Lecture 14: Secondary Processing: Decomposition of Residues: Catalytic Cracking

Hello and welcome to the 14th lecture of Petroleum Technology. In this lecture, we will learn about secondary processing, under which we will talk about catalytic cracking. This is also a unit where the residues, residue oils are decomposed and we get the lighter products. So, catalytic cracking is the process where low-valued high, boiling feedstocks are cracked into value-added products by using a catalyst. Usually, in catalytic cracking, the feedstock that is used mostly boils above 350 degrees centigrade temperature. The boiling point is more than 350 degrees centigrade temperature or somewhat less, but still, the feedstocks are heavier and because of that, they have a very low economic value.

To get the value-added products from these heavy residue feedstocks, the catalytic cracking operation is done, where the products are obtained by using a catalyst. Catalytic cracking is the process where low-valued boiling feedstocks are cracked into value-added products by using a catalyst. As the catalyst is used for this process, you understand that the temperature of the process is somewhat lower than the thermal cracking where no catalyst is used. Now, fluid catalytic cracking and its related cracking operation, residue fluid catalytic cracking (RFCC), are the two important cracking operations used in the petroleum industry.

Resid fluid catalytic cracking is important in the way that people are continuously drilling out the lighter crude oil from underground. So, the lighter crude oil is continuously depleting, and that is why the transportation fuel demand is increasing. Now, as people are getting heavier crude oil, the residue that we obtain from those heavier crude oils is also very heavy, and they contain many objectionable compounds such as metals, asphaltenes, sulfur, nitrogen, etc. But we have to go for the cracking of that high boiling residue fuel oil or residues to get the lighter oils, so RFCC is getting popular day by day, although it has many disadvantages. So, the demand for light transportation fuel also contributed to establishing the residual oil cracking at the end of 1970.

When people see that there is no other way but to go for residual fluidized cracking, the principal products from catalytic cracking are high-octane gasoline, which is the major product or major aim of the products, light distillate oil, and olefinic liquefied petroleum gas. These are the three major products that are the targeted products from the FCC unit. Fluid catalytic cracking can accept lots of feedstocks, including atmospheric gas oil obtained from the atmospheric distillation column as the straight-run product, vacuum gas oil from the vacuum distillation column as the straight-run product, coker gas oil from the coking unit fractionator bottoms as the heavier fractionator bottoms, thermally cracked gas oil from the thermal cracking unit, and the thermal cracking unit fractionator bottoms. Solvent deasphalted oils are those that remove asphaltene content from heavy feedstock, any heavy feedstock that contains the asphaltenes. Asphaltenes are the precursor of coke.

So, this removal is done by solvent extraction. Lube extract is also a heavy distillate; this is a straight-run distillate from the vacuum distillation column, and hydrocracker bottoms are the bottom distillate of the hydrocracker fractionator bottom. So, these are obviously, you understand all these are very heavy residues or residual oils or residual fuel oils which have very low value, and those can be upgraded through this fluidized cracking process. Feedstocks of RFCC: RFCC is Resid Fluid Catalytic Cracking; here the heavier residual fractions contaminated with asphaltenes, carbon residue, and metals such as nickel, vanadium, etc., are taken as the feedstock. These contaminants increase the yield of coke and poison the catalyst.

However, because of the presence of these objectionable impurities in the catalyst in the residual oil which are the feedstocks, there is a significant challenge in processing these resid fluids in the catalytic cracking unit. But still, this RFCC can give premium-grade light transportation fuel. To get this premium-grade light transportation fuel, depending on the amount of contamination, the residual oil may undergo treatment that is pretreatment of the residual oil, which includes hydro-treatment and solvent deasphalting. So, hydro-treatment and solvent deasphalting reduce the sulfur, nitrogen, and metals contained in the feedstock, and deasphalting reduces the carbon residue in the feedstock. Now, whenever the feedstock is passed through these pretreatment units, the products obtained after this RFCC may not require heavy post-treatment processes; that is, those feed products may contain very low amounts of these objectionable compounds, such as sulfur, nitrogen, and metal compounds, as well as the carbon residue of those products are not much appreciable.

Even the flue gas generated during this RFCC process may not be treated for sulfur dioxide removal. So, sulfur dioxide removal may be alleviated for flue gas. Feedstocks in this RFCC category are atmospheric residues and mixtures of residues and gas oils. Here, in this division, mixtures of residues and gas oil may be vacuum residue, which is diluted with some vacuum gas oil. Both of these combinations are very heavy, and they have almost no value. So, they are treated in the RFCC unit.

Residual oil cracking has two technologies running nowadays: one is UOP residual oil cracking, and the other is total catalytic cracking. UOP (Universal Oil Product) is one of the licensors of this residual oil cracking process, and Total is another company, another licensor, which also put forward this patented technology. These two are the competing technologies nowadays. Both of these technologies cope with the problem of excess coke production by using two-stage regeneration. As you understand, RFCC is handling residual oils; hence, the tendency for coke formation on the catalyst is very high. That's why the coke produced on the fine catalyst dust has to be burnt out in two-stage operations in the regeneration stage. That's why a two-stage regeneration process is installed for the RFCC.

Now, coming to the process chemistry, catalytic cracking proceeds over a porous solid catalyst containing acid sites. These acid sites provide the cracking property of the porous solid catalyst, and this process goes through a carbonium ion mechanism, that is, the C^+ carbonium ion mechanism. Typical cracking reaction conditions are : temperature is kept around 500 to 540 degrees Celsius, pressure is 2.3 to 3 bar absolute, the catalyst to hydrocarbon ratio is kept at 4 to 7 by weight, and dispersion of steam is required at 2 to 5 weight percent of hydrocarbon.

This process actually involves catalytic cracking, but at the same time, we cannot avoid the thermal cracking process at the high temperature of the catalytic cracking. This thermal cracking is a highly undesirable process while the catalytic cracking operation goes on because this thermal cracking produces a large amount of dry gas in the C1 to C3 range. This dry gas is of low value and is not used much in the refinery. During the production of C1 to C3, we lose some part of the feedstock in producing this undesired product. So, the production of dry gas is not wanted. It also produces olefins in the gasoline boiling range with little branching, resulting in a low octane rating.

Along with the C1 to C3 paraffinic hydrocarbons, some olefin double-bonded hydrocarbons are also produced in this low molecular weight range, which has very little or almost no branching. If branching is not present, then those compounds lower the octane number of the gasoline produced. At the same time, whatever paraffins are produced also lack branching. So, as a whole, thermal cracking is disadvantageous because it negatively impacts product quality. At the same time, this thermal cracking produces more aromaticity in the light cycle oil produced in the thermal than catalytic cracking process.

Light thermal cycle oil may be one of the desired products, but if aromaticity increases, then its cetane number decreases. This is another negative effect of thermal cracking. This is the catalytic cracking mechanism, where one compound is taken to show how the cracking occurs. The hydride ion H^- is abstracted in the initiation stage, leaving the carbonium ion. This carbonium ion undergoes beta-scission to form a low molecular weight olefinic compound and another carbonium ion. Apart from this pathway, several other reactions may occur during this process, such as hydride shift skeletal isomerization, or hydrogen transfer. Hydrogen transfer is not desired in the process, as it can lead to undesirable side reactions. In modern FCC units, thermal cracking and hydrogen transfer can be avoided by preventing local high-temperature heating at the catalyst and feedstock mixing zone and reducing the residence time in the reactor.

Now, let's turn to the FCC catalyst. FCC catalyst is a finely divided powdered solid that is fluidized by hydrocarbon vapors in the reactor. This FCC catalyst is a very fine powder with a particle diameter of about 60 to 70 micrometers. This powder is of very low density and can be easily fluidized by the hydrocarbon vapor produced in the reactor. Not only in the reactor, but the FCC catalyst is also very fluffy, so it can be easily fluidized in the catalyst stripper by steam and in the regenerator by combustion air. This catalyst has a high silica-to-alumina ratio, with Y zeolites bound in an amorphous matrix.

Y zeolite is a highly crystalline type of zeolite with a high silica-to-alumina ratio. Zeolites are sodium aluminosilicates, so the silica-to-alumina ratio is very high for Y zeolite, which is essential, and it is a major component for the cracking reaction, bound to an amorphous matrix. Typically, the percentage of Y zeolite in the whole catalyst is around 20 to 35 percent, but it has been observed that 70 to 80 percent of the cracking reaction depends on this Y zeolite. As mentioned, zeolite contains sodium, which is an important component, but the sodium content of zeolite is removed through rare earth exchange and ammonium exchange processes. Sodium zeolite is not effective for cracking reactions, so sodium is removed by rare earth metals and the ammonium ion NH_4^+ through these two different processes, resulting in two types of zeolite catalysts: rare earth exchanged zeolite and ammonium exchanged zeolite.

Ammonium ion exchanged zeolite is heated to remove ammonia to leave HY zeolite, and this H is highly effective for acid sites. HY zeolite has stronger acid sites and produces more gasoline-range olefin and LPG. So, HY zeolite, with its strong acid sites, improves the gasoline octane number and produces LPG, classifying it as an octane catalyst.

Rare earth exchange zeolite has a greater number of closely spaced sites, but they do not have very strong acid sites. However, they have more sites that are closely spaced, resulting in higher yields of gasoline, less LPG, and fewer gasoline-range olefins. Olefin production is lower with this catalyst, but gasoline production is higher, so it's called a gasoline catalyst.

To achieve optimum product quality, both rare earth and ammonium exchanged Y zeolites can be mixed together to make a composite catalyst, termed an octane barrel catalyst.

FCC can be operated in various modes to maximize different cuts. For instance, if the goal is to maximize gasoline production, the severity of operation is medium, with intermediate severity, and the temperature is maintained at around 520 to 540 degrees Celsius. High catalyst activity and a high catalyst-to-oil ratio are used, and usually, recycling is not done in this process to maximize gasoline production.

For maximizing middle distillates, such as kerosene and diesel fractions (light cycle oil), the severity of operation is lower, meaning a lower temperature compared to gasoline production. The temperature is maintained at around 490 to 510 degrees Celsius, with a reduced catalyst-to-oil ratio compared to gasoline production. Recycling of unconverted feed is done in this case. The feed is partially converted in one pass, and then the mixture of converted and unconverted feed is sent to the fractionator. The fractionator bottom, which is obtained, is a heavier product and almost unconverted feedstock, which is undesired. The unconverted feedstock from the bottom of the fractionator is recycled with fresh feed, and the combined stock is injected into the reactor.

Another mode of operation aims to maximize LPG production. Here, the operation severity is very high, and the cracking temperature range is 535 to 565 degrees Celsius. The typical production is C3 and C4 hydrocarbons, which are a mixture of propane, propylene, butane, and butylene. These hydrocarbons have two markets: the LPG market and the petrochemical market. In the petrochemical market, C3 propylene and C4 butylene can be used as feedstock for first-generation petrochemicals.

Except for C4, which is butylene, this cut can be separated from the gas mixture and used as feedstock for methyl tertiary butyl ether (MTBE), an octane enhancer used in gasoline to improve the octane number. Additionally, C4 can be used to produce alkylate, which serves the same purpose as an octane enhancer in gasoline. In this mode of operation, the ZSM-5 zeolite catalyst is mixed with the Y zeolite to adjust the severity of the operation. Maximum LPG production requires effective feed injection and effluent separation to minimize thermal cracking at high operating temperatures. Since this is a high-severity operation, there is a high chance of obtaining thermally cracked products, which is undesirable because thermal cracking produces C1 and C2 gases, referred to as dry gases, which are non-condensable and not desired.

Looking at the figure, it shows the FCC operating modes at different severities and their corresponding yields. Gasoline yields increase as severity increases, and at a certain point of severity, gasoline yield reaches its maximum. Beyond that point, with further increase in severity, gasoline yield declines. Middle distillate production is maximum at the lowest severity, and as severity increases, the distillate yield decreases. However, when examining the formation of C3 and C4 olefinic products, their yield increases as severity increases. It's highly unpredictable to determine exact yields due to various operating parameters, variations in product unsaturation, feedstock characteristics, and the cleanliness of the charge stock, whether it's free of asphaltenes or contains sulfur and nitrogen content. The entrainment of asphaltene material into the feed contributes to coke deposition because asphaltenes are precursors of coke; they form coke as they are highly carbonaceous materials in the feedstock. Similarly, sulfur, nitrogen, etc., act as mild inhibitors to the cracking reaction because they passivate or deactivate the catalyst.

Yields are more directly influenced by the percentage of conversion achieved in a single pass. Severity can be expressed using this formula: catalyst-to-oil weight ratio divided by the space velocity, which is the weight of oil per hour per weight of the catalyst. This formula represents the severity of the operation. If the catalyst-to-oil ratio increases, the severity will also increase. Efficiency for the process is represented by the percentage of gasoline, by the percentage of conversion, multiplied by 100, as gasoline is typically the major product in most FCC operations.

Efficiency is expressed in terms of the percentage of gasoline yield. This chart shows how heat is consumed at different points of operation during the FCC process.

Heat up and vaporize fresh feed: This stage consumes a large amount of heat, totaling 40 to 50 percent of the total heat. Heat for recycling oil: The oil obtained from the fractionator bottom is recycled and mixed with the fresh feed. Since the fresh feed is already at a high temperature, the recycled oil needs to gain heat to mix with it. The percentage of heat consumed for heating the recycled oil is 0 to 10 percent. Reaction temperature control: The reaction is endothermic, so a continuous supply of heat is required to control and maintain the temperature in the reactor. This stage requires 15 to 30 percent of the total heat. Steam generation: Steam generation requires 2 to 8 percent of the total heat. Heat loss compensation: Some heat is lost during the process, and to compensate for this heat loss, 2 to 5 percent of heat needs to be supplied to the process. Regeneration section: In the regeneration section of the catalyst, air is required to burn the coke. The air needs to be heated to reach the regeneration temperature, and this stage requires 15 to 25 percent of the heat for that purpose. Temperature adjustment: There is a temperature jump from the reactor temperature to the regeneration temperature, as the reactor temperature is lower than the regeneration temperature. To achieve this temperature adjustment, 1 to 2 percent of heat is required for the regenerator. The total heat required ranges from 1162 to 2325 kilojoules per kilogram of the feedstock.

These are the references. Thank you for your attention.