Lecture 12: Coking, Gasification and Steam Cracking

Hello and welcome to the 12th lecture on Petroleum Technology. In this lecture, we will learn about Coking, Gasification, and Steam Cracking. In the last lecture, we have already learned that coking is of two major types: fluid coking and delayed coking. So, at the beginning, we will concentrate on fluid coking. Fluid coking involves a fluidized bed, and it is a continuous process. Here, the heated feedstock is spread into a fluidized bed of hot coke particles. Very tiny coke particles are fluidized in the coking reactor, and whenever the heated heavy feedstock is introduced into the fluidized coking reactor, it is spread into the coking reactor. The very small droplets of the feedstock sit on each of the hot coke particles, and on the hot coke particles, the cracking reaction occurs.

You can say that each of the coke particles acts as one reactor, and on each of the coke particles, the reaction occurs. Gaseous products are formed, as well as liquid products and coke is also formed on the coke particles. As the reaction progresses, the coke particles grow in size as the layers on them also grow one after another. Ultimately, at one point in time, the entire coke from the coking reactor is removed, and a new batch of hot coke particles is fluidized in the reactor. This is the whole mechanism of the process. The reactor is maintained at a pressure of 20 to 40 psi, and the temperature is maintained at more than 500 ℃. At this high temperature and pressure, the coking reaction occurs.

The main unit of the fluid coking process is the combined scrubber reactor assembly, where the scrubber is fixed above the coker reactor. The hot residue-heavy feedstock is introduced into the scrubber section, where it comes in contact with the reactor effluent from the reactor, and here, heat exchange occurs. As heat exchange occurs, the residue feed attains a temperature of about 570 ℃, and due to the heat exchange, the reactor effluent gets cooled to that temperature. The heavy hydrocarbons, poly-nuclear aromatic hydrocarbons, condense and are scrubbed out by the residue feed, hence the name "scrubber." This condensed part is sent back to the reactor as a recycle. After the reaction takes place, the lighter products in vapor form are taken out from the top of the scrubber and sent to the fractionator. In the fractionator, the lighter products are fractionated into gas, gasoline, gas oil, and heavy residue. The coke taken out from the bottom of the reactor is sent to a burner where approximately 20 percent of the coke is burned with air introduced into the burner. This is done because coking is an endothermic process, and burning 20 percent of the coke in the exothermic reaction provides the necessary heat for controlling the reactor's temperature. Some amount of coke is returned from the burner to maintain the fluidized bed in the reactor, and the remaining coke is extracted as a marketable product. The flue gas produced by burning the coke in the burner is taken out from the top of the burner and used for steam generation in the steam boiler. This constitutes the overall fluid coking unit flow diagram.

Now, another coking operation, which is one of the preferred choices of many refiners, is delayed coking, as it offers the advantage of handling very heavy residue feedstock. Delayed coking accepts heavy residue, which is low-value and contains a significant amount of sulfur and unwanted metals. This delayed coking process produces a substantial amount of naphtha and diesel products, namely naphtha and metal distillate products. The percentage yield of these products can be adjusted by changing the recycle rate and modifying the operating conditions. The name of the process, "delayed," comes from the fact that the coking reaction occurs in the coke drum rather than in the heater. Unlike other coking processes, in delayed coking, the feedstock is introduced into a furnace where it reaches the required temperature, and coking is not allowed to happen in the furnace tubes. Once the feedstock reaches the necessary temperature, it is promptly removed from the furnace and transferred into a coke drum. The coking reaction occurs in the coke drum instead of the furnace. Hence, the term "delayed," as the coking reaction is intentionally delayed in the coke drum. Coke drums are employed to hold or delay the heated feedstock while cracking takes place. Apart from the coke drum, there are several other units in the delayed coking process, including the furnace's complete blow-down system, the coke separation and recovery system, and the water recovery system, in addition to the coke drums. Two coke drums are used in the process. Delayed coking is not a continuous process; it is a semi-batch process because once one coke drum becomes full of coke, it is removed from the line, and an idle coke drum, which was empty of coke, is then replaced by the full coke drum.

The cracking and carbonization reactions involve dehydrogenation, rearrangement, and polymerization. Various types of reactions take place in the coking process. Here is a simplified flow diagram of the delayed coking unit: Heavy feedstock, along with the recycle stream from the bottom of the fractionator, is sent to the furnace to reach the required temperature. Once the feedstock reaches the desired temperature, it is swiftly transferred to one of the coke drums, where the coking reaction occurs. Inside the coke drum, the coking reaction takes place, producing lighter hydrocarbons that are removed from the top of the coke drum and sent to a fractionator. The bottom product from the coke drum is primarily coke, which solidifies within the drum. When a coke drum becomes full of coke, it is removed from the process line. An empty coke drum is then placed into the line, and the operation continues. This cycle repeats to maintain a continuous coking process.

The gaseous product from the top of the coke drum is extracted and sent to the fractionator. In the fractionator, various products are obtained: Gas and unstabilized gasoline. This gasoline needs to undergo stabilization to remove lighter hydrocarbons. Steam stripping is employed for this purpose; Gas oil is another product obtained from the fractionator. Heavy distillate fraction: The bottom product of the fractionator. A portion of the heavy distillate is taken as a recycle and mixed with the feed for the coking process. Once a coke drum becomes full of coke, it is removed from the processing line and cooled down. During the cooling process, steam is introduced into the coke drum to remove hydrocarbons. The resulting steam and hydrocarbon mixture is sent to the blowdown section, where the hydrocarbon vapor is compressed, and water is separated from it. After cooling, the coke drum is opened, and high-pressure steam and high-pressure water jets are used to detach the coke from the drum's walls. Sharp knives may also be employed to assist in cutting the coke from the coke drum.

After the coke is recovered from the coke drum, it is collected in a coke pit at the bottom of the coke drum. The coke is separated from water, and then it is sent for the next phase of treatment. The table provided shows the maximum conversion in delayed coking of two types of residues: atmospheric residue feedstock and vacuum residue feedstock. If you examine the products, they include Gas (up to C_2), LPG (a mixture of C_3 and C_4 hydrocarbons), Naphtha (boiling in the range of C_5 to 170 ℃), Light cycle gas oil (boiling in the range of 170 to 350 ℃), Heavy cycle gas oil (boiling above 350 ℃), Coke. These are all the products of the coking operation.

Comparing the atmospheric residue and vacuum residue, you can observe differences in the weight percentages of lower molecular weight gas (up to C_2). Atmospheric residue produces 3.4 percent, while vacuum residue produces 4.9 percent more. However, when it comes to lighter products like LPG, naphtha, and light cycle gas oil, atmospheric residue produces a much higher percentage of these products compared to vacuum residue. This difference is due to atmospheric residue containing lighter hydrocarbons remaining in it compared to vacuum residue.

Heavy cycle gas oil is not obtained from atmospheric residue because atmospheric residue does not contain a higher percentage of heavy fractions, unlike vacuum residue, which produces a substantial quantity of heavy gas oil. The same trend holds for coke production; coke production is much less from atmospheric residue compared to vacuum residue. Petroleum coke is a coal-like substance known as "green coke," and it is primarily used as a fuel in power plants. Petroleum coke can be classified into two distinct types: calcined (or green coke) and fuel-grade (or pet coke).

This fuel-grade coke, also known as pet coke, is primarily used as a fuel in power generation. Pet coke has a spongy texture and contains a significant amount of sulfur. When fuel-grade pet coke is burned, it produces sulfur dioxide gas. Therefore, whenever fuel-grade coke is used in power generation, a sulfur-capturing unit must be associated with the power generation system to capture the sulfur and maintain clean air specifications. Calcined or green coke is obtained by roasting or calcining petroleum coke at a temperature just below the melting point of the coke. It finds various applications in the smelting industry for the production of metals such as titanium, aluminum, and steel. Additionally, it is used in motor brushes and dry cells. Despite being a low-grade fuel compared to transportation fuels, coke has a high demand as it is economical, readily available, and easily produced, even though it contains a significant amount of sulfur.

Calcined or green coke is produced in the Barauni, Digboy, and Guwahati refineries of the Indian Oil Corporation, while fuel-grade or pet coke is produced in the Panipat refinery of the Indian Oil Corporation. Another process practiced in refineries is the gasification of heavy residues, which involves gasifying heavy residue fractions such as heavy oils and refinery residues. This process is also known as partial oxidation. Gasification has several advantages, including the ability to process low-quality, highly viscous, and sulfur and metal-rich residues. Gasification or partial oxidation can convert these high-sulfur residues into a clean synthesis gas, which is a mixture of hydrogen and carbon monoxide. This synthesis gas serves as the feedstock for many chemical processes.

From this hydrogen and carbon monoxide mixture, hydrogen can be separated out as the content of hydrogen is very high in this synthesis gas and can be used in different application points in the refinery. This synthesis gas is the feedstock for the production of various chemicals such as ammonia, where we need hydrogen, methanol, both carbon monoxide and hydrogen, acetic acid, oxo-alcohols, etc. All these are the highly demanding chemicals in the process industries. Chemistry of partial oxidation of hydrocarbons in this, we will see that partial oxidation is the reaction of hydrocarbons with an amount of oxygen that is insufficient for complete combustion; that is why the name partial oxidation is given. The temperature is kept at a very high 1250 to 1600 ℃ and pressure is kept at around 15 mega Pascal. This process may be autothermic. This autothermic partial oxidation is an endothermic process and to compensate for the heat requirement, some part of the feedstock is burnt in the reactor. This reactor is called an auto thermal reactor, where the feedstock is burnt in the upper part of the reactor and the heat produced due to this burning is taken in the lower part of the reactor where the partial oxidation process is going on. It is seen that, as a whole, the process is slightly exothermic. So, this process may be autothermic. Here, steam is introduced as a moderator; steam has many functions. Steam is introduced as the heat carrier as well and steam gives mobility to the feedstock; steam reduces the partial pressure of the hydrocarbon and this way, it reduces the coke deposition in the furnace coil. The product is a mixture of not only carbon monoxide and hydrogen; it is a mixture of carbon monoxide, carbon dioxide, hydrogen, water vapor, methane, hydrogen sulfide and carbonyl sulfide. So, before the synthesis gas is utilized for making any chemicals, the whole gas mixture has to pass through a sulfur-removing process to remove the sulfur-containing compounds. Otherwise, these sulfur-containing compounds may passivate the catalyst of the secondary processes. Now, another type of process is usually practiced in the refinery, which refinery has associated petrochemical units with it. Steam cracking or pyrolysis of hydrocarbons is one of the major processes to get the first generation of petrochemicals. Mainly, it produces small unsaturated hydrocarbons. It is a non-catalytic thermal decomposition process. A catalyst is not used in this process in which the saturated hydrocarbons are broken down into smaller unsaturated olefinic hydrocarbons. So, long chain saturated hydrocarbons are decomposed and they give the shorter-chain olefinic hydrocarbons and these small olefinic hydrocarbons are the feedstock for the petrochemical's next generation petrochemicals. The temperature range varies between 750 to 900 degrees centigrade. This high temperature does not allow the feedstock to reside in the furnace for a longer period of time because this residence time is kept very low, 0.1 to 10. The reason for this is that this short residence time at this high temperature can avoid many unwanted side reactions as well as the coke formation reaction. Steam is introduced in the feedstock; steam suppresses the partial pressure of hydrocarbons, and decreases the possibility of polymerization of the dioliphenic products and the coke deposition in the cracker. As we get the unsaturated hydrocarbons, this unsaturated hydrocarbons may be the monounsaturated or polyunsaturated. In polyunsaturated compounds hydrocarbons, some dioliphenic products are also obtained.

Dioliphenes contain hydrocarbons that are highly prone to polymerization, but steam reduces the partial pressure of these hydrocarbons. So, the polymerization reaction possibility is decreased. This is a flow diagram of the steam cracking process. The raw materials may be various kinds of ethane, propane, butane, very low molecular weight hydrocarbons, as well as naphtha. In fact, naphtha is the major feedstock for the steam cracking process.

Gas condensate is the mixture of C4 and C5 hydrocarbons, which condensate is obtained by condensing the refinery off gases. Gas oil is the heavy hydrocarbon feedstock. This may be introduced in the pyrolysis process when the reactor temperature is 750 to 900^0C and pressure is kept at 2 to 4 bar. The steam is introduced into the furnace, and water vapor is kept more than 40 percent. Time: residence time is kept very low, 1 second and conversion per pass is allowed by 60 to 80 percent.

After the product is formed, the products are separated in the separation section. The first stage is cooling up to 300 ℃. After this, the carbon dioxide, hydrogen sulfide and water vapor are removed from the products. After this, gas mixtures are taken to the cooling section and low-temperature fractionation. The second stage is the cold separation unit, where different hydrocarbons and low molecular hydrocarbons are separated at very low pressure and temperature. The ethane and propane, which are unconverted or produced by this cracking process, are recycled back to the pyrolysis reactor and we get a range of products. These are the products obtained usually in the steam cracking process: ethylene, propylene, 1-butene, 2-butenes, and isobutane. These are the mono-unsaturated small-chain hydrocarbons that are the major feedstock for the petrochemical unit. Except that this is the polyolefinic compound, which is butadiene, this is also an important feedstock for petrochemicals. So, one example may be the preparation of styrene butadiene rubber. After this olefinic hydrocarbons, we will consider hydrogen production. Hydrogen is produced by this process, which can be utilized for many other processes.

Methane is utilized as a fuel as it is a high calorific value gas and pyrolysis gasoline is a liquid cut that boils in the gasoline range and contains lots of aromatic compounds, mostly benzene, toluene and xylene. This pyrolysis gasoline is taken as a product from the steam cracking and mixed with the other gasoline obtained from various other processes. This slide shows the product distribution along the steam cracker tube. As the feedstock is flowing through the steam cracker tube, different reactions occur and temperature varies at different points. So, with the change in temperature within the furnace coil or cracker coil, the rate of the reaction changes and as the rate of the reaction changes the rate constants also change. It is actually one factor is introduced to get the idea of the severity of the operation, which is called kinetic severity function KSF, which is represented as $2.303\log 1/(1-x) = kT$ where x is the fractional conversion, k is the average rate constant, T is the time. According to the value of KSF, the process of steam cracking can be divided into zones like zone 1, which is the least severe process where the KSF value is less than 1. Here in this zone, primary reactions occur, which are the basic reactions in the steam cracking process. Zone 2 is somewhat more severe, where the KSF value ranges from 1 to 2.5, more than 1 less than 2.5 and the third one is the highest severity section, zone 3, where KSF is more than 2.5. In this section, the secondary reaction and coke formation take place. As we look at this figure, we see that various products are formed at different zones at different yields. Look at the ethylene, the most important product from the steam cracking. The ethylene production increases as the severity increases and after a certain severity, the production is leveled off.

Look at the hydrogen and methane here. The hydrogen and methane production increases as the severity increases, but after a certain time, the production rate increase is not much appreciable. Propylene, butane, butene and butadiene follow a similar trend at the beginning. The production increases as the severity increases and after a certain time, as the severity goes very high, the percentage yield decreases. As we see the gasoline, gasoline yield decreases as the severity increases, but after a certain severity, gasoline increases, but not a very high trend. This is the whole process of getting different yields of products at different severity in the steam cracking process.

These are the references. Thank you for your attention.