Lecture 27: Upgradation of straight run cuts from atmospheric distillation unit (Contd.)

Hello and welcome to the lecture number 27 of Petroleum Technology. In this lecture, we will learn about the Upgradation of Straight Run Cuts from the Atmospheric Distillation Unit. You know that we have already learned about the catalytic reforming process chemistry and what reactions usually happen in the catalytic reforming unit. So, let us come to one of those units which carry the catalytic reforming process, which is semi-regenerative catalytic reforming. From the name, you can understand whether it is a semi-batch process or almost it is not a continuous process. A regenerative process indicates that the unit is periodically shut down to regenerate the catalyst.

As the reaction progresses in the catalytic reforming reactor, the catalyst loaded in the reactor continuously accumulates coke deposits, leading to a gradual degradation of its activity. This reduction in activity not only affects the yield but also impacts the quality of the reformate product. Therefore, in a semi-regenerative process, the unit is periodically taken offline for catalyst regeneration. When it becomes evident that the catalyst is no longer producing the desired reformate, the entire system is shut down to facilitate the regeneration of the catalyst. After regeneration, the revitalized catalyst is reintroduced into the reactor to continue the process.

In the process, the naphtha feed undergoes hydrotreatment to reduce sulfur and nitrogen levels to nominal values. This treated naphtha is then combined with hydrogen, which is generated within the process and is subsequently pumped through a fired heater before entering the first reactor. It's important to note that there are multiple reactors arranged in series, and each reactor is equipped with an associated fired heater to achieve and maintain the required reaction temperature. The purpose of hydrotreating the naphtha is to remove sulfur and nitrogen compounds, which act as catalyst poisons.

The naphtha feed initially undergoes hydrotreatment and is then mixed with the hydrogen generated within the process. Subsequently, it is pumped through a fired heater before entering the first reactor. In the first reactor, the temperature is maintained at approximately 500 degrees Celsius, with a pressure of up to 3450 kiloPascals (500 psig). It's worth noting that this first reactor involves an endothermic naphthene dehydrogenation reaction, which absorbs heat and causes a temperature drop in the reaction mixture.

To restore the temperature to the required level, the mixture then passes through a second-fired heater before entering the second reactor. In the second reactor, there is a further, albeit lesser, temperature drop. After the initial stage of reaction in the first reactor, the temperature of the reaction mixture drops below the desired level for the second reactor. Therefore, the mixture from the first reactor is sent to the second-fired heater to regain the appropriate temperature before entering the second reactor. In the second reactor, another stage of reaction occurs, causing a temperature drop, although it is less significant than in the first reactor. The reaction mixture exiting the second reactor is then passed through a third heater before entering the third reactor, where the final reactions take place. This sequential arrangement of reactors and heaters ensures that the reaction temperature is controlled and maintained throughout the process.

It's important to note that in some cases, even after the third reactor, the quality and quantity of the reformate may not meet the desired level. In such situations, a fourth reactor can be added alongside the third reactor to achieve the desired reformate quality. Now, let's take a look at the flow diagram of the semi-regenerative catalytic reforming process. The process begins with the feed, which is hydrotreated naphtha mixed with the process hydrogen. This mixture then enters the combined feed heat exchanger, where it exchanges heat with the reformate from the last stage of the reactor, which is very hot. This heat exchange cools the reformate and heats up the feed.

Next, the feed, now at the appropriate temperature, is directed to the first stage of the fired heater. In the fired heater, the feed reaches the required temperature level before being introduced into the first reactor. Within the first reactor, an endothermic reaction occurs, resulting in a temperature drop. To compensate for this temperature drop, the reaction mixture passes through the second stage of the fired heater.

From the second stage of the fired heater, the reaction mixture, now at the desired temperature, enters the second reactor, where further reactions occur. As the temperature drops again at the bottom of the second reactor, the reaction mixture proceeds to the third heater. In the third heater, the mixture is once again heated to the appropriate temperature before entering the third reactor, where the final reactions take place. This sequential arrangement of reactors and heaters helps maintain and control the reaction temperature throughout the process.

The process continues with the third heater raising the temperature of the reaction mixture, which is then introduced into the top of the third reactor. If the third reactor successfully produces reformate, which is fully reformed naphtha of the desired quality, the reformate is drawn from the bottom of this last reactor. The reformate then undergoes heat exchange with the feed and is subsequently directed into a cooler to reduce its temperature. After cooling, the reformate is sent to a separator. In the separator, hydrogen-rich gases are extracted from the top, while the bottom of the separator contains the reformate.

The hydrogen-rich gas extracted from the separator is mixed with the feed naphtha. Any surplus hydrogen can be directed to other process units, such as hydrodesulfurization. However, the reformate obtained from the bottom of the separator still contains some gases mixed with it. To separate these gases, the reformate undergoes a fractionation process in a stabilizer. The refinery gases are taken out from the top of the stabilizer, including the C3 (propane) and C4 (butane) fractions, while fully reformed naphtha, known as stabilized naphtha, is obtained from the bottom. The Reid Vapor Pressure (RVP) of the stabilized naphtha is typically maintained at around 4 psig. Throughout the reaction, coke is deposited on the catalyst, reducing its activity. This coke deposition occurs as the reaction progresses. To minimize the need for catalyst reactivation, a high hydrogen-to-hydrocarbon molar ratio is maintained during the process.

Maintaining a high hydrogen-to-hydrocarbon molar ratio, typically around 6:1, helps control coke deposition to some extent. However, as the reaction proceeds, the catalytic activity of the catalyst decreases due to coke deposition. This reduction in catalytic activity necessitates raising the reactor temperature to sustain the desired octane number of the reformate, albeit at the expense of lower reformate yield. In other words, as coke accumulates and hinders the catalyst's effectiveness, increasing the reactor temperature becomes necessary to ensure that the reaction proceeds smoothly and at an acceptable rate. This temperature adjustment is made to maintain the desired quality of the reformate, particularly its octane number. However, it results in a reduced quantity of reformate being produced, as the catalyst's activity has decreased due to coke accumulation.

As the loss of yield in the desired octane number reformate becomes significant, there comes a point where the entire plant must be shut down, and the catalyst needs regeneration. Continuous increases in temperature will eventually fail to maintain both the desired octane number and the yield of reformate. This situation arises because, as the temperature is raised, catalyst activity keeps decreasing, and coke deposition continues. Regenerating the catalyst can be achieved through either in situ burning of the coke or replacing the catalyst with fresh material. In the case of in situ burning, the coke deposited on the catalyst is ignited with oxygen. This process burns off the coke, converting it into carbon dioxide, and leaves the catalyst surface regenerated and ready for further use.

In some cases, the catalyst may become so severely deactivated that even after regeneration, it cannot produce the desired quality of the product. In such situations, the entire batch of catalysts is replaced with a fresh catalyst. To address the economic feasibility of this process and reduce downtime, an improvement called cyclic reforming was developed. In cyclic reforming, an extra swing reactor is introduced alongside the main reactor. When the primary reactor's catalyst becomes deactivated and can't produce the desired reformate quality, the swing reactor with a fresh catalyst can be used to maintain continuous production without the need for a complete unit shutdown. This approach reduces downtime and is more economically efficient.

The swinging process involves replacing a deactivated reactor with a freshly loaded catalytic reactor to maintain continuous production. This approach helps reduce downtime and improve the overall efficiency of the catalytic reforming unit. It's known that reformates with higher aromatic content tend to have a higher octane number. Lower-pressure, lower-severity operations can produce reformates with more aromatics and higher octane numbers. However, one limiting factor in such operations is the increased coking of the catalyst. To counteract this limitation, bimetallic catalysts were introduced as an improvement. These catalysts allowed operations at pressures ranging from 200 to 300 psig, resulting in reformates with octane ratings of 95 to 98 under a cycle length of 1 year in a Semi-Regenerative Catalytic Reforming (SRE) unit.

The introduction of bimetallic catalysts marked an improvement in the catalytic reforming process. These catalysts, unlike single metal catalysts, operate at much lower pressures, typically in the range of 200 to 300 psig. They can produce reformates with octane ratings of 95 to 98. Bimetallic catalysts are more robust than single metal catalysts and have a longer cycle life, typically around 1 year in a Semi-Regenerative (SR) unit, as opposed to the 8 to 12 months observed with single metal catalysts. Now, let's move on to the Continuous Catalytic Regeneration (CCR) process. This process allows for operation at lower pressures compared to the SR process and utilizes a much lower hydrogen-to-hydrocarbon ratio. In the CCR process, catalyst regeneration is continuous, meaning that as soon as the catalyst becomes coked, it is regenerated in real time and then recycled back to the reactor. This continuous regeneration eliminates the limitation posed by rapidly deposited coke on the catalyst.

In the Continuous Catalytic Regeneration (CCR) process, coke deposition on the catalyst is not a significant issue because the catalyst is continuously and in real-time regenerated within the process. Unlike the Semi-Regenerative (SR) process, which lacked a catalytic regeneration unit, the CCR process has a catalyst regenerator integrated with the reactor. This allows for the continuous regeneration of the catalyst within the system. In the CCR system, the reactors are vertically stacked on top of each other rather than being arranged side by side, as in the SR process. The entire reactant mixture and catalyst flow from the top reactor to the bottom reactor in a continuous manner, facilitating ongoing catalytic reactions. A stream of spent catalyst is transported by hydrogen lift from the bottom reactor to a regenerator system and then back to the topmost reactor, ensuring a continuous cycle of catalyst regeneration and use.

The spent or deactivated catalyst is removed from the bottom of the last reactor using a hydrogen lift mechanism, and it is then transported to a regenerator system. After the regeneration process, the catalyst is returned to the topmost reactor, ensuring that the catalyst within the reactors is essentially fresh at all times. This continuous regeneration process allows the unit to operate at a much lower pressure, as low as 50 psig, compared to the 200 to 300 psig or higher pressure range in the Semi-Regenerative (SR) process.

The continuous regeneration of the catalyst mitigates the impact of coke deposition on catalyst activity. In the Continuous Catalytic Regeneration (CCR) process flow diagram, you can observe that the reactors are vertically stacked one above another. The naphtha feed, after being hydro-treated and mixed with process hydrogen, undergoes heat exchange with the hot reformate from the process in the feed heat exchanger. After this heat exchange, the naphtha feed, along with hydrogen, is introduced into the first reactor, where the endothermic reaction takes place.

The temperature of the reaction mixture drops after the endothermic reaction in the first reactor. The mixture is then taken from the bottom of the first reactor and passed through a heat exchanger to regain the appropriate heat required for the second reactor. After heating, it is sent to the second reactor, where further reactions occur. This process is repeated for each subsequent reactor in the series. Once the reactions are complete and the desired quality of reformate is obtained, the reformate is withdrawn from the bottom of the last reactor. Simultaneously, the spent or deactivated catalyst is removed from the bottom of the last reactor. The spent catalyst is then sent to the regenerator. In the regenerator, the coke deposited on the catalyst is burned off, effectively activating and regenerating the catalyst. The regenerated catalyst is subsequently reintroduced at the top of the first reactor, completing the continuous cycle of catalyst regeneration and reuse. This process allows for the catalyst to remain fresh and continuously regenerated, which is a key feature of the Continuous Catalytic Regeneration (CCR) process.

In the CCR (Continuous Catalytic Regeneration) process, the other part of the process is similar to the SR (Semi-Regenerative) unit. After the reformate has undergone heat exchange with the feed, it is sent to a separator. The separator's primary function is to separate the hydrogen-rich gas from the reformate. Some of the hydrogen is taken back into the process, while the remaining portion is directed to other refinery processes that require hydrogen, such as hydro-treatment units (e.g., hydrodesulfurization, hydronitrogenation, hydrodeoxygenation) or hydrocracking. The reformate, which still contains some dissolved gases, is then sent to the stabilizer. In the stabilizer, the reformate is stabilized, resulting in fully reformed naphtha. Off-gases are removed from the stabilizer to maintain the reformate's Reed Vapor Pressure (RVP). The key difference between the semi-regenerative and continuous catalytic regeneration processes lies in the importance of selectivity towards aromatics. In the CCR process, selectivity towards producing aromatic compounds is crucial because coke deposition on the catalyst is minimized due to continuous regeneration. This allows for more control over the reformate's composition and quality in the CCR process compared to the SR process.

Hence, if selectivity goes towards the aromatics rather than the SR process, where the SR process cannot give only the aromatics, and aromatics should be the more desirable compounds in the reformate, as its octane number is very high. Tolerance of high coke deposition of the catalyst is one of the prime factors in SR, as the regeneration cycle time is much higher than that of the CCR. Hence, in the SR process, catalyst development plays a big role because the catalyst in the SR process has to withstand the coke deposition on it, although it has to give the octane number of the reformate at the desired level. So, it should have a robust nature, or it should maintain its quality, activity, and selectivity more than the catalyst that is used in the CCR process.

Now, coming to the feed and process variables. Naphtha feed is generally in the boiling range of 80 to 185 degrees Celsius. This is the feedstock for the catalytic reforming unit. Usually, as the FBP (final boiling point), this is the IBP (initial boiling point) of naphtha maintained. The IBP is the initial boiling point in the ASTM distillation unit, and FBP is the final boiling point in the ASTM distillation unit. So, this is the range usually maintained for the naphtha feed, but the thing is, this 185 is kept as the FBP because of the reason that in the reforming process, it is always seen that some 15 to 20 degrees Celsius rise in FBP is observed after the final reformate is obtained from the last reactor.

Hence, in the specification of the reformate, it is seen that the FBP is said to be 210 degrees Celsius, usually for the reformate, not for the feed. For the IBP, usually, many refiners in many countries prohibit naphtha feed with the C6 and C7 components because these C6 and C7 components or compounds are benzene precursors, and benzene is a poisonous or carcinogenic material. After the naphtha reformate is burnt in the engine, it produces benzene vapor, which is not desirable because this benzene vapor mixes with the atmospheric air, polluting the air. Hence, C6 and C7 compounds are highly prohibited in the reformate. Usually, C6 is maintained at less than 1 volume percent, and C7 is maintained at less than 5 volume percent. For this reason, in those countries, the IBP goes up to 90 to 100 degrees Celsius, and this is also specified. C5 and C6 hydrocarbons are excluded from the feed because they mostly go to the isomerization process. C7 paraffins boiling up to about 90 degrees Celsius may also be excluded from the naphtha feed as benzene precursors, as I have already mentioned. Bigger C7 paraffin is allowed, but the C7 paraffin with a lower boiling range, up to about 90 degrees Celsius, or with a lower molecular weight is excluded from the naphtha feed because it produces benzene. Now, coming to the reactor temperature, the primary control for product quality in catalytic reforming is the catalyst temperature, which can be adjusted by the heater outlet temperature. This reactor temperature is controlled by the thermodynamic equilibrium, and typically, SR units operate in the 490 to 525 degrees Celsius range, while CCR units operate in the 525 to 540 degrees Celsius range.

This higher temperature in the CCR unit and lower pressure in the CCR unit have the advantage of yielding a higher quality reformate than the SR unit. Now, coming to the space velocity operated in the reactors of CCR is an indication of the contact time between the feed and the catalyst. It is expressed as liquid hourly space velocity (LHSV), which is the volume of naphtha charged per hour per volume of the catalyst. The higher the LHSV, the more temperature is required for the process. Space velocities of the order of 2 per hour are typical.

Next, it comes to the hydrogen-to-hydrocarbon molar ratio. This is the ratio of the moles of hydrogen in the recycled gas to moles of naphtha charged to the unit. The process hydrogen used removes the reaction products from the catalyst surface, and hydrogen-to-hydrocarbon molar ratios of up to 8 to 1 have been used in SR units. However, the ratio can be as low as 1.6 to 1 in the CCR system. A high hydrogen-to-hydrocarbon ratio is required in the SR unit to resist coke formation or coke deposition on the catalyst. Still, as the CCR unit does not face the problem of catalyst deposition all the time, less hydrogen can also carry out the reaction. So, a hydrogen-to-hydrocarbon ratio of 1.6 to 1, which is much lower compared to 8 to 1, can be used in the CCR system easily.

Now, coming to the catalyst. Reforming catalysts are composed of a base support material, generally alumina (Al2O3), on which catalytically active metals, less than 1 weight percent, are evenly distributed.

Alumina is the base support; it is an alkaline material, a basic type of material on which catalytically active metals are highly dispersed, and this dispersion occurs at a very low quantity, typically around 1 weight percent maximum. This low quantity is maintained due to the high cost of the metals. For monometallic catalysts, platinum is the active metal, and you can understand that platinum is a very costly metal. Rhenium is also very costly and is normally added to bimetallic catalysts for more severe processing requirements. An example of a bimetallic catalyst used today contains 0.35 weight percent platinum and 0.4 weight percent rhenium. Even a very low quantity of these active metals can work wonders in the reaction.

A special requirement introduced by the CCR process was the necessity for the catalyst to be resistant to attrition. In the CCR process, the catalyst flows from the top to the bottom through the reaction reactors one after another, exposing the catalyst to attrition. Therefore, the catalyst should be resistant to attrition and should not break. Mechanically strong spherical catalysts are preferred over the more conventional cylindrical extrudates. Spherical catalysts, being devoid of corners, are less susceptible to attrition and breakage compared to conventional cylindrical extrudates, which have edges and are more prone to attrition.

An innovation in which two different catalysts are used in the same SR plant, exploiting the better features of each catalyst, is known as staged loading.

In this approach, two or three different types of catalysts are used in the same SR (Selective Reforming) plant. Each of these catalysts is tailored to work specifically for one or two types of reactions where they exhibit superior performance. This design aims to enhance the overall performance of SR plants.

The first catalyst is loaded into the first and second reactors, where the primary reactions involve the dehydrogenation of naphthenes and the dehydrocyclization of long-chain paraffin. These reactions have high rates and result in relatively little coke formation on the catalyst. The catalyst used in these reactors demonstrates high selectivity toward producing aromatics and low selectivity toward cracking during the conversion of naphthenes and paraffin. This catalyst is unique because it prioritizes the production of aromatics and doesn't act as a cracking catalyst in the reactor during the conversion of naphthenes and paraffin.

In the last reactor, shorter-chain paraffins are dehydrocyclized to aromatics, and cracked products are formed, requiring higher temperatures. In this final reactor, the cracking reaction predominates, and higher temperatures lead to increased coke formation on the catalyst. Because of the elevated temperature, more catalyst deactivation is observed due to the higher coke formation. Therefore, a catalyst with high activity and stability is loaded in the last reactor. This catalyst needs to have both high activity and stability to endure the coke formation and maintain the desired quality of the reformate. These are the references you can consult with. Thank you for your attention.