it in a solvent whatever is precipitated is called as asphaltenes.

So it is easy to separate out this fraction so because of these two reasons asphaltene is one of the most commonly studied components of bitumen and we can see the molecular weight here ranges from 800 to 3500. So they are really, really big molecules, so this is the chemical composition of all these four fractions which are present in bitumen. Again all of them are hypothetical; people have some measurements in relation to all of them but nobody has any verified structure for each of this fraction.

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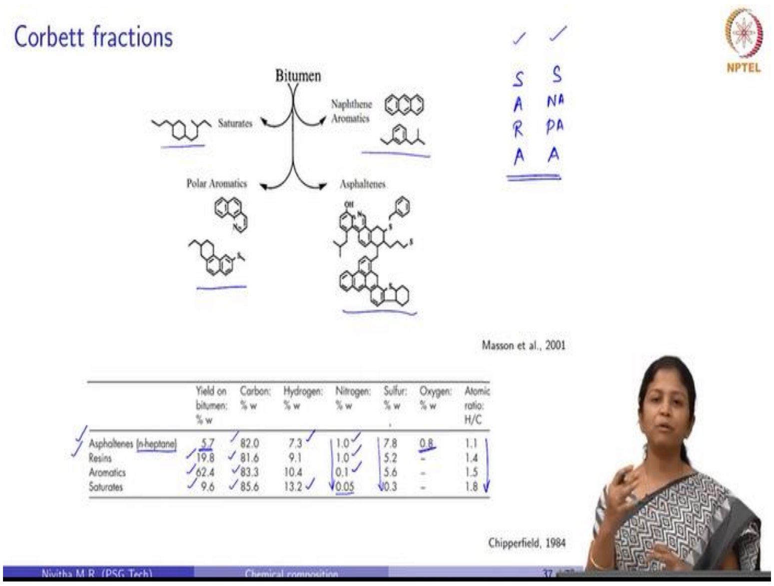

Corbett fractions

Masson et al., 2001

	Yield on bitumen: % w	Carbon: % w	Hydrogen: % w	Nitrogen: % w	Sulfur: % w	Oxygen: % w	Atomic ratio: H/C
Asphaltenes (n-heptane)	5.7	82.0	7.3	1.0	7.8	0.8	1.1
Resins	19.8	81.6	9.1	1.0	5.2	-	1.4
Aromatics	62.4	83.3	10.4	0.1	5.6	-	1.5
Saturates	9.6	85.6	13.2	0.05	0.3	-	1.8

Chipperfield, 1984

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So in summary we will see bitumen has saturates we have seen what they are; naphthene aromatics, polar aromatics and asphaltenes. We can see how the size of the molecule increases from saturates to asphaltenes. This is a study in which they have said, what is the percentage of carbon, hydrogen, nitrogen, sulphur, oxygen and this hydrocarbon ratio in these four fractions.

So we have asphaltenes, they are specific here asphaltenes which are insoluble in n-heptane as a solvent. So this is called as n-heptane asphaltenes that is how they are defined; n-heptane asphaltenes and n-pentane asphaltenes specifying what is the solvent which is used here and they have also said resins, these resins are nothing but the polar aromatics fraction. So these polar aromatic fraction in some literature is also referred as resins.

So this comes from crude oil literature where they have SARA fraction, saturates, aromatics, resins, asphaltenes right? Similar to saturates, naphthene aromatics, polar aromatics and asphaltenes. Again the fractions are similar but we have to mind what is the solvent and what is the procedure which is used in both the cases. Now if we see what is their percentage contribution in the whole bitumen?

We can see asphaltenes are present only as 5 % right? Only 5 % of the whole bitumen is composed of asphaltenes. We have resins about 20 % we have aromatics about 60 % and saturates as 10 %. So this is the contribution; again this is specific to this particular study when we have different type of bitumen this can vary over a range.

And we see what is the carbon which is present here; the percentage weight of carbon; the asphaltenes have 82 % carbon, resins 81, aromatics 83 and saturates have higher percentage of carbon about 85 % of carbon is present in the saturates fraction and when you look at hydrogen the amount of hydrogen is very less in the case of asphaltenes whereas it is high in the case of saturates.

So previously we said right the number of hydrogen atom is less in a bigger molecule because one bond is always taken by one or many bonds are taken by a carbon atom. So in a big molecule the amount of hydrogen atoms are lesser. So when we look at this hydrocarbon ratio it keeps increasing for materials with larger molecules lesser hydrogen content the hydrocarbon ratio is lesser whereas in the case of saturates fraction we can see this hydrocarbon ratio is about 1.8 %.

Now let us look at the hetero atoms; we see that nitrogen is about 1 % in the case of asphaltenes and resins, 0.1 % in the case of aromatics and 0.05 % in the case of saturates. So we said that this saturates fraction may have very small amount or traces or may not have any of these hetero atoms at all. So like we said the hetero atom nitrogen content keeps decreasing as we move from asphaltenes to saturates.

The next fraction is sulphur. Again in sulphur, we can see the sulphur content reduces as we move from asphaltenes to saturates, the oxygen content they were observed only in the asphaltenes fraction and in this study they did not observe oxygen in the remaining three fractions. So these asphaltene as proposed has more number of hetero atoms and they seem to have bigger molecules.

So only based on some understanding like this people tend to propose hypothetical structures for all these four fractions.

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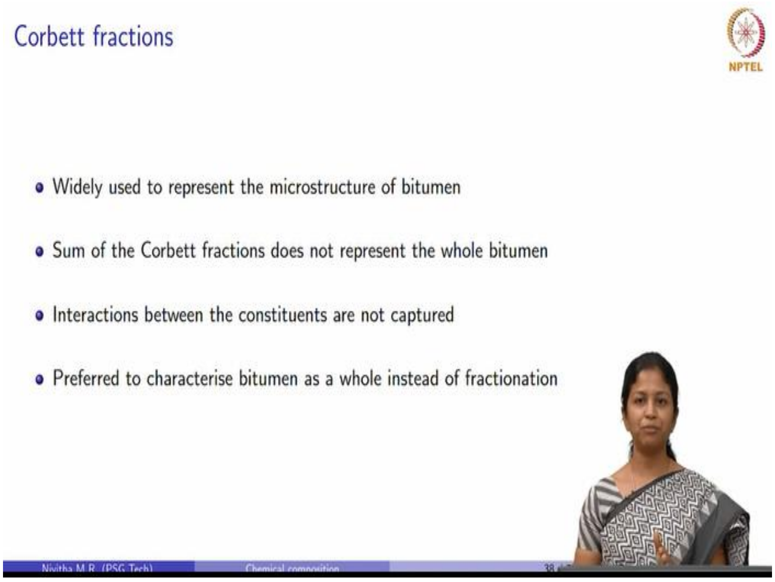

Corbett fractions

- Widely used to represent the microstructure of bitumen
- Sum of the Corbett fractions does not represent the whole bitumen
- Interactions between the constituents are not captured
- Preferred to characterise bitumen as a whole instead of fractionation

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So these Corbett fractions are widely used to represent the microstructure of bitumen, but there is something which we have to remember here, there was a study which was conducted by Harrison et al. as part of an SHRP program. So they had measured DSC on bitumen and each of these four fractions. I will tell you what a DSC what DSC is in a while so you just remember that it captures the thermal events in bitumen.

So they tried to capture the thermal events in bitumen as a whole and each of these four fractions of bitumen; but when they put together the information of each of these four fractions they did not get the thermal evens for the whole bitumen. So then people started saying that the interactions between these four fractions are also important and they are lost when we separate them into fractions.

So the affinity of one fraction to other and the interactions which arise due to them is lost when the fractionation is done. So that is a reason why we are not able to see a whole response when we sum up the response of the individual fractions. So that is something we need to take in mind but again irrespective of this factor, people still prefer this fractionation procedure to represent the chemical composition.