Lecture 13: Secondary Processing: Decomposition of Residues: Hydrocracking

Hello, and welcome to the lecture number 13 of Petroleum Technology. In this lecture, we will learn about the secondary processing of hydrocarbon. This is one of the processes where we will see the decomposition of the residues. Nitrogen is utilized in the refinery at various utilization points such as giving very high-quality low-boiling products from heavy and high-boiling feedstock. It can reduce the nonhydrocarbon compounds such as sulfur, nitrogen, oxygen, etcetera from the feedstock and give the product an acceptable quality. Except that the hydrogen can crack the polynuclear heavy aromatic hydrocarbons to give the product color stability and stability towards various other operations, and it can give us a good lubricating oil-based stock.

Other applications of hydrogen utilization are to obtain a good-quality fluidized catalytic cracking feedstock, a good feedstock for the steam reformer process, and many other secondary processing feedstocks. Hydrocracking is the cracking operation where hydrogen is introduced during the cracking. So, it is not only cracking; it is a combination of hydrogenation and cracking. Here, the low-value gas oil with a high percentage of polynuclear aromatics is simultaneously cracked and hydrogenated to produce low-boiling and mid-boiling distillates of high value.

So, the low-demand and low-valued high-polynuclear aromatic-containing hydrocarbon fractions can be converted to high-demand valued low-boiling products. It selectively produces gasoline, diesel fuel, or jet oil without producing any unwanted low-molecular-weight gases. This is one of the advantages of hydrocracking: any portion or percentage of feedstock is not lost by producing unwanted low-molecular-weight gases, which almost have no use in the refinery. The major product, which is desired or wanted products, are the low-boiling transportation fuels. These are gasoline, diesel fuel, and jet fuel, which are the major products of the hydrocracking process.

Hydrocracking feedstocks may be straight-run vacuum gas oil, coker gas oil, solvent-deasphalted oil, or vacuum gas oil, which we obtain directly from the vacuum distillation unit. Coker gas oil is obtained from the fractionating tower of the coking process. Solvent-deasphalted oils are those oils that are heavy in asphaltene content, and thus, asphaltene or heavy carbon-precursor materials are removed by solvent extraction. This is the solvent-deasphalted oil. Hydrocracking reactions are inhibited by the presence of nitrogen and sulfur compounds.

This is one of the advantages of a hydrocracking reaction because if the feedstock contains nitrogen and sulfur compounds, the hydrocracking produces ammonia and hydrogen sulfides, which can deactivate the catalyst of hydrocracking. So, the feedstock should be devoid of any sulfur and nitrogen compounds, and then the hydrocracking catalyst can run with a long catalyst life, and the product quality will be much better. This is a general flow scheme of the hydrocracking process. This is called a single-stage once-through process (SSOT). This hydrocracking configuration is the least costly scheme per barrel of feed but more costly per barrel of light products generated.

Here, the unconverted oil, obtained from this process, can be used as one of the good-quality feedstocks for the next stage of secondary operations, such as catalytic cracking or steam cracking. If the refiner wishes to add more value to this unconverted oil, then they can run this process for hydrocracking. This unconverted oil can act as a good-quality lube oil base stock because it is hydrogen-rich. The process involves mixing the fresh heavy feed with makeup or recycled hydrogen, heating it, and then trickling it downward toward a multi-bed reactor. This is a multi-bed reactor.

As the reaction is highly exothermic, a device is introduced into the reactor to redistribute the phases—liquid feed and hydrogen—within the beds, and quenched hydrogen is injected between the beds to control the temperature. After the hydrocracking, the products are taken out from the bottom and sent to a high-pressure separator where the liquid products are formed, and the gaseous products are extracted. This includes the recycled gas, and hydrogen is introduced as the quenched hydrogen to the reactor, along with some portions mixed with the fresh feed for the reaction. In this process, if the feed contains lots of sulfur and nitrogen, then the product also contains sulfur, hydrogen sulfide, and ammonia. Additionally, the recycled gas also contains these two unwanted gases. Injecting this recycled gas along with hydrogen will obviously deactivate the hydrocracker catalyst in the reactor.

This is one disadvantage of the single-stage once-through process. From the bottom of the separator, the liquid product is taken out and sent to a fractionator. From the top of the fractionator, we obtain product gas, various light gases, light naphtha, heavy naphtha, kerosene, and diesel as side streams. The unconverted oil is collected as the bottom stream and taken for the next stage of processing. There are several other types of hydrocracking processes. One is the single-stage recycling process. In this process, the refiner aims to convert all the feedstock into light products, and the fractionator's bottom stream is recycled back with the fresh feed. This is the single-stage recycling system. This single-stage recycle system can be divided into two types: a single-reactor system and a two-reactor system. In the single-reactor system, the fractionator's bottom stream is recycled and co-processed with the fresh feed, while in the two-reactor system, the first reactor is the treating reactor where the feed is introduced, and two reactors are placed side by side for demetallation, desulfurization, and denitrogenation processes.

This is the hydrotreatment unit. Here, sulfur, nitrogen, and metals are removed through the use of high-pressure hydrogen. After the unwanted materials are removed from the feed, the feed is introduced into a hydrocracking reactor. Therefore, this hydrocracking catalyst does not have to endure the ammonia and hydrogen sulfide environment, resulting in a longer catalyst life. The bottom of the hydrocracker is sent to a fractionator to obtain different side cuts as well as the bottom cut. Another process is the two-stage recycling process.

Here, the fractionator bottoms of the SSOT are sent to another reactor in which the remaining heavy oil is converted. If you look at this process, the dotted portion represents the SSOT system where the fresh feed is mixed with recycled hydrogen and sent to a multi-bed reactor. The bottom of the reactor is separated in a high-pressure separator. The hydrogen, along with other gases, is recycled, and quenched hydrogen is injected into the beds of the reactor. The product is the first-stage product, which is sent to a fractionator to obtain various light cuts as well as the heavy cut.

The heavy cut, instead of recycling with the fresh feed, is sent to another hydrocracker where it is mixed with some portion of the makeup hydrogen. In this hydrocracker, the catalyst does not have to face the ammonia and hydrogen sulfide environment because this unconverted oil does not contain ammonia and H_2S; these impurities have already been removed in the first stage of the process. Now, the reactor bottom is taken out in a similar way; it is separated in a separator, and the separator bottom, which is a liquid, is sent to the same fractionator where the first-stage product is fractionated. This process is called the isocracking process, and it was first introduced by the company Chevron. This process is known as the Chevron isocracking process.

They introduced this process long before 1959, and since then, the hydrocracking process has been a highly popular process in the refinery because it produces very high-quality feedstock for secondary processing units. Now, let's consider an example of hydrocracking for lube oil base stock. We have observed that the SSOT hydrocracker produces a very high-quality lube oil base stock from the unconverted oil at the bottom of the fractionator. This lube oil base stock has excellent properties. For example, the viscosity index of the heavy feedstock used in the SSOT system maybe 40. However, after hydrocracking in the SSOT, the viscosity index value of the unconverted oil has improved to 130. So, there is a significant increase in the viscosity index, going from 40 to 130.

For lube oil, the property of the viscosity index is crucial. It measures the rate of change of viscosity with temperature. Lubricating oil is used in situations where two moving parts require lubrication to reduce friction and dissipate the heat generated by their movement. Between these two moving parts, such as gears and others, lubricating oil is applied. As the temperature increases, the lubricating oil's temperature also rises, and with rising temperature, the viscosity of the lubricating oil typically decreases. This is a common property of most oils. However, when the viscosity index of lubricating oil is high, it can resist significant changes in viscosity with temperature. In other words, a higher viscosity index indicates better resistance to viscosity changes as temperature varies. This improvement in the viscosity index is achieved through the saturation and cracking of heavy aromatic compounds, leading to the selective production of isoparaffins. The presence of isoparaffins contributes to a higher viscosity index in lubricating oil. Typically, paraffins are known for providing a high viscosity index to lubricating oil. In the hydrocracking process, heavy aromatic compounds are cracked and saturated to produce isoparaffins, thereby enhancing the viscosity index value of the lubricating oil.

Normal paraffins also provide a good viscosity index value, but they have an associated problem: normal paraffin is a precursor of wax formation. Long-chain, straight-chain normal paraffins tend to form wax when the lubricating oil is cooled to a certain temperature. This is measured by a property called the pour point. If the pour point is high, it indicates that the lubricating oil contains a significant amount of normal paraffins, which are prone to wax formation. When lubricating oil is transported through a pipeline from a hotter region to a colder region, there is a risk of freezing within the pipeline due to the increase in viscosity at low temperatures and the formation of wax. Normal paraffins are responsible for wax formation. However, if normal paraffin can be removed through the dewaxing process, the viscosity property of the lubricating oil will be improved. Alternatively, if normal paraffin can be converted into isoparaffins, the viscosity index value can be retained, and the tendency for wax formation will be minimized. Dewaxing by hydroisomerization is another advantage by using hydrogen in the process. Dewaxing by hydroisomerization offers advantages over solvent dewaxing and catalytic dewaxing. While solvent dewaxing or catalytic dewaxing removes normal paraffins from the lubricating oil cut, hydroisomerization retains these paraffins in the form of isoparaffins. This allows for the retention of the viscosity index value and the reduction of wax formation tendencies in the lubricating oil. Now, let's delve into the chemistry of hydrocracking. Hydrocracking feedstocks are complex mixtures of hydrocarbons. They are heavy, and the reaction processes can be best understood by considering three types of hydrocarbon compounds.

If we divide the entire hydrocarbon range into three major types—paraffins, naphthenes, and aromatics—their responses to hydrogen differ as the cracking reaction progresses. Consider a feedstock that boils above 345 degrees Celsius and may contain 18 percent paraffins, 20 percent naphthenes, and 56 percent aromatics. When this feedstock is introduced into the hydrocracking process, we can observe the yield and hydrogen consumption as shown in this figure. As the feedstock is introduced into the hydrocracking reactor, which contains paraffins, naphthenes, and aromatics, the aromatics are the first to react with the hydrogen. Aromatics are more reactive than the other compounds. Initially, the aromatics become saturated and form naphthenes that have a similar boiling range to aromatics.

That means, at 345 degrees Celsius or higher, the cut is not reducing its boiling range initially. However, after some time, when almost all polynuclear aromatics are saturated by the hydrogen and transformed into naphthenes, the naphthene content starts to decrease. In the SSOT (Single Stage Once Through) process, paraffins do not respond well. They remain largely unchanged from the beginning. As the reactor length increases, we observe an increase in conversion. The aromatics content is significantly reduced, and then naphthenes and paraffins become nearly the same. Now, let's discuss the benefits of a clean second-stage operation, as shown in the picture.

Here, hydrocracking is performed in two stages: the first stage is in the presence of ammonia and H_2S, and the next stage is without these contaminants. In the initial two-stage recycle system, in the first stage, aromatics are similarly saturated to produce naphthenes, while paraffins remain largely unchanged. After a certain reactor length or a specific percentage of conversion, typically around 37 to 40 percent, the product is extracted and sent to a second reactor where it is free from ammonia and hydrogen sulfide—a second-stage reactor. When the feedstock is in an environment free of ammonia and H_2S, it can yield a better product composition at significantly lower temperatures compared to the first stage. In the picture, you can see that the content of aromatics suddenly decreases to almost zero, naphthene content also decreases, and even paraffin content is lower in the second stage. Overall, the reaction rate is nearly 30 times faster in the second stage process without sulfur and nitrogen contaminants than in the first stage. This illustrates the advantage of operating the hydrocracking reaction without sulfur and nitrogen. The following slide displays the operating conditions for different feedstocks in residue hydrocracking and distillate hydrocracking. Residue hydrocracking is typically more demanding, with stricter conditions than distillate hydrocracking.

Residue hydrocracking consumes hydrogen in the range of 1200 to 1600 cubic feet, while distillate hydrocracking may consume 1000 to 2400 cubic feet, depending on the type of feedstock and the desired extent of the reaction. Liquid hourly space velocity is lower for residue hydrocracking, whereas in distillate hydrocracking, it may be higher. The lower temperature range is higher for residue hydrocracking, typically in the range of 400 to 425 degrees Celsius, while distillate hydrocracking covers a temperature range of 250 to 480 degrees Celsius for similar products. The required hydrogen pressure is higher for residue hydrocracking and distillate hydrocracking, and it can vary significantly depending on the desired end product.

Now, the catalyst also plays a significant role in determining the range of products produced in hydrocracking. Depending on the type of catalyst used, hydrocracking can either produce 100 percent naphtha or maximize the production of middle distillates. The middle distillate is a mixture of kerosene and diesel. Two types of catalysts are commonly used in hydrocracking: amorphous catalysts and zeolite catalysts. Amorphous catalysts are non-crystalline, whereas zeolite catalysts are crystalline.

When zeolite is used, only naphtha can be produced in hydrocracking, depending on the operating conditions of the reaction, without producing any byproduct light gas. This is of utmost importance. Zeolite catalysts can exclusively produce naphtha without generating any byproduct light gas. Among various types of zeolites, Y-type zeolite in impregnated form with rare earth metals is highly preferred for obtaining the naphtha fraction. Amorphous catalysts tend to yield more middle distillate, but when zeolite is added to amorphous catalysts, a combination of the catalysts results in a higher ratio of light to heavier liquid products. This allows us to customize the product yield depending on the type of catalyst used.

Hydrocracking catalysts offer long operating cycles since hydrogen is used in the process, and the catalyst's lifespan can extend up to 2 years or even longer in the case of distillate hydrocracking. However, if it is a residue hydrocracking process, the catalyst's life may be reduced to 1 and a half years. In the following slide, we will explore the impact of catalyst type on liquid yields in the hydrocracking process, specifically in a two-stage recycle process. When zeolite is used as the catalyst, it is possible to achieve 100 percent naphtha production. The specific type of zeolite used and the adjustment of the recycle cut point, at which point recycled material is mixed with the fresh feed, can influence the product mix. By fine-tuning the operating conditions and selecting the appropriate zeolite type, it is possible to obtain a mixture of naphtha and kerosene, or if desired, increase the middle distillate fraction while reducing the naphtha fraction.

Indeed, everything depends on the type of catalyst, operating conditions, and the recycle cut point in hydrocracking. Amorphous catalysts typically yield a mixture of naphtha and middle distillate. However, the specific yields of naphtha and middle distillate, as well as their combination, can be adjusted based on the type of amorphous catalyst being used. The choice of catalyst and fine-tuning of process parameters allow for flexibility in tailoring the product state to meet specific refinery requirements and market demands.

These are the references. Thank you for your attention.