Lecture 4: Composition of Crude Petroleum and Evaluation of Oil Stocks

Hello and welcome to the 4th lecture on petroleum technology. In this lecture, I will cover the composition of crude petroleum and the evaluation of oil stocks. Let us first start with the composition of crude petroleum. Already we know that petroleum is not a uniform material, it is a complex mixture of hydrocarbons and hydrocarbon derivatives with different organometallic and organosulfur, oxygen and nitrogen compounds. The metals contained are mostly vanadium, nickel, iron and copper. Hydrocarbon content may be as high as 97 percent. This we find for the light petroleum crude mostly and as low as 50 percent, and this we find for heavy asphaltic crude. This is what I am saying in general. Now, this table gives us the elemental composition of crude oil or it is done by the ultimate analysis of crude oil. Here if we see through the column, left, in the first column, carbon, hydrogen, sulfur, nitrogen, oxygen and metals, carbon content is the highest which is 83.9 to 86.8, very high compared to the others and next coming to the hydrogen content. So, you can see that in crude oil, we mostly find carbon and hydrogen content, but sulfur, nitrogen, oxygen and metals are observed to be there in crude oil in trace amounts. Now, coming to the hydrocarbon content of crude petroleum. The hydrocarbons remain in the crude petroleum in the form of straight chain, branched chain, fused cyclic structure, saturated or unsaturated.

Among those compounds, we can differentiate three major ones. One is the paraffin. Paraffin, you know paraffin is a compound that is a straight chain or branched chain compound without any ring structure. We find in the crude petroleum, paraffin at around 15 to 25 percent on average. In the lighter crude, we mostly find the straight chain compounds from C1 carbon number 1 to around C40.

As we go towards the higher molecular weight paraffinic compound, we find the paraffins are waxy in nature. That means if crude contains a higher molecular weight of paraffin, then, while transporting that crude through the pipeline from one locality to another locality, there is a possibility of temperature difference. And if the temperature goes down, that crude may freeze within the pipeline. So, this is the disadvantage of containing higher molecular weight straight chain paraffin. Those actually have a waxy nature.

Now, actually, at lighter crude, these C1 to C40 straight-chain compounds remain up to around 35 percent compared to the heavy crude. This is for light crude and for heavy crude, they may be very low, around 15 percent or lower. Now, coming to the branched-chain paraffin. Branched-chain paraffins range of various molecular weight. Branched-chain paraffin observed in crude petroleum. And this branching starts from C 4.

Straight-chain paraffins are found in the molecular range C1 to C40 in the light petroleum crude and the percentage may vary up to 35 percent. As we go towards the higher molecular weight paraffins, we find these paraffins show a waxy nature. That means, if crude petroleum contains a higher molecular weight of straight-chain paraffins when they are transported through pipelines, there is a tendency to freeze within the pipeline if the temperature drops down in a locality. So, this waxy nature of petroleum paraffinic compounds is not very desirable in a crude component. Now, coming to the branched-chain paraffin.

Branched chain starts from C4 from butane. And you know that branched-chain paraffin we usually denote by iso. So, isobutane is the first branched-chain paraffin in petroleum fraction. In a light petroleum crude, we usually find C 6 to C 8 branched paraffin with methyl group as the branching. As the molecular weight increases, this branching may be longer.

Now, coming to the naphthene. Naphthene is the closed ring saturated molecule. And in petroleum crude, we usually see alkyl cyclopentane and alkyl cyclohexane. All these are very simple mononuclear structures of naphthenes. Usually, naphthenes content vary more or less 50 percent of the petroleum crude. These naphthenes may be mononuclear or polynuclear, depending on the density of the crude oil.

If it is a light crude then we find a lesser molecular weight naphthenes in that. And if it is a heavier crude then polynuclear and condensed ring structures are observed even up to 8 condensed ring structure is observed in naphthenes. Now, coming to the aromatics. Aromatics or arenes are the ring structures with unsaturation in them. The first aromatic compound is benzene and we find in the lighter crude, the benzene and its homologs such as toluene, xylene etcetera or some higher derivatives, as well as some polynuclear aromatic compounds, I have shown, the naphthalene, phenanthrene etcetera. Not only will more condensed ring structures be found, but the percentage of aromatics in crude oil will not go beyond 15 percent. Now, coming to the nonhydrocarbon components of crude petroleum. Nonhydrocarbon components are organic sulfur compounds, nitrogen compounds, oxygen compounds, and some metals. Mostly in metals, we find vanadium and nickel compounds that remain in the form of porphyrin.

Porphyrins are a very complex ring structure where in the middle we find these metal atoms. In sulfur compounds, we mostly find mercaptan. Mercaptans have functional group SH. Then sulfides, sulfides are RSR, R is the alkyl group. Disulfides, disulfides are RSSR and thiophene. Thiophene, you know, this is an aromatic compound with 5-membered ring unsaturation with sulfur and one sulfur atom at one position.

But all the sulfur compounds are not this simple. They are complex in nature, having their derivatives, alkyl derivatives, bulky structure may be there. Now coming to the nitrogen compounds. We find pyridine and quinoline which are 6-membered unsaturated ring structures, then pyrrole indole etcetera, and even carbazol. So, all these are different kinds of nitrogenous compounds with their ring heavily loaded with some alkyl groups. Now coming to the oxygenated compounds, the examples are given, pyran furan etcetera. All these sulfur, nitrogen, oxygen and metals remain in a very trace amount, but their effect is very important on the crude petroleum as well as their fractions.

Sulfur compounds, nitrogen compounds, and oxygen compounds corrode the metallic parts of the processing equipment as well as deactivate the catalysts of the secondary processing units in the refinery. These compounds sit on the catalyst's active centers and passivate the catalyst. Oxygen compounds form sticky gums in the petroleum fractions if we store the petroleum fraction for a time and oxygen compounds also have these bad effects. They even cause some discoloration in the finished products and affect the stability of the finished product as well as the efficiency of the finished product.

Now we will talk about the evaluation of oil stocks.

Oil stocks or crude petroleum can be characterized by various factors. In that, characterization factor which is denoted by K is that, which is defined by Universal Oil Products, UOP and so, many times this characterization factor is said as UOP characterization factor. K is equal to the cube root of T_B/S where T_B is the molal average boiling point in degree Rankin and S is the specific gravity at 60 by 60 degrees Fahrenheit or 15 by 15 degrees centigrade. Average boiling point is a characteristic boiling point of a mixture of hydrocarbons which has a range of boiling points. This characteristic boiling point or average boiling point helps in detecting many physical properties and characterization of petroleum stocks.

There are several types of average boiling points: weight average boiling point which is abbreviated as WABP. Volume average boiling point which is called VABP and molal average boiling point, which is called MABP. Now here it is said, molal average boiling point. So, molal average boiling point T_B we can represent this way: $T_1x_1+T_2 x_2+T_3x_3/x_1+x_2+x_3$, where T is the boiling point of the component and x is the mole fraction of that component. And degree Rankin you know, degree Rankin is the Fahrenheit plus 460, as we do for the determination of Kelvin, centigrade plus 273 and S is the specific gravity at 60 by 60 degrees Fahrenheit on or 15 by 15 degrees centigrade. It means that both the water and oil are kept at a single temperature that is 60 degrees Fahrenheit or 15 degrees centigrade.We determine specific gravity in comparison to water.

Now coming to the API gravity of a crude petroleum fraction. API has a full form of the American Petroleum Institute. This institute has given this name. They represented this gravity of petroleum fractions which is represented by 141.5 by specific gravity at 60 by 60 degrees Fahrenheit minus 131.5.

And degree API is used to express the gravity or density of crude oil or a petroleum fraction. For petroleum fractions, to determine the gravity, we give the API gravity value. Why API gravity, not specific gravity? This is because, the difference in specific gravity between two adjacent petroleum fractions is very low, very small. Say, one fraction has a specific gravity of 0.79 and the adjacent fraction has a specific gravity of 0.8. So, it is very difficult to distinguish between those two fractions depending on the specific gravity. Hence, we say about the API gravity where you see the specific gravity is coming at the denominator of the API gravity formula and hence it magnifies the values. So, it broadens the scale.

Now, coming to the discussion on the basis of crude oil. According to the U.S. Bureau of Mines, 8 bases of crude oil are designated depending on the distillation characteristics.

U.S. Bureau of Mines distinguishes different types of crude oil we get, different types of crude oil throughout the world. So, they distinguish these crude oil depending on their distillation characteristics. Distillation is done in the laboratory at a standard distillation apparatus which is said to be a Hempel distillation apparatus. Now, I have to say about the key fractions. So, these are the distillation characteristics. Key fraction 1 is the fraction of crude oil, which boils between 482 to 527 degrees Fahrenheit at atmospheric pressure and key fraction 2 is the fraction which boils between 527 to 572 degrees Fahrenheit at 40 millimeter mercury pressure that means, at vacuum in standard Hempel at distillation apparatus. So, whenever we get a crude oil, we can do the distillation in the laboratory in that standard apparatus and find out the key fraction 1 and key fraction 2 of that particular crude oil. Then we can determine the composition of key fraction 1 and key fraction 2 as well as their API gravity and UOP characterization factor. So, look at this table where you in the leftmost column it is given the base of crude oil and then API gravity at 60 degrees Fahrenheit and next is K factor. Under this base of crude oil, the first column is a low boiling part, which is key fraction number 1 and the next part is the high boiling part which is key fraction number 2.

Next, API gravity is determined for both these fractions, the same as for the UOP characterization factor. The first one, for example, let me take this one which is paraffin. So, both the low boiling part and high boiling part, both the key fraction number 1 and key fraction number 2 have the composition paraffinic in nature. The API gravity for key fraction 1 is 40 plus, the same as the key fraction 2 is 30 plus, as key fraction 2 is heavier. So, if API gravity is lower than the key fraction number one, but the UOP characterization factors are the same, 12.2 plus and 12.2 plus, more than 12.2. Now, if you go down through the column you see the different natures of crude oil, different compositions of crude oil, paraffin-intermediate (intermediate means a mixture of paraffin, naphthene and various others). Then you will find that only paraffin has a UOP characterization factor of 12.2 whereas, only naphthene is a UOP characterization factor of 11.4 minus less than 11.4. So, the characterization factor varies from more than 12 to less than 11, starting from paraffin to naphthene. Similar to the API gravity, depending on the specific gravity and composition of the crude petroleum of its key fraction 1 and key fraction 2, API gravity varies throughout the column. Now, the nature of crude oil in terms of sulfur content. We usually say it is sour crude, it is sweet crude. What is sour crude? Sour crude is when the crude contains dissolved hydrogen sulfide in it, 0.05 foot cube of hydrogen sulfide in 100 gallons of crude oil. This is the definition of sour crude. If the hydrogen sulfide content is lesser than this defined one, then we cannot say the crude is sour. And if the content of hydrogen sulfide is far less than obvious, we can say it is sweet crude, and even some sweet crude does not contain any hydrogen sulfide in them. High sulfur crude is that, which crude oil contains disulfides, mercaptans, and thiophenes in a sufficient amount. So, high sulfur crude cannot be sour crude because those two are different. Sour crude has hydrogen sulfide content and high sulfur crude has sulfur compound content.

These are the references. Thank you for your attention.