Mechanical Characterization of Bituminous Materials

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Lecture No 18
Chemical composition of bitumen Part-02

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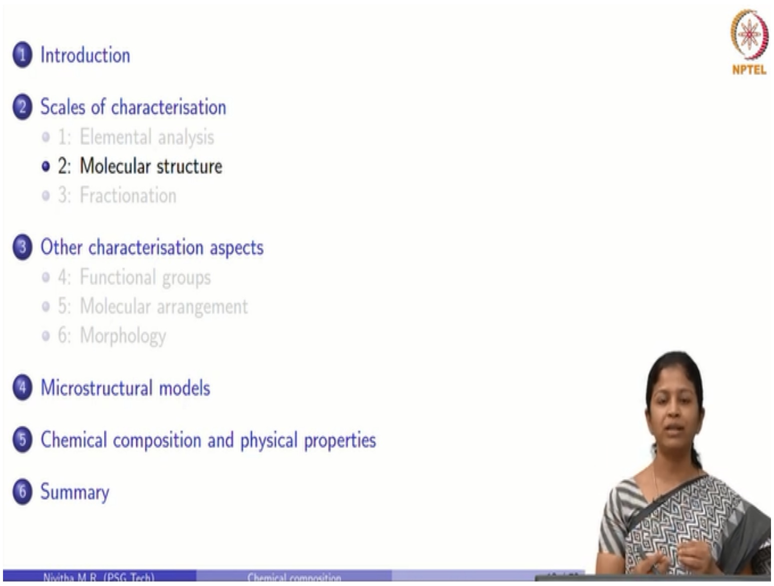

Next we will move on to the molecular structure. Molecular structure says how these elements are joined together to form molecules. So if I have two bitumen of exactly identical elemental composition, can we say that they are going to have identical molecular structure? It may not be possible it may or may not happen right? How these molecules, associate with each other, is going to be important, rather than the proportion of each of these elements. So for that purpose we need to study the molecular structure.

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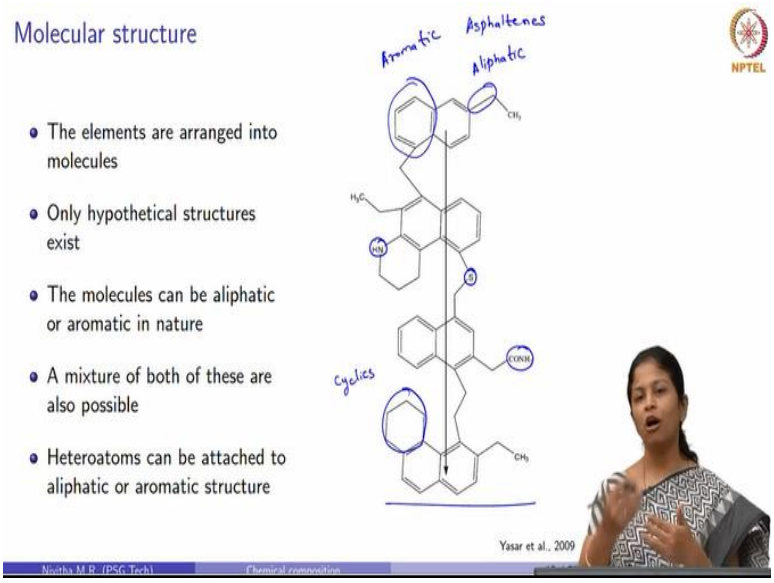

The elements are arranged into different molecules. So this is a hypothetical structure for asphaltenes one of the component which is present in bitumen. When we discuss the fractionation technique, I will tell you what these asphaltenes are; but as of now you can just keep it as one of the components which is present in bitumen. If I divide into a number of fractions, this is one of the component.

So people tried to propose what will be the molecular structure of this one molecule of asphaltene. So as far as molecular structure is concerned only hypothetical structures exist. People say that this can be the possible structure of asphaltene molecule. So these molecules can be aliphatic, aromatic or cyclic in nature. So I will tell you what these aliphatics and aromatics are. And a mixture of all of them is also possible.

So the hetero atoms can be attached to this molecule at different positions. Let us now have a closer look at this particular asphaltene molecule. So we see that we have a ring like structure something like this here. So we know that it is a benzene ring. So which is an aromatic structure and we also have some chains like this, which are aliphatic structures right? We also have something like this without a ring here; these are called as cyclics right?

And then we also have some hetero atoms which are attached. We can see a sulphur molecule which is present here; we can see an NH which is present here. We can also see a $CONH_2$ which is present here, so they also have hetero atoms. So this asphaltene molecule has aliphatics, has aromatics, has cyclics and hetero atoms attached to each of them. So again, this is only a hypothesis and where this particular hetero atom is attached and in what form it is present; all of them have significant influence on its physical properties. So let us now have a closer look at what these aliphatics are, aromatics are and cyclic are.

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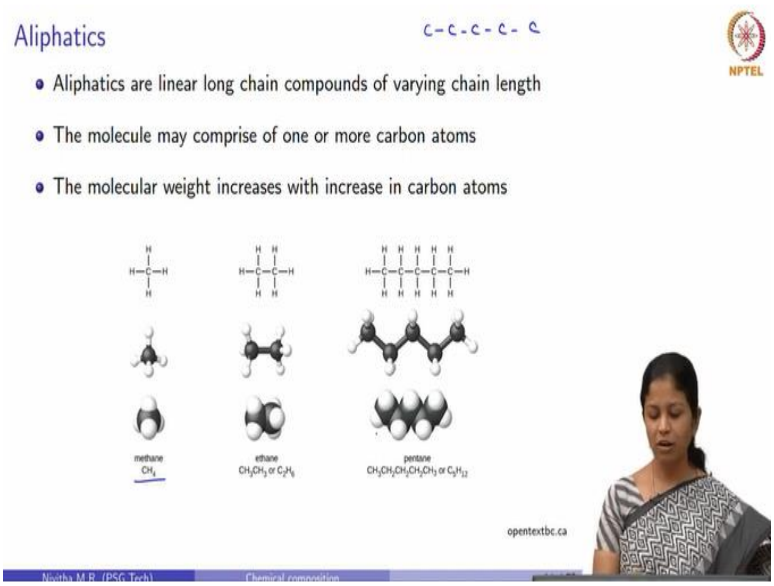

These aliphatics are linear long chain compounds, they have different chain lengths. So what do we mean by linear, we have carbon atoms attached in row. They are present in a linear form; those are called as aliphatics. The molecule can comprise of one or more carbon atoms. So if we have 1 carbon atom, we call it as methane, so we can see 1 carbon atom and 4 hydrogen atoms here.

Similarly, we have ethane, where we have 2 carbon atoms and 6 hydrogen atoms. We also have pentane here. So these are called as aliphatics - linear long chain molecules.

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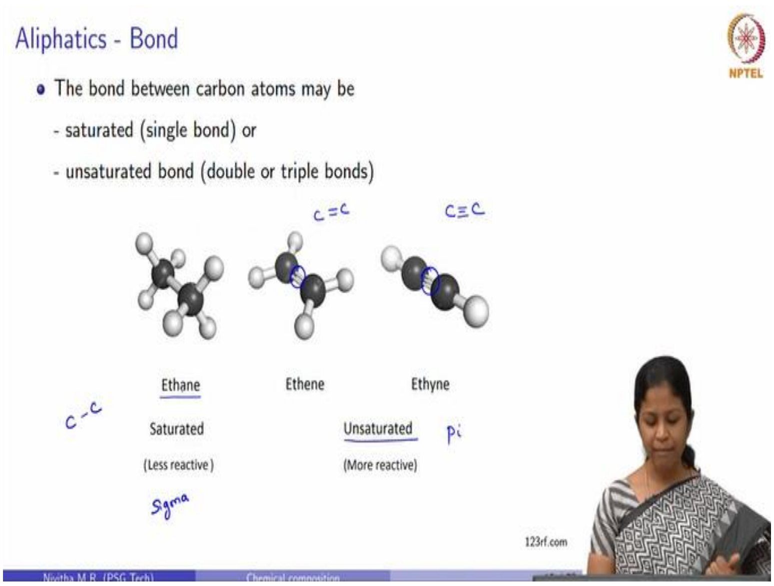

The bond between two different carbon atoms can be of three types. So we should have studied this in Higher Secondary chemistry- a single bond, double bond and a triple bond. So depending upon the type of bond, the reactivity is going to be different. A single bond is what is called as a saturated bond. So we have ethane which is present here. Carbon single bonded to carbon, right?

So this is ethane and these saturated bonds are mostly sigma bonds. So these sigma bonds are less reactive. Next we have unsaturated compounds which will have a double bond or a triple bond something like carbon double bonded to carbon, or carbon triple bonded to carbon. So these bonds are mostly pi bonds. So because of this pi bond, they are highly reactive and they are called as unsaturated compounds.

So we have same carbon bonded to carbon but with three different types of bonds and depending upon the type of bond, the reactivity is going to be different.

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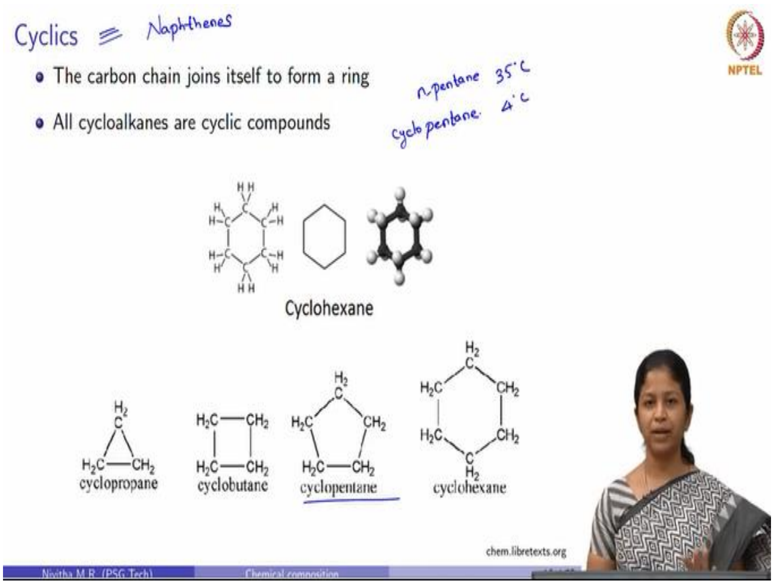

We also have something which are called as cyclics. These cyclics are when this aliphatics join together to form a ring like structure. So we have again the same pentane where there are 5 carbon atoms, but these 5 carbon atoms will come together and form a ring like structure where we can see here right? Again we have the same five carbon atoms and same number of hydrogen, hydrogen atom which we have seen in this particular slide right?

We have the same number of hydrogen and carbon atoms but the structure is different. So these are called as cyclics, these cyclics are also called as naphthenes. These naphthenes are different from naphthalenes. When I discuss about aromatics I will tell you what these naphthalenes are but these cyclics are also called as naphthenes, right? So the property of pentane when it is present in a straight chain is completely different from when it forms a ring like structure.

Let us take n-pentane, where there are five carbon atoms attached in a straight row. So the boiling point of n-pentane is about 35 degree Celsius, whereas the boiling point of cyclopentane is four degree Celsius. So this is for n-pentane and this is for cyclopentane right? So, this is again pentane but depending upon the form in which it is present, the boiling point is going to be different. So this is one type of molecules which are present in bitumen.

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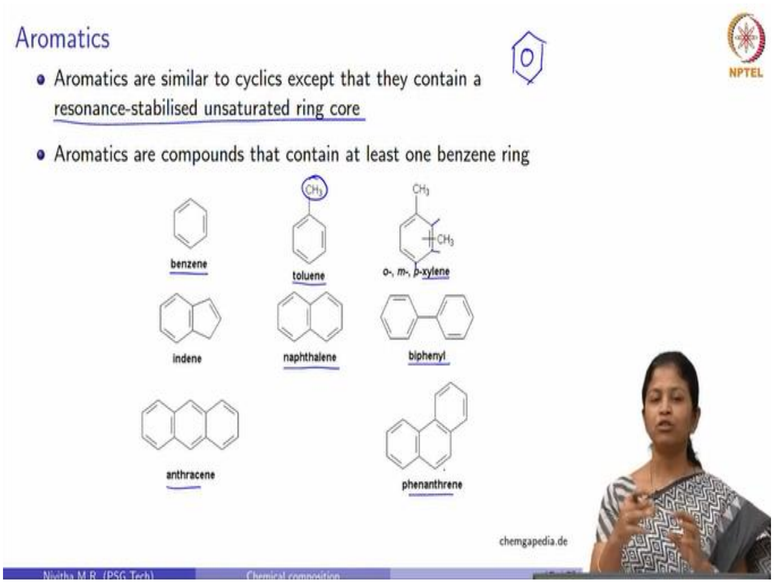

And the other type is aromatics. So these aromatics are similar to cyclics except that they have a resonance stabilized unsaturated ring core. So we draw something like this, this is a cyclic when they have a ring core which is present in it, then this is aromatic compound. So what this resonance stabilization is, it is a process which reduces the molecular weight of that particular molecule and makes it more stable.

So these aromatics are highly reactive. The basic requirement, when we call a molecule as an aromatic is that it should have at least one benzene ring. So we have benzene which is just one ring. We also have toluene where CH_3 is attached to this particular benzene ring. We also have xylene, xylene is defined when there are two CH_3 attached to a benzene ring and depending upon the position, whether it is attached here, here, or here and it can be called as Ortho, Meta or Para xylene.

Then we also have indene, where there is a six member ring attached to a five membered ring which is present here. Here we have naphthalene; previously I told you that was napthene, here we have naphthalene where there are two benzene rings attached together. We also have biphenyl, anthracene and phenanthrene. So these are some forms of aromatics, which are present in bitumen.

Now, we have looked into different types of components, aliphatics, cyclics, aromatics. Many designed materials will have any one of these property. It will be either an aliphatic or it will be a cyclic or it will be an aromatic. But bitumen, being a complex material with lot of different types of molecules, has all of them. It has some amount of aliphatics, it has some amount of aromatics, it has some amount of cyclics.

So it is a mixture of all of them. So it has molecules of different sizes, shapes, characteristics, and molecular weights.

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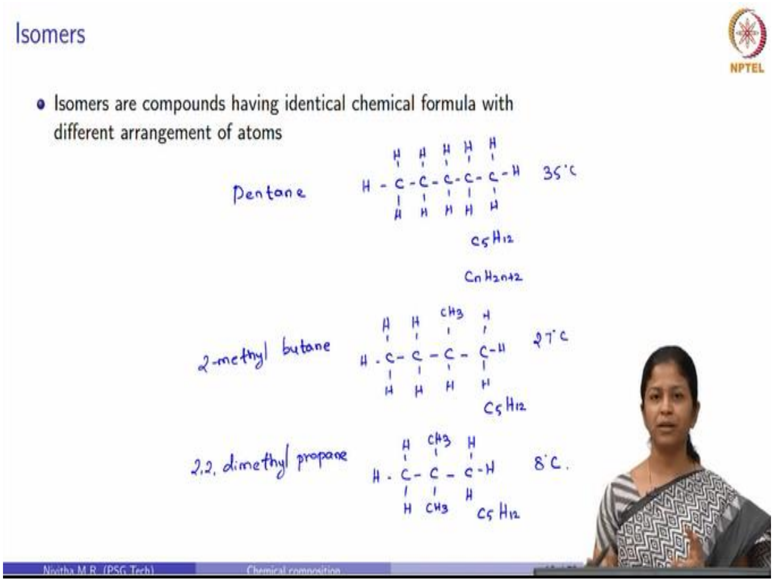

So trying to identify the number of molecules which are present in bitumen, is like trying to count how many particles are there in a handful of sand. It is not impossible, but it is very tedious. Next we look into another interesting aspect of this molecular structure. These are called as isomers; Isomers are compounds which have the same chemical formula but different arrangement of atoms.

So let us take pentane, so we have pentane, so it is C_5H_{12} right? The formula of pentane is C_nH_{2n+2}. So we have 5 carbon atoms and 12 hydrogen atoms. So this forms, pentane, like I already told you, the boiling point of pentane is 35 degree Celsius. Now, we will have a small variation, we will have 2-methyl butane. So this is four carbon atom in the second position we have CH_3 again Hydrogen atoms.

Now if I count the carbon and hydrogen, we are going to have 5 carbon atoms and again 12 hydrogen atoms 3 here 5, 8, 9, 10, 11 and 12. So again this is C_5H_{12}. It has similar number of carbon and hydrogen, except that it is arranged in a different form. So the boiling point of this particular compound 2- methyl butane is about 27 degree Celsius. We will define some other form, which is 2, 2 dimethyl propane.

So here we have three carbon atoms one CH_3 here, one CH_3 here. If I count here again I have 3, 4 and 5 carbon atoms, 3, 6, 9 again 12 hydrogen atoms C_5H_{12}. But the boiling point of this particular material is 8 degree Celsius. So, depending upon the structural arrangement of this particular molecule the physical property is going to be completely different. So this is the significance of isomers.

Two molecules can have the same chemical formula, but depending upon the arrangement, their physical properties will be completely different. So it is very important that we study the isomeric properties of molecules to understand its physical properties.

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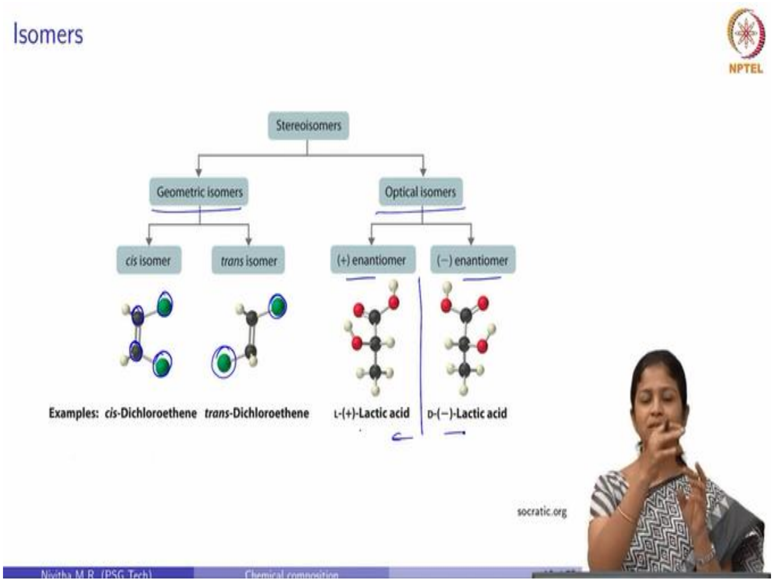

So there is something called as stereoisomers. Stereoisomers are compounds which have different structural arrangement and the isomerism is because of their structural arrangement. Again, we have two classes of stereoisomers, geometric isomers and optical isomers. In geometric isomers we have a cis form and a trans form. So what do I mean by a cis isomer, this is carbon atom and this is chlorine atom. So this is dichloroethene right?

We have two carbon atoms bonded by a double bond and we have two chlorine atoms. This is also dichloroethene but we see that one chlorine atom is present in one side and the other chlorine atom is present on the other side. So depending upon the position where the second chlorine atom is present, it can be called as a cis form or in a trans form. Similarly we have optical isomers. This is a positive enantiomer and it is a negative enantiomer. This is for lactic acid.

If I draw a vertical line here, this one is going to be a mirror image of this particular one. So these are different forms in which isomers are present. So previously we have seen that the properties of a simple molecule like pentane is going to be completely different depending upon the structural arrangement. Now we said bitumen has aliphatics, aromatics and cyclics.

So depending upon how this molecule is or how the carbon and hydrogen arranged, we are going to have n number of isomers which are available for bitumen.

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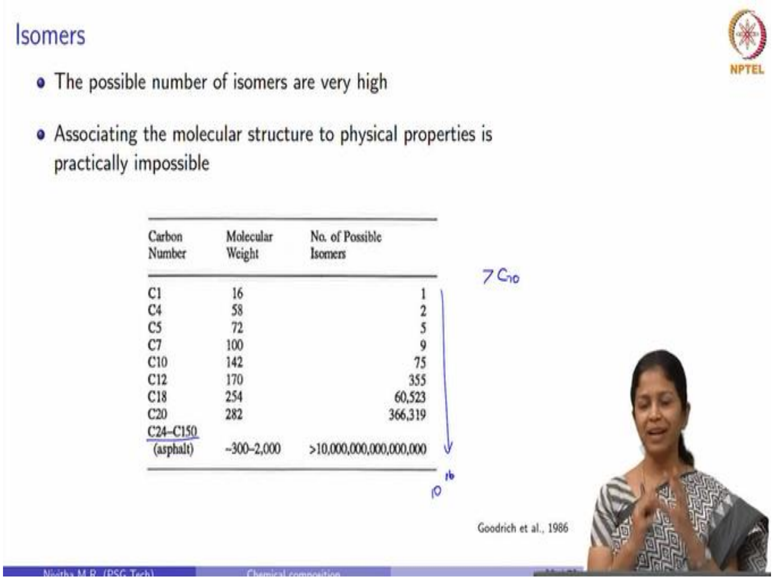

So, this is a table which shows what are the possible numbers of isomers depending upon the carbon number. So the possible number of isomers are very high as far as bitumen is concerned. If we come down the carbon number from 1 to a carbon number of 24 to 150, we can see the molecular weight obviously increases. Higher the number of carbon atoms bonded together they form a very strong bond, so the molecular weight keeps increasing.

And we can see what is the possible number of isomers. It is something like 10 to the power 3, 6, 9, 12, 15 and 16. So we have 10 to the power 16 isomers for a molecule, with carbon number between 24 and 150. So we had defined bitumen with carbon number greater than 70 right? So we can imagine how many forms of isomers will be present in bitumen and each of them will have physical properties.

So the combined the physical property that we see for bitumen is the combined influence of all those individual molecules, their isomer forms and all the other aspects. So it is very difficult to associate a particular molecular structure to bitumen and define its physical properties in terms of its molecular structure.

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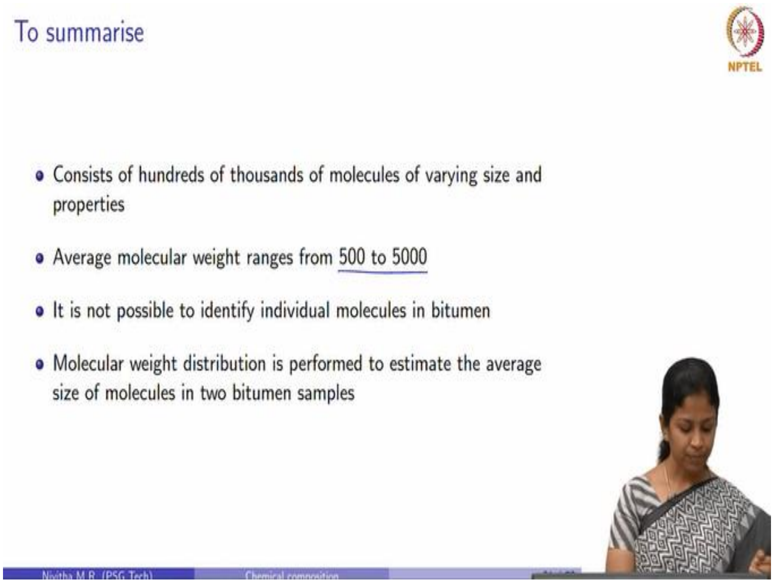

So to summarize, bitumen consists of hundreds of thousands of molecules of varying size and properties. So that is what we said, it has aliphatics, aromatics and cyclics. Again each of them of different sizes, the carbon number can vary. So then depending on that they will have different types of isomers and so we will have different physical properties for each of these molecules.

The average molecular weight will range from 500 to 5000. This is an average molecular weight, we can have molecules as small as with a molecular weight of 500 again we can have molecules with a molecular weight of 5000. So it can range anywhere in between them. And it is not possible to identify individual molecules in bitumen. So like I said earlier, we can measure it, but it is practically not possible to identify the molecules in bitumen.

So what we do is; we do a molecular weight distribution. We identify how many molecules are of a particular size, how many molecules are of a particular another size, so we define the molecules based on their molecular weight. So it is not possible to propose a structure to these molecules, but we can identify and separate them based on their molecular weight.

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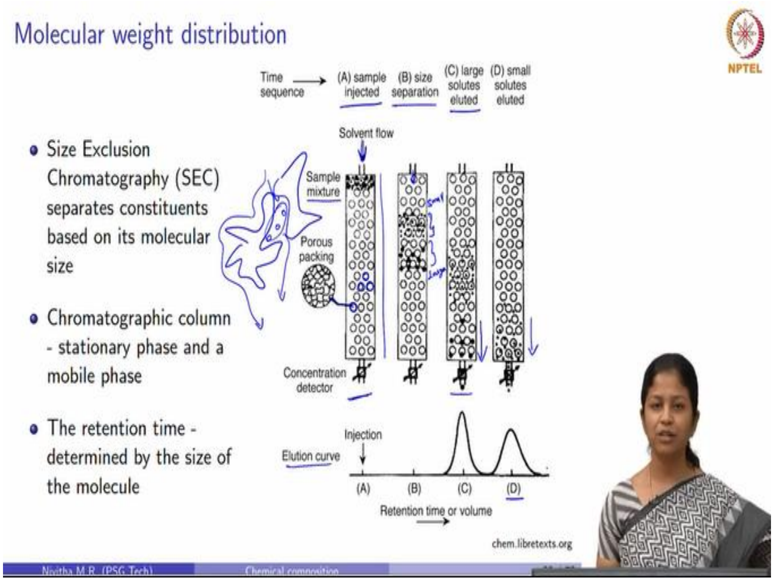

So to find out the molecular weight distribution of bitumen, we use a size exclusion chromatography. So this is a technique which is used to separate the constituents of bitumen based on their molecular size. So once we separate them based on the molecular size, we can calculate their molecular weight. So for this purpose, we use a chromatographic column.

So this chromatographic column is something like what is shown here, so it has a stationary phase and a mobile phase. So let us start with this figure. Let us move from the left end to the right end. There are four phases which is present here. So first I will define what a chromatographic column is. It is nothing but a vertical column which is present here with a porous packing.

You can see these circles which are present here, so these are porous packing. When I enlarge one particular circle, we see something like this. So it is something like something like this, lot of porous particles which are combined together. Now what we do here is we take bitumen, mix it with a solvent and allow it to pass through this chromatographic column. So when bitumen passes through this chromatographic column, what happens is we said it has molecules of different sizes.

So the smaller molecules will try to pass through this, right, will try to spend more time here, whereas the bigger molecule will come out of this porous packing. The size is large that it cannot enter that porous packing and it will just come out. Whereas these smaller molecules can enter into these pores which are present here, they will spend some time inside these pores here and then they will come out.

So what happens here is the larger molecules will come out first, whereas the smaller molecules depending upon the size of the molecules, they will leave this chromatographic column at different time. So this is used to separate molecules of different sizes. So let us now look at this figure here. The first phase which is defined as A, the sample is injected into the chromatographic column.

We have bitumen mixed with a solvent, so this is injected into this chromatographic column so it is a sample mixture, mixture of molecules of different sizes. So this now flows into this chromatographic column. In the second phase, the size separation happens. So once it starts passing through this point, the smaller molecules will try to spend more time here, whereas larger molecules will be leaving.

So here you can see the smaller molecules are present here, whereas the larger molecules have already come down. So depending upon the size, these molecules will be separated. So as they come down the larger solutes are eluted. So what do we call as an elute? Whatever comes out, we call that as a elute. So the larger solutes, solutes is what we dissolve in a solvent. So the component of bitumen which is larger in size. So that is what they mean by larger solutes.

So this larger solutes comes out of the chromatographic column initially. After some time, this smaller molecules comes out. So when we draw an elution curve with time, what happens is initially there is nothing that is coming out. After some point of time again in the second phase is also there is nothing that is coming out. In the third phase we have larger molecules which is present here, so we see a distribution here.

And then the D phase we have the smaller molecules which are coming out. Again we have a distribution here. So this is the principle which we use to separate molecules of different sizes using this chromatographic principle.

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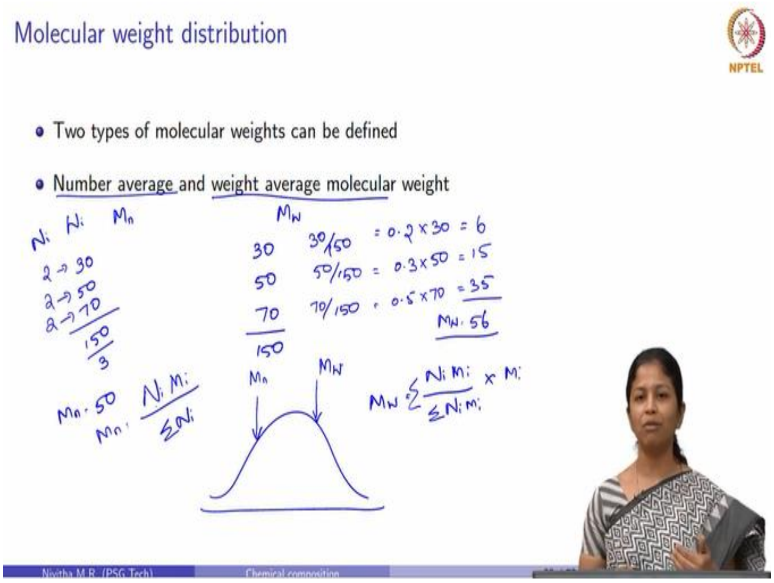

There are two types of molecular weight, so this is based on size. Now we have to calculate the molecular weight. There are two types of molecular weight that can be calculated for bitumen. A number average molecular weight, which is defined as M suffix n and weight average molecular weight, which is defined as M suffix w. When you look into the literature which talks about molecular weight for distribution you can see, they always refer to number average and weight average molecular weight.

So what does this number average and weight average molecular weight, and why is it important to study each of them. Let us take an example; the number average molecular weight is like kind of averaging the weight of 3 different people in a class. Let us take 3 people with weights 30, 50 and 70, the number average molecular weight, will just kind of average these 3 numbers. So what we get here is 150.

So we have 3 people in the class. So 150 divided by 3, we will get 50. So this is number average molecular weight. So if we have 2 people with weight 30, 2 people with weight 50, 2 people with weight 70, so this becomes number of people with weight, and this becomes the weight of people. So what we get here is $Ni \times Mi/\sum Ni$. So that is what is my number average molecular weight, so that we have it as 50 here.

Let us see what is this weight average molecular weight? This weight average molecular weight gives more weightage to people with higher weights. So if we take this particular case whatever be the end when we average out, the effect of the lower weight people and the effect of higher weight people are going to be averaged out but we do not want that because in bitumen we say molecules with higher weight and higher sizes are contributing differently to its chemical composition compared to molecules of smaller sizes.

So when we average it out, we are going to remove all these effects in this particular parameter. So, to take into consideration we are calculating something as a weight average molecular weight. So what we do in this case is, we have again 30, we have 50, we have 70, so totally I have 150, I am going to find out what is the contribution of this person with a weight of 30 to the total weight.

So I do 30 divided by 150, so I get something about 0.2. I do the second case, which is 50, divided by 150. So it is something about 0.3, let us ignore the second digit. The third one we have 70 divided by 150 again I will take it as, 0.5 roughly right? Now what I do is I multiply this 0.2 into 30, so I will have 6 here. I multiply this 0.3 into 50, so I will get 15 here, and I multiply this 0.5 into 70, so I get 35 here.

So when I add this I am going to get 56, which is the weight average molecular weight. So you can see the difference here when I calculate a number average molecular weight, I am getting 50, whereas when I calculate a weight average molecule weight it is 56. So it is giving a slightly higher weightage to the person with a higher weight. So this is defined as $Ni \times Mi$ for a particular case, divided by $\sum(Ni \times Mi)/(\sum Ni \times Mi) \times Mi$.

So this is like a whole summation. So this is the difference between a number average and weight average molecular weight. So when we do for bitumen; If we have a molecular weight distribution something like this, this number average molecular weight is going to be on the lower side, whereas a weight average molecular weight is, this is my number average molecular weight, and this is going to be my weight average molecular weight right?

So, this is we need to remember this particular difference between these two molecular weights, when we are looking at the molecular weight information, which is given for different types of bitumen.

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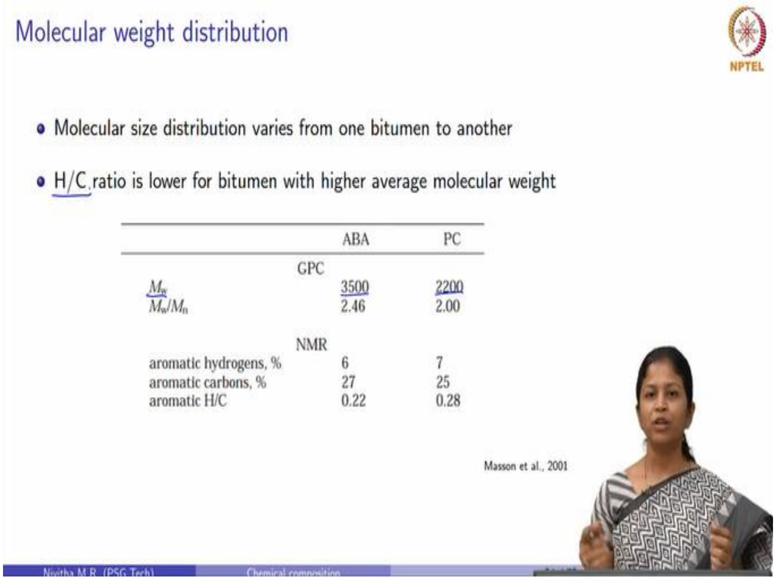

So this is one information from the study which we had seen earlier, we had seen the elemental composition for the same two type of bitumen. So we are going to see its molecular weight the number average molecular weight and the weight average molecular weight. So we see that for these two type of bitumen, the weight average molecular weight is higher for bitumen ABA, whereas it is lower for bitumen PC.

So what does this information tell us? This says that there are more molecules with higher molecular weight in ABA compared to PC. So that is the information which we will be able to derive from this particular molecular weight information, and we have already seen that the hydrocarbon ratio is lower for bitumen with higher average molecular weight. So we said that when we have lower number of hydrogen atoms, there are more number of carbon atoms present, so the molecule is bigger.

So we can relate the hydrocarbon ratio information to the molecule weight information. So again, there we had seen that the hydrocarbon ratio was different for these two type of bitumen. And there is another technique which is NMR spectroscopy, which can tell us, how much is the hydrogen content which are present in aromatic molecules and how much is the hydrogen content which is present in aliphatic molecules.

So this says, 6% of hydrogen in bitumen ABA is present as aromatic hydrogen and 27% is present as aromatic carbon, so this will tell us how many aromatic, the percentage of aromatics components and the percentage of aliphatic components which are present in bitumen.

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Next we will move on to the fractionation technique, which will tell how molecules of identical nature, again I said we have to be very careful when I said identical nature are grouped together to different fractions, we will do that in the next lecture. I will stop this lecture with this. In the next lecture, we will continue about the fractionation technique and few other aspects which are used to characterize the chemical composition of bitumen. Thank you.