Lecture 28: Upgradation of straight run cuts from atmospheric distillation unit (Contd.)

Hello and welcome to the 28th lecture of Petroleum Technology. In this lecture, we will learn about the Upgradation of Straight Run Cuts from Atmospheric Distillation Units. Today we will discuss the isomerization of the naphtha fraction. The isomerization process is required to isomerize some of the normal chain paraffinic compounds which have very low octane numbers and convert them into isoparaffins which have higher octane numbers. Virgin light straight-run naphtha typically boiling 30 to 75 degree centigrade consists mainly of C5 and C6 paraffinic hydrocarbons with possibly some cyclic cyclopentane and methyl cyclopentane. C5 normal chain and C6 normal chain along with that the cyclopentane and methyl cyclopentane.

These are the two cyclic compounds that may be present in light straight-run naphtha. It is evident that the branched-chain isomers of normal paraffins have significantly higher octane numbers than the normal paraffins. It is clear that when normal paraffin is converted into isoparaffins, which are the branched-chain isomers of normal paraffin, they acquire higher octane numbers than their parent normal paraffin. The greater the degree of branching, the higher the octane number.

The isomerization process is designed to increase the proportion of naturally occurring branched-chain paraffin in light straight-run naphtha, thereby increasing its octane number. In the isomerization process, normal or straight-chain paraffinic compounds are converted into branched-chain paraffins. Typically, the goal is to eliminate all normal paraffins and convert them into isoparaffins, ultimately increasing the octane number of LSR (Light Straight-Run) naphtha. In more advanced processes, the objective is to increase the content of highly branched paraffins and eliminate normal paraffins entirely. It's worth noting that the sensitivity of paraffin is very low compared to that of cyclic compounds.

"Sensitivity" in this context refers to the difference between the Research Octane Number (RON) and the Motor Octane Number (MON). Typically, the RON is somewhat higher than the MON, and this difference is consistently observed. The reason for this difference is that the Motor Octane Number is measured under more demanding conditions, including engine load and harsher operating conditions, compared to the Research Octane Number, which is measured under more normal engine operating conditions.

What this means is that paraffins, specifically branched-chain paraffins, exhibit very low sensitivity. In other words, they show a minimal difference between the Research Octane Number and the Motor Octane Number. This characteristic makes branched-chain paraffins highly efficient in achieving higher octane numbers because they maintain similar octane ratings under both normal engine operating conditions and under load, making them desirable components for improving fuel quality.

Since the two main components of the gasoline pool, catalytically cracked gasoline and catalytic reformate, have much higher sensitivity, this makes reformate a valuable component in the pool. In a refinery, gasoline is obtained from various production points, including straight-run gasoline, catalytically cracked gasoline, hydrocracker gasoline, coker gasoline, catalytic reformate, and more. All of these components collectively constitute the gasoline pool. It is observed that the major components of the gasoline pool are catalytically cracked gasoline and catalytic reformate, both of which have higher sensitivity. This means that the difference between the Research Octane Number (RON) and Motor Octane Number (MON) is greater for these components. Therefore, to enhance the pool's properties, isomerate, which consists of isomerized compounds, is often added.

Indeed, adding isomerate to the gasoline pool improves the octane number of gasoline, making isomerate a valuable component in the pool. It's worth noting that all isoparaffins have lower boiling points than their corresponding normal paraffins, which means that isoparaffins have higher volatility compared to their parent normal paraffins. As a result, the Reid Vapor Pressure (RVP) of gasoline can be adjusted by adding a very small quantity of butane, typically around 5 volume percent.

However, it's important to consider that isomerization can increase the RVP, which needs to be taken into account during subsequent gasoline blending operations. Gasoline blending can be carried out with isomerate so that the addition of butane to adjust the RVP may not be necessary. The isomerization process is a relatively straightforward procedure involving the passage of Light Straight-Run (LSR) naphtha over a suitable catalyst in the presence of hydrogen, all under temperature and pressure conditions appropriate for the catalyst. This process is designed to convert normal paraffin into isoparaffins, improving the overall quality and octane rating of the gasoline product.

Isomerization is a relatively simple process. In this process, Light Straight-Run (LSR) naphtha is mixed with hydrogen and passed through a catalyst bed at specific temperature and pressure conditions that are suitable for the catalyst. The goal of this process is to produce isomerate compounds by converting normal paraffin into their corresponding isoparaffin forms. For the example of pentane isomerization, it's important to note that the equilibrium mixture of normal and isopentane contains approximately 80 percent isopentane at a temperature of 300 degrees Celsius, and this percentage slightly increases to about 85 percent at 100 degrees Celsius. This equilibrium mixture is controlled by the thermodynamic equilibrium of the reaction. In the case of pentane isomerization, when the normal and isopentane mixture is at equilibrium, with normal pentane as the reactant and isopentane as the product, it's observed that at a lower temperature of 100 degrees Celsius, the production of isopentane increases to 85 percent. This observation indicates that lower temperatures favor higher isomer production, which is a fundamental aspect of the isomerization process.

For the mixture of 2-methylpentane and 3-methylpentane isomers, both of which have the same octane number of 75, lower temperatures favor the formation of the higher-octane double-branched compound 2,2-dimethylbutane (2,2-DMB) and reduce the concentration of normal hexane, whose research octane number is 25. In this reaction, when 2-methylpentane and 3-methylpentane react together, they produce 2, 2-dimethylbutane, a highly branched and high-octane compound, as well as normal hexane, which has a lower octane rating. At lower temperatures, there is a higher quantity of the high-octane product, 2, 2-DMB, compared to the lower yield of normal hexane. Conversely, at higher temperatures, there is a continuous increase in the production of normal hexane, which has a low octane number, while the yield of 2, 2-DMB decreases compared to the lower temperature. Therefore, for the isomerization of C5 and C6 mixtures, as found in Light Straight-Run (LSR) naphtha, there is a clear advantage in operating at lower temperatures. The development of catalysts has been oriented in this direction to maximize the production of high-octane isomers like 2, 2-DMB.

In the development of a catalyst for isomerization processes, it is essential to consider three major qualities: catalyst activity, catalyst selectivity, and catalyst stability.

Catalyst Activity: Higher activity means that the catalyst can efficiently produce the desired compounds at the desired quality. In other words, it promotes the chemical reactions necessary to create the desired products effectively.

Catalyst Selectivity: Higher selectivity indicates that the catalyst can produce the desired compounds selectively, minimizing the formation of unwanted byproducts. This results in higher yields of the desired products.

Catalyst Stability: A stable catalyst can withstand adverse conditions over an extended period. It remains active and effective for a longer duration, contributing to the longevity of the catalyst's life and overall process efficiency.

Now, regarding the discussion on catalysts used in isomerization processes, two distinct types of catalysts are commonly employed:

Platinum-Bearing Zeolite Catalyst: This type of catalyst consists of platinum supported on a zeolite substrate. It requires an operating temperature of approximately 260 degrees Celsius and operates at a pressure range of 260 to 500 pounds per square inch gauge (psig). The crystalline nature of this catalyst helps in producing isomerate compounds efficiently. Amorphous Platinum-Bearing Chlorided Alumina Catalyst: Unlike the crystalline zeolite catalyst, this catalyst is amorphous in nature. It operates at a lower temperature range of 120 to 180 degrees Celsius, favoring the formation of branched isomers. However, a challenge with this catalyst is that it requires the continuous addition of organic chloride to keep it activated and functioning effectively. The choice of catalyst depends on various factors, including the desired product specifications, operating conditions, and process requirements. Both types of catalysts have their advantages and drawbacks, and the selection is made based on the specific needs of the isomerization process.

The third type of catalyst developed is the platinum-on sulfated metal oxide catalyst. Unlike the amorphous catalyst, this type does not require continuous revival by the addition of external compounds. It operates at a medium temperature and pressure range, falling between the other two catalyst types in terms of operating conditions. The increase in the Research Octane Number (RON) for a 68 to 70 Light Straight-Run (LSR) naphtha typically reaches up to 78 to 80 when using the zeolite catalyst and up to 82 to 84 for the amorphous catalyst. However, for the platinum on sulfated metal oxide catalyst, the obtained RON is in the range of 80 to 82. Now, let's move on to another process, which is alkylation.

Alkylation is a process used to produce components of motor gasoline. In this process, light olefins, typically propylene and butylene (C3 and C4 olefins), are combined with isobutene to form branched-chain isoparaffins with a high octane number. This alkylation process involves adding alkyl groups to the reactant molecules, resulting in the formation of isoparaffins. Propylene and butylene are typically produced from a fluid catalytic cracking (FCC) plant, which is known for producing olefinic compounds during the cracking process. On the other hand, the source of isobutene may come from various units, including the FCC unit, catalytic reformer unit, or crude oil distillation unit. Isobutene is a saturated hydrocarbon with a branched-chain structure, and it serves as a key component in the alkylation process for producing high-octane isoparaffins used in gasoline blending.

Isobutene is obtained in significant quantities from the crude oil distillation unit because it is often associated with the naphtha fraction. In the overhead of the atmospheric distillation unit, the first liquid side draw stream is the naphtha, and this is where isobutene is mixed with it. However, during the process, isobutene is separated from the naphtha in the Debutanizer column to obtain naphtha that is free from isobutene. This separation process provides a source of isobutene for alkylation. The catalysts commonly used in the alkylation process are either sulfuric acid (H2SO4) or hydrofluoric acid (HF). These catalysts facilitate the addition of alkyl groups to the reactant molecules, resulting in the formation of alkylates. Alkylates are highly valued components in the gasoline pool because they possess a high octane number and low sensitivity, which makes them desirable for blending into gasoline to improve its quality and performance.

Indeed, alkylates are highly valued in the gasoline pool because they are branched-chain compounds produced after the alkylation reaction. These compounds inherently have a high octane number, and their branched structure leads to low sensitivity, meaning there is a minimal difference between the Research Octane Number (RON) and Motor Octane Number (MON). Alkylate ranks as the third largest component in the gasoline pool, following catalytic crack naphtha and catalytic reformate. Its significance lies in its ability to improve the overall octane number of the gasoline pool, contributing to its overall quality.

In terms of process chemistry, the primary reactions in alkylation involve the interaction between isobutane and C3/C4 olefins. For instance, the reaction between isobutane and propylene (a C3 olefin) produces 2, 3-dimethylpentane, which has a Research Octane Number of 89. This reaction yields a compound with a high Research Octane Number due to the combination of isobutane and propylene. Similarly, the reaction between isobutylene and isobutane results in the formation of 2, 4-trimethylpentane or isooctane, which possesses a Research Octane Number of 100, making it an extremely high-octane compound. These reactions demonstrate the capability of alkylation to produce valuable high-octane components for gasoline blending.

In the octane number scale, 2, 2, 4-trimethylpentane, also known as isooctane, is considered the reference point with the highest octane number of 100. When isobutylene and isobutane react, they produce isooctane, which is another high-octane component. Additionally, the reactions between 1-butene and 2-butene with isobutene result in the formation of branched-chain dimethylhexane. This product has a research octane number of 79, and it includes isomers of trimethylpentane, whose research octane numbers vary between 96 and 100, respectively. These reactions demonstrate that while the carbon number of the product is the sum of the carbon numbers of the reactants, the product has a different molecular configuration. Secondary reactions, such as isomerization, also occur, which involves the conversion of 1-butene to 2-butene, further affecting the product composition and octane rating.

In the context of fuel and octane number improvement, polymerization reactions that lead to the production of heavier paraffins with reduced octane numbers are typically not desirable. Instead, processes such as cracking and alkylation are favored. Cracking involves breaking down larger polymer molecules into smaller fragments. These smaller fragments can then participate in alkylation reactions. This is a complex process that includes disintegrating polymer molecules into smaller fragments, which can subsequently recombine and participate in alkylation reactions. Additionally, hydrogen transfer reactions between propylene and isobutene can produce butylene and propane.

These reactions, including polymerization, cracking, alkylation, and hydrogen transfer, are various secondary reactions that may or may not be favorable for improving the octane number of a fuel. It's essential to carefully control and optimize these reactions to achieve the desired fuel properties, including the octane number.

Polymerization plays an essential role in improving the octane number of gasoline. This process typically begins with a C3-C4 olefin stream obtained from thermal or catalytic cracking. The goal is to polymerize these olefins to form C6, C7, and C8 olefins that fall within the gasoline boiling range. This slight increase in the carbon number helps enhance the properties of the gasoline.

The process of slight polymerization or oligomerization involves joining 1, 2, or 3 monomers together to form oligomers. It is sometimes referred to as catalytic condensation. The resulting product is commonly known as "poly gasoline." There are two main types of process operations for this purpose. The primary one is the UOP catalytic condensation process, which employs a solid catalyst. This process can be applied not only to polymerize C3-C4 olefins into the gasoline range but also to create jet fuel or diesel oil boiling range products. It is a versatile method for improving the properties of various fuel products.

In the UOP licensed process, often referred to as the UOP catalytic condensation process, a solid catalyst is used to enhance the quality of jet fuel or diesel oil by polymerizing C3-C4 olefins. While this process transforms C3-C4 olefins into C6, C7, and C8 olefins, these fuels still contain a significant amount of unsaturated olefins. To meet the requirements for jet fuel or diesel oil, these unsaturated olefins need to undergo hydrotreating, which involves hydrogenation to convert them into straight-chain paraffin. This is essential to improve their octane number. On the other hand, the Dimersol process relies on a consumable liquid-phase catalyst. This process primarily converts C3 olefins into dimers.

Dimet indeed refers to hexane, which is produced by combining two C3 olefins together. Hexane is commonly used in gasoline blending. Benzene reduction is a crucial aspect of controlling toxic emissions. Gasoline containing high levels of C6 and C7 hydrocarbons, including aromatics and naphthenes, can lead to the formation of benzene through various reactions. When gasoline with significant C6 and C7 content is burned in automobile engines, it can produce benzene emissions in the exhaust gases. These benzene emissions can mix with the atmosphere and pose a health risk, as benzene is known to be carcinogenic. Therefore, minimizing benzene content in gasoline is essential for environmental and health reasons.

The major source of benzene in the gasoline pool is catalytic reformate, which typically contributes 50 to 75 percent to the pool. So, catalytic reformate should be refined before it is added to the pool to remove the benzene. Two basic approaches can reduce the benzene production. One is to remove the benzene precursors charged to the reformer before the gasoline is charged to the reforming unit. The benzene is removed, not only benzene but also benzene precursors. Precursors mean benzene-producing components are to be removed beforehand or fractionate a benzene-rich light reformate stream for subsequent benzene conversion or extraction. These are the two important processes to reduce the benzene production afterward of gasoline use.

So, let's first discuss light reformate processing. This naphtha is straight-run naphtha coming from the atmospheric distillation unit. It goes to the naphtha splitter, which, if you remember, removes the C5-C6 fractions from the top of the naphtha splitter. From the bottom, we obtain C6 or C6+ naphtha, which goes to the reformer unit. After reforming, we get the reformate, and a reformate splitter is installed. From the top of the reformate splitter, some C6 and C7 hydrocarbon compounds are removed after reforming is completed. These C6-C7 hydrocarbons are then directed to various processes. Isomerization: This process aims to produce isomerates from the C6-C7 hydrocarbons, enhancing their stability and safety.

Saturation: Hydrogen is used to saturate the compounds, making them more stable and safer.

Alkylation: Alkylation is performed using FCC C3 olefin compounds to produce alkylate.

Extraction: The process extracts C6-C7 components.

At the bottom of the reformate splitter, we find the heavy reformate, which is free of any C6-C7 components. Another process is the prefractionation of C6 cycles. Before the naphtha is sent to the reformer unit, the C6-C7 compounds are separated in the naphtha splitter. C5-C6 components are removed, and the naphtha sent to the reformer contains C7 plus compounds, with C6 cycles kept very low, below 0.5 percent. The C7 plus components, which are the heavier naphtha, are sent to the reformer unit to produce safe reformate. The C5-C6 and some C7 are sent to the isomerization unit to produce isomerate or to the benzene saturation unit to saturate benzene and obtain the saturated light straight-run cut. This process may yield a light straight-run cut, which contains C5, C6, and C7 components.

These are the references which you can consult. Thank you for your attention.