Lecture 26: Upgradation of straight run cuts from atmospheric distillation unit

Hello and welcome to the 26th lecture on Petroleum Technology. In this lecture, we will learn about the Upgradation of Straight Run Cuts from the Atmospheric Distillation Unit. In this lecture, let us first discuss the Gasoline processes. You know gasoline is one of the most important straight-run cuts obtained from the atmospheric distillation unit. It is the first liquid cut coming out from the overhead of the atmospheric distillation unit. Gasoline-producing processes start with oil fed to the atmospheric distillation column, where crude oil is split into a naphtha fraction that boils up to 180 degrees centigrade.

This is the cut you have already read. From the overhead, we get the gaseous fraction and the naphtha fraction. Naphtha is obtained from the dehumanizer and splitter after removing the butane part from the naphtha. Then, the naphtha is split into light naphtha and heavy naphtha. And the whole complete cut of naphtha is C5 to 180-degree centigrade. In between, the naphtha is split into two cuts: one is light naphtha, which boils up to 90 degrees centigrade and another one is heavy naphtha, which boils up to 180 degrees centigrade is C5 to 90 and 90 to 180-degree centigrade. Now gasoline producing processes produce gasoline up to 180 degrees centigrade cut, mostly the straight-run cut coming from the atmospheric distillation column. This straight-run cut is insufficient to meet the demand for gasoline worldwide.

Moreover, about 40 percent of all naphtha produced from crude oil by simple distillation is required to satisfy the demand for petrochemical feedstock. So, most of the light naphtha part that is C5 to 90 degrees, around 40 percent of the total naphtha we get, goes to the petrochemical feedstock preparation. The balance of this naphtha is converted to gasoline. Whatever naphtha remains after being sent to the petrochemical unit, the balance is converted to gasoline. The gasoline shortfall is then made up from the various conversion processes of heavy residual products. You know that not only does the straight run naphtha fraction from various secondary processing units in the refinery, such as thermal cracking or Visbreaking and catalytic cracking, but we also get the naphtha fraction from the coker unit. So, all these secondary processing units produce the naphtha fraction and these all together produce the total naphtha of the refinery. This total naphtha is converted to gasoline. Gasoline is the motor fuel. You know gasoline is the motor fuel that is used in the motor engine and the various conversion processes make up the gasoline shortfall. The C4 fraction or butanes from naphtha are obtained as the lighter head of the butane, that the C4 fraction, which was actually associated with the lighter naphtha that is stripped off in the debutanizer unit. Still, this C4 fraction has an octane number very close to 100. Hence, the small amount of C4 fraction dissolved in the naphtha is welcome because of raising the octane number, but this C4 fraction is a lighter fraction. So, it has high raid vapor pressure. So, the limit is that the 5 percent of the C4 fraction is allowed to mix with the gasoline permitted to blend with the gasoline to one side. It limits the vapor pressure specification of the gasoline and improves the octane number to some extent.

Surplus butanes may be used as an LPG component with propane. So, butane propane C3 C4 is the LPG fraction that you also know by now. The isobutene is the unsaturated paraffin isobutene component of the butane stream and is a necessary feedstock to the alkylation unit. Alkylation is another unit where alkylates or alkylated compounds are produced by the reaction between the isobutene and other compounds and those alkylated products are the high-octane products. Those are called alkylates and those alkylates are also a necessary component of the total gasoline produced in the refinery to improve the octane number of the gasoline pool.

C3 C4 olefin stream that is derived mainly from FCC unit is used for the production of MTBE. MTBE is methyl tertiary butyl ether. This is an oxygenate, and this is an octane number improver. C3 C4 olefin stream that is derived mainly from FCC unit is used for the production of MTBE. MTBE is methyl tertiary butyl ether. This is an octane improver. You know that alkylate lead alkyl compounds are highly toxic in nature. Whenever the gasoline is burned in an automobile engine, the lead compounds form the poisonous gas in the exhaust. As the exhaust goes out from the exhaust line of the car mixes with the air, it causes heavy air pollution. So, lead compounds are banned and prohibited from being mixed with gasoline instead of the MTBE, one of the major octane improvers used as the octane improver to increase the octane number of the gasoline pool. And that is obtained by the reaction with C3 C4 olefins with methanol. Methanol has to be obtained from other sources of the refinery.

One stream that exists in the C5 C6 fraction is isopentane. Isopentane is another isoparaffin hydrocarbon of 93 research octane number and a valuable component for aviation gasoline. You understand that C5 is a very lighter fraction, but isopentane has a high octane number and aviation gasoline is a lighter cut of the gasoline. So, isopentane is one of the most essential components of aviation gasoline. The virgin LSR naphtha light straight run naphtha may be absorbed directly in the gasoline pool if octane quality permits.

So, the light straight-run naphtha is a lighter component of naphtha light naphtha, which I said can be directly blended in the gasoline pool if the octane quality is good. Otherwise, in most cases, this LSR naphtha is sent to the isomerization unit to produce the isomerates. Isomerates are the compounds that are formed by the isomerization reaction and the isomerization reaction produces high-octane products. Those isomerates are high-octane compounds that are again mixed into the gasoline pool to improve the total octane number. A large proportion of straight-run naphtha goes outside the fuel refinery for petrochemical production. This is one part that goes to the non-fuel refinery or petrochemical production.

We are now coming to the reforming of naphtha. What is reforming? Reforming is the process by which the low-octane naphtha is upgraded to high-octane naphtha or motor fuel. So, reforming is a refinery process to upgrade low octane naphtha to high-octane motor fuel and this upgraded fuel obtained after reforming is termed reformate. Reforming is an essential process in the refinery to increase the octane number of naphtha by several reactions. Reforming is done by the by passing the feedstock, that is, the naphtha, through a reactor containing mostly the platinum catalyst at a suitable temperature and in this process, several reactions occur in the range of C5 to C12, but without altering the boiling point of the parent naphtha we get the product which is the reformate.

This is the reforming reaction or reforming process in short. So, the naphtha contains paraffins, naphthenes and aromatics in the C5 to C12 range and naphtha obtained from catalytic or thermal cracking operations contains some olefins also. We handle the naphtha, which comes from the gasoline pool and contains various types of naphtha coming from many points or units of the refinery. Hence, the gasoline pool can contain paraffin, naphthenes and aromatics and some olefins and olefins. You know, olefinic compounds are produced from the cracking operation. So, we can expect that in naphtha, paraffins, naphthenes, aromatics, and olefins in the C5 to C12 range are there and sent to the reforming process.

The reform naphtha or reformate is rich in aromatics and isoparaffins. Aromatics and isoparaffins have a high octane number in the paraffin, naphthenes and aromatics series. So, reform naphtha contains reformates that are rich in aromatics and isoparaffins that are desirable. Hydrogen produced in this process is used in the hydro processing of different cuts in the refinery. In the reforming process, we will see that hydrogen is produced and that hydrogen is used for various other operations that need the hydrogen, such as hydroprocessing of various cuts, hydro-desulfurization, hydro-denitrogenation, hydrocracking, and hydro finishing etcetera.

Reforming is accomplished by processing the naphtha feed at an elevated temperature of 450 to 520 degrees centigrade and moderate pressure of 4 to 30 bar in the presence of hydrogen. Reforming is done in the presence of hydrogen at high temperatures and pressure. The catalyst used is mainly platinum-based platinum on alumina catalyst is used and the reforming unit practiced in the refinery are of two types. Two types of reforming units are used in the refinery; one is semi-regenerative reforming, another one is the continuous regeneration type. In the semi regenerative reforming, the catalyst is allowed to work for a long period until the catalyst is totally deactivated and cannot produce the required or desirable amount of or yield of reformate as well as cannot keep the quality of the reformate.

After that, the whole process unit is shut down and the catalyst is regenerated. After regeneration, the catalyst is again filled in the reactor and then the process starts. In the continuous regeneration type, what happens is that the catalyst is continuously getting regenerated and hence, what happens is that we do not need to regenerate the catalyst in between. That means it does not need to shut down the whole process from time to time. UOP universal oil products first commercialized the reforming process in 1949 and coined the process as platforming after the name of the platinum catalyst used by them. UOP is a world-known universal oil product. One world-known company or licensors first commercialized the platforming process and worldwide, more than 1000 platforming processes are running at present. UOP licenses some 700 out of them, and along with that platforming process, they also introduced a continuous catalyst regeneration system and this system produces the gasoline having a very high octane number around 108, which is almost meeting the theoretical expectation.

Now, coming to the reaction chemistry of reforming. Four principal reactions which are undergone by naphthenes and paraffin are as follows. Dehydrogenation of naphthenes produces aromatics isomerization of naphthenes and paraffin, which produce the isomerates. Dehydrocyclization of paraffin produces naphthene and cracking of paraffin. They produce the branched chain or isoparaffins. Aromatics pass virtually unchanged and naphthenes had dehydrogenated easily to aromatics.

Aromatics has nothing to do with these reactions because aromatics are the most required compound in the gasoline as they have the highest octane number. Hence, aromatics pass through virtually unchanged and naphthenes are converted to aromatics and that is a very easy process. Napthas with high paraffin content give less favorable yields in terms of octane number. If the naphtha contains high paraffin, then only this paraffin can be changed or converted to isoparaffin. Still, it is difficult to convert paraffin into aromatics because paraffin is a straight-chain compound and aromatics are closed-chain compounds. So, it is a strained structure thermodynamically it is not very favorable.

Now, coming to the reactions dehydrogenation of naphthenes. The conversion of naphthenes to the corresponding aromatics is the dehydrogenation process, which is a fast process. This is an endothermic process favored by high temperature and low pressure. This is an example of the dehydrogenation of naphthenes. Here, you see that methylcyclohexane, which has research octane number 75, is converted to toluene, having research octane number 100 plus. So this is the naphthene converted to aromatic toluene along with 3 moles of hydrogen per mole of toluene produced. The next reaction is the isomerization of naphthenes. An example of isomerization of naphthenes is the conversion of alkyl cyclopentane to cyclohexane. Here, you see the methyl cyclopentane methyl group is the branch that is converted to cyclohexane. This is of 6 membered ring. So, 6 membered ring is produced from the 5 membered ring, taking the branch CH_3 into it and making this 6-membered ring. It is thermodynamically somewhat favorable because the 5 membered ring is a strained structure compared to the 6-membered ring. Aromatization of cyclohexane The next step will be the aromatization of cyclohexane to produce the aromatics. Then, aromatics must be produced from naphthene from naphthene aromatics will be produced in the next step. And whenever aromatics are produced, that will improve the overall octane number. Isomerization of naphthenes involves ring opening and ring rearrangement. It is seen that this 5 membered ring has to open and it has to take this CH3 branch with it to form the ring rearrangement to form the 6-membered ring.

The next reaction is the isomerization of paraffin. Paraffin isomerization reactions occur rapidly at typical operating temperatures. Isomerization of paraffin produces isoparaffins from normal paraffin, thereby increasing the octane number. You know that normal paraffin has a very low octane number and isoparaffins have a high octane number. Here, the example is normal hexane C_6H_{14} having octane number research octane number 25, which is converted to the 2 methyl pentane with this branching containing the same formula having the same formula C_6H_{14}. Still, the research octane number has been improved to 74.

Another reaction is the dehydrocyclization of paraffins. This reaction is a difficult reaction as it involves both cyclization and dehydrogenation of paraffin. You see, this is normal heptane whose research octane number is 0. You know, in the octane number scale, normal heptane is taken as the lowest octane number, which is fixed as 0. This normal heptane is converted to methyl cyclohexane, whose research octane number is 75 with 1 mole of hydrogen.

This reaction is difficult in the sense that from a straight chain compound, a ring structure is formed and after that, along with this ring structure formation, hydrogen is also liberated. So, it is a process where both cyclization and dehydrogenation of paraffin occur, which is a somewhat difficult reaction. It is favored by low pressure and high temperature. A high temperature is required to make the reaction progress toward cyclization and dehydrogenation.

The next reaction is the cracking of paraffin. It is, in fact, hydrocracking. Hydrogen is used in this process to saturate the olefinic compound produced in the cracking reaction. Hydrocracking of paraffin is a reaction that occurs with the hydrogen liberated from other reactions of the reforming. You have seen that in the reforming process in many reactions, we get hydrogen as the product that hydrogen is utilized in this reaction. It is a high-temperature and high-pressure process because of the reason that it is a cracking reaction.

So, it is favored by high temperature and high pressure and you see this normal decane having a research octane number minus 53; it is a very low research octane number. Along with the reaction with hydrogen, it produces 3 methyl pentane one cracked product having research octane number 75 and a shorter chain product, butane, having a research octane number very high 94. And here, as the hydrogen is used, the olefin, which was supposed to form in the cracking reaction, has been saturated to give the two straight-chain paraffins or one. This is an iso compound and this is the straight-chain compound of normal paraffin. Now, this last slide shows the effect of crude quality on naphtha reformate. Let us see the table. Here, you see that crude sources are given Arabian light, Arabian heavy, bonny light from Nigeria and Maya crude from Mexico and naphtha compositions paraffin naphthene olefin paraffin naphthene aromatic content by volume percent at this. Arabian light is 68 percent paraffin, 19 percent naphthene and 13 percent aromatics, whereas Arabian heavy has 77 percent paraffin, 12 percent naphthene and 11 percent aromatics. Bonny light Nigerian crude has 41 percent paraffin, 48 percent naphthenes and 11 percent aromatics and this Maya crude gives 59 percent paraffin, 28 percent naphthenes and 13 percent aromatics. If you compare all these crudes, you can see that they give this Arabian heavy as it has very high paraffin content. So, this Arabian heavy crude will not give us a very high improvement in octane number as these paraffins do not react much in the reforming reaction; only they form the isoparaffins. Rather than this bonny light crude, which has a higher naphthene content, this naphthenes can produce aromatics very easily. Hence, this bonny light the naphtha produced from bonny light after reforming will give a good octane number improvement. Look at this figure here: the reformate research octane number of reformate is given on the x-axis and the y-axis, reformate C5 plus yield in weight percent of the feed is shown. Here, you see when the reformate research octane number is 90, there are two naphtha qualities. We find this dotted line is called the rich naphtha as it shows a very small decrease in the weight percent yield. As the reformate percent reformate number increases, the reformate research octane number is increasing. Rather, the bold line naphtha, which has the 90 research octane number, is much higher compared to the rich naphtha. Moreover, this lean naphtha production is lesser. It is 80 percent compared to the rich naphtha, which is 90 percent at the same octane number. Now, types of reforming processes semi regenerative reforming is the most common type of catalytic reforming unit. Here, as I said, the reforming reaction is allowed to occur up to such a point until the catalyst is not deactivated fully. So, it cannot give the reformate's desired yield and octane number. This process is continuously carried out for a long period of time and catalyst activity gets reduced due to coke deposition. The catalysts are regenerated in the period of 6 months to 1 year, depending on the type of naphtha. The whole unit has to shut down.

The catalyst is regenerated. Coke is burnt out from the catalyst to get the regenerated catalyst and again, the catalyst is reused. As the activity of the catalyst decreases, naphthene conversion and yield of hydrogen decreases. That means, as the catalyst activity decreases, naphthene conversion towards aromatics, which is the most desirable reaction, decreases as well and hydrogen yield decreases. The continuous catalytic regeneration process is the most modern type of catalytic reforming unit. In this process, the regeneration of the catalyst is done continuously in a special regenerator and then the regenerated catalyst is charged to the operating reactor.

So, at any point in time, the feedstock is not facing any trouble because of the deactivated catalyst and it produces almost the constant grade of reformate. These are the references you can consult. Thank you for your attention.