Lecture 11: Secondary Processing: Decomposition of Residues: Thermal Cracking

Hello and welcome to Lecture Number 11 of Petroleum Technology. Today, we will learn about secondary processing, specifically the decomposition of residues by thermal cracking operations. In thermal cracking, heat is applied to a heavy feedstock to break it into smaller fragments and lighter products. Therefore, thermal cracking is a secondary process in the refinery where changes in the composition of petroleum fractions are achieved solely through the action of heat. In this process, catalysts are not used; only heat serves as the energy source to break the molecules, reduce viscosity, or transform a low-value product into a high-value one. This process involves the decomposition of carbon-carbon bonds in hydrocarbon molecules.

Usually, heavy feedstocks are charged into the thermal cracking process to obtain lighter products. The primary or first-stage products are mainly olefinic in nature, consisting of double-bonded hydrocarbons. In the second stage of the process, we get products with the same molecular weight as the feedstock or higher than the feedstock. The typical temperature for thermal cracking is around 425 to 500 ℃. The severity of thermal cracking depends on the type of feedstock, residence time (how long the feedstock remains in the cracking furnace), and the desired degree of conversion. The outcome, whether it's a lighter product, gas, or liquid, depends on the parameters chosen for the thermal cracking process.

Mild thermal cracking is known as visbreaking, a type of thermal cracking commonly employed in refineries. Another thermal cracking process, which is more severe, is called coking.

Visbreaking and coking are both popular thermal cracking operations in the refinery. In fact, pure thermal cracking has not been widely used in the refinery for the past several decades, but visbreaking and coking are the two very popular methods, popular processes used in the refinery. Thermal cracking is indispensable as a source of primary petrochemical, ethylene. Ethylene is the first grade of petrochemical, the first in a series of petrochemical starting materials obtained through the thermal cracking of mostly naphtha. In the thermal cracking process, steam is introduced into the thermal cracking furnace. This process is called steam cracking of naphtha, where steam serves the dual purpose of providing heat and suppressing coke formation in the process. Here is a table that compiles various types of thermal cracking processes, their temperature ranges, and the resulting products: Visbreaking operates in the temperature range of 425 to 460 ℃, which is the lowest among all, with the major product being fuel oil. This is the most desired product from the visbreaking operation.

Thermal Cracking: Operates at somewhat higher temperatures, ranging from 460 to 520 ℃. The products obtained from thermal cracking include gas, gasoline, and fuel oil. These thermal cracking processes are selected based on their temperature ranges and the desired product outcomes, with visbreaking suitable for fuel oil production and thermal cracking yielding a mixture of gas, gasoline, and fuel oil.

As the temperature is higher, lighter products are also formed along with the heavier products. Fuel oil, gas, and gasoline are the lighter products. The next stage of cracking operation may be low-temperature coking; it operates in the range of 520 to 600 ℃. Here again, we may get gas and gasoline as the lighter end products and soft coke, which is a spongy type of coke used for burning purposes, as another higher-end product, a higher molecular-end product. The temperature of 600 to 800 ℃ is for gas production. Mostly, gases are produced at this very high temperature, and unsaturated compounds, that is, olefinic compounds are produced in this production process.

800 to 1000 ℃ temperature is operated for high-temperature coking. Here, we mostly get coke (hard coke) and also "peach," which is a carbonaceous material. It is a semi-solid type of material obtained, and heavy aromatics are formed—high molecular aromatics. These heavy aromatics, peach, and coke, are on the higher molecular weight side. In the lower molecular weight, the side product is the gas. So, coke is also a carbonaceous compound, having a very high carbon-to-hydrogen ratio. Hydrogen content is very low, but it is not completely carbon. Peach has a somewhat higher hydrogen content than coke; that's why it is semi-solid. Heavy aromatics contain polynuclear aromatics with many rings together and polymerized aromatics. These are the higher-end products. Above 1000 degrees, complete decomposition of the hydrocarbons occurs to produce hydrogen and small molecular weight gases. In the higher molecular weight range is the carbon black, which is almost pure carbon. These are the components of various types of thermal cracking operations in the refinery. All these processes are performed depending on the demand in the market and the refiner's choice. This is the flow diagram of a typical thermal cracking operation, where both long residue and short residues are used as feedstock. The long residue is actually atmospheric residue, and the short residue is vacuum residue. Atmospheric residue is termed "long residue" because it contains many distillate fractions. This classification is made because atmospheric residue can yield far more distillates and valuable products compared to vacuum residue. In contrast, vacuum residue is referred to as "short residue" because it is less capable of yielding valuable cuts or distillate products. Regardless of whether it's long residue or short residue, it is charged into the cracking furnace. In the case of long residue, after cracking, it will not only yield distillate products but also a significant amount of lighter products and cracked residue.

So, lighter products are sent through a cyclone separator to the fractionator. From the fractionator, we obtain gas and gasoline as the lighter products from the top and gas oil as the side-stream product. Heavy distillate products are recycled; they are sent through a furnace or heat exchanger and then recycled to the bottom of the fractionator. From the bottom, we get the cracked residue. Similarly, in the case of short residue, it is cracked in the furnace and then suddenly sent to the fractionator. From the top of the fractionator, we get lighter products, gas and gasoline. The side stream is gas oil, and the bottom stream is the cracked residue. Various kinds of reactions occur in thermal cracking: dehydrogenation, dealkylation, isomerization, cyclization, alkylation, polymerization, hydrogenation, etc. All these reactions may occur together at a time during the cracking process, or they may occur sequentially, one after another, depending on the type of feedstock, the hydrocarbon composition in the feedstock, the residence time in the furnace, the temperature, etc.

Thermal cracking is an endothermic process, and it follows a free radical mechanism. As it is an endothermic process, we need to make arrangements for a continuous supply of heat to maintain the temperature. The thermal cracking reaction rate increases as the molecular size decreases but decreases with aromaticity, since aromatics are harder to crack. The rate of thermal cracking is exponentially related to temperature; this is quite obvious because these thermal cracking reactions always follow the Arrhenius principle and exhibit an exponential dependence on temperature.

Let's delve into the mechanism of thermal cracking, which is a free radical process. First, in the initiation stage, normal paraffin, nonane (C_9H_{20}) is heated, producing two radicals: an ethyl radical and a C_7H_{15} radical. This marks the beginning of the process. Moving on to propagation, the ethyl radical combines with another feed molecule, extracting one hydrogen from nonane to form ethylene. It then departs, leaving behind a large free radical, the C_9 free radical, which undergoes beta scission. Beta carbon, the one-two carbon away from the electron, undergoes beta scission, leading to the formation of propylene, an ethyl olefinic compound, and another free radical. This free radical undergoes beta scission as well as alpha scission. Alpha scission involves breaking the bond of the carbon adjacent to the electron. Both beta scission and alpha scission produce olefins. Alpha scission results in propylene, while beta scission yields ethylene and other free radicals. This process continues, ultimately producing ethylene as the end product, along with olefinic products, methyl radicals, and ethyl radicals. In the termination stage, various reactions can occur. For example, two methyl radicals can combine to produce methane, ethane, and ethyl radical. Alternatively, a methyl radical and an ethyl radical can combine to produce propane or ethylene and methane. These are examples of termination reactions in the free radical mechanism of thermal cracking. Now, let's discuss visbreaking, which is a mild thermal cracking process used in refineries to reduce viscosity and improve the pour point of heavy oils, primarily atmospheric residue, vacuum residue, or both. The name "visbreaking" derives from its purpose of breaking down the viscosity of heavy residues during thermal cracking. As longer-chain hydrocarbons are cracked into shorter chains, lighter products are produced, resulting in a decrease in viscosity compared to the feedstock. Additionally, visbreaking helps lower the pour point, which is the temperature at which oil solidifies or forms wax crystals. Heavy residues often contain long-chain paraffinic compounds that can lead to wax crystal formation, causing pipeline blockages in cold regions. Visbreaking yields gas, distillates, and stable fuel oil. The stable fuel oil is a valuable product as it does not produce vapor at moderate temperatures, making it safe for use. This process is employed to increase the net distillate yield in refineries while reducing the volume of heavy oil produced. Visbreaking is considered a mild thermal cracking process, and its associated costs are not very high because the operating temperatures are not extremely elevated. In the table provided, you can see the products obtained from visbreaking when using atmospheric and vacuum residue as feedstock, including gas, naphtha, gas oil, and residual fuel oil. The typical process scheme for a visbreaking unit involves charging either atmospheric residue or vacuum residue into a visbreaker heater or furnace. The temperature is then raised to the desired level, and the stream is quickly transferred to a soaking drum, where the cracking reactions take place.

The quick transfer is essential because, if cracking occurs within the visbreaker heater or furnace, the equipment will become coated with coke deposits. Therefore, all cracking reactions and the required residence time are allowed to take place in the soaking drum. Once the desired degree of reaction and residence time is reached, the stream is rapidly quenched with a gas oil stream or cooled visbroken tar to halt the reaction. Afterward, the entire stream is routed to the visbreaker fractionator. In the fractionator, fractionation occurs, and from the top, the visbreaker off-gases are obtained. After they are cooled, their vapors are condensed. From the reflux drum (shown here), one liquid stream is directed to the top of the tower to serve as reflux, and the other stream is collected as unstabilized naphtha. Unstabilized naphtha requires steam stripping to remove the light ends. The side stream is visbreaker gas oil, which undergoes steam stripping in the stripper unit. From the bottom of the fractionator, visbreaker fuel oil is obtained. This comprises the entire visbreaking operation.

The distillate fraction from the visbreaking process is used as a blending agent for heavy straight-run residual fuel oil to reduce its viscosity. The distillate fraction obtained from the visbreaker unit is blended with the heavy straight-run residual fuel oil, effectively lowering the cutter stock requirement for residual fuel oil blending. In the refinery, instead of visbreaking, another approach is sometimes employed, where the heavy residue is mixed with a lighter stock to reduce viscosity. This transformation of low-value residues into high-value products involves mixing the very heavy residual fuel oil with a lighter product or distillate product, making it suitable for use as burner fuel. The cutter stock used here typically refers to the diesel fraction of the refinery. Diesel is a higher-value product compared to residual fuel oil. However, when cutter stock is mixed with residual fuel oil, the value of diesel decreases, even though the value of the residual fuel oil increases. In this process, some valuable cuts are effectively lost. Conversely, if visbreaking is practiced in the refinery, distillate fractions are obtained from the visbreaking unit, which can be used as blending agents for residual fuel oil to reduce viscosity and enhance its value. Consequently, the use of cutter stock can be minimized. The severity of visbreaking is constrained by the stability of the high-sulfur residual fuel oil. Objectionable compounds, such as sulfur compounds, tend to accumulate in the heavier fractions of residual fuel oil. Therefore, if the residual fuel oil contains a high sulfur content, its stability becomes questionable. As a result, the severity of the visbreaking process, which includes factors like temperature and residence time, is selected carefully to address these considerations.

As a result, the residual fuel oil product ultimately becomes a stable product. The economics of the process are strongly influenced by the use of visbreaker distillate in place of cutter stock. Visbreaker distillate is not significantly more expensive than the cutter stock produced in the refinery. Therefore, if visbreaker distillate can replace cutter stock, it can lead to overall economic improvement. Despite efforts to prevent coke formation in the Visbreaker furnace, some amount of coke still forms in the Visbreaker furnace coils. This coke formation is inevitable and cannot be entirely avoided.

To decoke the visbreaker furnace and ensure good heat transfer, steam and air are introduced into the furnace coils for the purpose of burning off the coke buildup. Steam is introduced from the beginning to reduce the hydrocarbon partial pressure, thereby restricting coke formation right from the start. After a certain period of operation, when some coke has already accumulated in the visbreaker furnace coils, hindering efficient heat transfer, the air is introduced to burn off some of the coke for decoking. Additionally, a thermal shock is applied to the furnace walls to dislodge the coke deposits on the coil walls. The broken particles are then carried away by the high-velocity steam. This process can remove approximately 80 to 90 percent of the coke, effectively decoking the visbreaking furnace. These are the various steps employed for the decoking of the visbreaking furnace.

Now, let's discuss coking. Coking is a high-severity process operated in the refinery, characterized by high temperatures and extended residence times. Coking serves to upgrade low-value bottoms, such as atmospheric or vacuum residue, into higher-value petroleum coke. When atmospheric or vacuum residues do not offer good utilization or value-added benefits, they are directed to the coking operation. Petroleum coke is a highly valuable product due to its substantial calorific value. It is widely used in various industries as a fuel for combustion. Petroleum coke shares similarities with high-carbon coal in terms of its material properties.

So, petroleum coke provides us with a valuable fuel source. In addition to coke, coker gas oil is another significant product of the coking process. Coker gas oil holds importance because it can be blended with the gas oil stream from other refinery processes. Ultimately, through blending, it contributes to the production of diesel cuts and can also serve as a cutter stock. The production of coke is achieved by prolonging the duration of the liquid phase cracking process. This extended time leads to the generation of polymerization and condensation products. As mentioned before, coke is a highly carbonaceous material characterized by very low hydrogen content. It is obtained through the extended exposure of hydrocarbons to high-temperature conditions during the coking process, which requires a lengthy duration at high temperatures.

In the coking process, large molecules undergo polymerization and condensation, resulting in the formation of compounds with very high molecular weights and very low hydrogen content but a significant amount of carbon. This ultimately leads to the production of coke. Coke itself may take the form of a fluffy material, not a sticky one. Sticky products are typically referred to as "peach." The temperature range used in the coking process typically falls between 500 to 650 ℃.

At the high temperatures mentioned, coking occurs, and coking operations can be classified into two types: fluid coking and delayed coking. Fluid coking involves fluidizing very tiny coke particles within the coking furnace at high temperatures. These small coke particles act as the reaction points, and more coke is deposited on them during the cooking process. On the other hand, delayed coking is a process where, after the feedstock is heated at a high temperature in a furnace, it is rapidly transferred to a coking drum. In this coking drum, coking reactions take place for an extended period of time. This process is termed "delayed coking" because the coking reactions do not occur within the furnace where the feedstock is initially heated.

These are the references. Thank you for your attention.