Lecture 29: Upgradation of straight run cuts from atmospheric distillation unit (Contd.)

Hello and welcome to lecture number 29 of Petroleum Technology. In this lecture, we will learn about the Upgradation of Straight Run Cards from the Atmospheric Distillation Unit. Let us come to the solvent deasphalting process. Solvent deasphalting is a physical separation process employed to remove asphalt from vacuum residues. You know that the vacuum residue that is produced from the vacuum distillation unit bottom contains lots of carbonaceous materials which are as a whole called asphalts, which are highly condensed and polymerized compounds and have a very high carbon: hydrogen ratio. So, these asphalts are the precursors of coke.

Whenever any heavy oil, whether it is vacuum residue or it is visbroken tar, or even if it is atmospheric residue, is sent to another secondary processing stage, these asphalts are the cause of producing coke in the unit. Hence, deasphalting is to be done to remove these undesirable component asphalts. So, solvent deasphalting is a physical separation process; it is an extraction process employed to remove asphalt from vacuum residues as well as many other residues as well. Typical usage for the deasphalted oil product includes lube bright stock, lube hydrocracker feed, fuel hydrocracker feed, fluid catalytic cracker feed, or fuel oil blending.

So, deasphalted oil is produced from vacuum residue to produce the lube bright stock. Lube bright stock is produced from the vacuum distillation bottom which is the vacuum residue after the solvent deasphalting process. Lube hydrocracker feed, if the lubricating oil-based stock is sent to the hydrocracker, then it will be called the lube hydrocracker feed. Fuel hydrocracker feed is when the vacuum residue is produced from a fuel oil-bearing crude oil, then the vacuum residue is called the fuel vacuum residue, and fuel hydrocracker feed is composed of that vacuum residue. FCC unit feedstock is required to be deasphalted for fuel oil blending.

Depending on the operation, the asphaltene product may be suitable for use as a blending component for various grades of asphalt, as a fuel oil blending component, or as feedstock to a heavy oil conversion unit such as a coker or a resid cracker. Asphaltene may also be used as a blending component for various units. This solvent deasphalting process is flexible enough to enable the processing of both long and short residue. Long residue refers to the atmospheric residue, and short residue refers to the vacuum residue.

In the solvent deasphalting process, a suitable solvent is mixed with the residue or heavy oil to be deasphalted in a mixer. Then, the mixture of solvent and the feed is introduced from the top of the asphaltene separator. Additional solvent is introduced from the bottom of the asphaltene separator. During the separation process, asphaltene, being insoluble in the solvent, separates from the liquid part. Some of the solvent, along with the solvent-rich and oil-rich liquid sections, is taken out from the top of the asphaltene separator. The solvent is subsequently removed through various processes, including heating or vacuum evaporation.

And the asphaltene-solvent mixture, where asphaltene is the major component, has the solvent removed by stripping. Solvent deasphalting is an extraction process in which the charge is separated based on the solubility of the more desirable deasphalted oil and the less desirable asphaltene material by using a solvent. The oil part of the feedstock is mostly soluble in the solvent, but asphaltene is not. Typically, light paraffinic solvents like propane, isobutene, butane, and pentane are used in the solvent deasphalting process. Sometimes, olefinic solvents are also employed for solvent deasphalting. The choice of solvent composition, operating temperature, and solvent-to-oil ratio is made to achieve the desired separation between the lighter deasphalted oil and the heavier asphaltene product.

The cut point, where the deasphalted oil is separated, and the cut point at which the heavy asphaltene is removed from the bottom is determined by the process parameters. These parameters include solvent composition, operating temperature, and solvent-to-oil ratio. Propane or a blend of propane and isobutene is commonly used as the solvent for producing lube oil bright stock from vacuum residue.

For applications where the deasphalted oil is sent to conversion processes like FCC, the solvent is more likely to be butane, pentane, or a mixture of both. When deasphalted oil is destined for conversion processes like FCC, it must be free of asphaltene because asphaltene can serve as a precursor to coke formation, which can deposit on the FCC unit's catalyst. Therefore, a more rigorous separation process is necessary for producing deasphalted oil in such cases.

Now, regarding process variables: At properly selected pressures and solvent-to-feed ratios, the separation of asphaltene constituents can occur at temperatures ranging from 40 to 90 degrees Celsius. Typically, lower temperatures are used because low molecular weight paraffinic solvents are employed for separation. To achieve the maximum extraction of valuable hydrocarbons from the feed, the temperature in the extractor is maintained at 50 to 65 degrees Celsius at the bottom and 75 to 85 degrees Celsius at the top. In the extractor where asphaltene and deasphalted oil are separated, two different temperatures are used. The lower temperature, between 50 to 65 degrees Celsius, is maintained at the bottom, while the higher temperature, around 75 to 85 degrees Celsius, is maintained at the top. This temperature difference within the extractor is achieved by heating the oil-solvent mixture using steam coils at the top of the extractor.

The use of steam coils is essential for providing the necessary temperature control. At higher temperatures, with the same solvent-to-feed ratio, asphaltene constituents readily separate into the lower layer. This separation process improves the color, reduces viscosity, lowers density, and decreases the coking potential of the deasphalted oil. However, it also results in a lower yield of deasphalted oil.

When the extraction temperature increases while keeping other parameters constant, asphaltene substances rapidly precipitate from the deasphalted oil. This leads to an improved quality of deasphalted oil in terms of color, viscosity, density, and coking potential. Clearly, as deasphalted oil does not contain asphaltene or contains only trace amounts of it, the desired quality of deasphalted oil is enhanced. However, it's important to note that running the process at higher temperatures reduces the overall yield of deasphalted oil.

On the other hand, if a lower temperature is used for the process, it may help restore yield, but it can negatively impact the quality of the deasphalted oil. The pressure in the extractor is typically maintained at a level of 3.5 to 4 mega Pascals, depending on the extraction temperature. Temperature and pressure are interrelated, but temperature is more sensitive in this process compared to pressure.

The solvent-to-feed ratio is determined by the nature of the feedstock and the deasphalting temperature. The amount of solvent to be used for a specific type of feed depends on the nature of the feedstock. If the feedstock contains a higher amount of asphaltene, then a larger amount of solvent should be used. In such cases, the solvent-to-feed ratio should be higher. This ratio is also referred to as the treat ratio or treat percentage, which represents the percentage of solvent based on the feed. Temperature is, as mentioned earlier, the most sensitive parameter in the asphaltene solvent deasphalting process.

This ratio is lower when there is a higher concentration of asphaltene in the feedstock and vice versa. When the feedstock has a higher concentration of asphaltene and a lower oil content, less solvent is required to dissolve the oil. Increasing the solvent-to-feed ratio under specific operating conditions can lead to an increase in the yield of deasphalted oil. Therefore, both yield and quality are dependent on process variables.

However, when the yield is increased beyond a certain range, the metal content of the deasphalted oil increases rapidly. Increased yield, achieved through lower temperature operation, results in higher metal content in the deasphalted oil derived from the feed, although the removal of sulfur and nitrogen is not significantly affected.

Deasphalted oil intended for use in lubricants must contain significantly less asphaltene compared to deasphalted oil intended for use as a fuel. For lubricant feedstock, the desirable asphaltene content should be very low, whereas deasphalted oil used as fuel oil can have a higher asphaltene content.

Now, let's move on to the base oil manufacturing process. Base oil serves as the primary component of lubricating oil, and a significant portion of base oil production still originates from vacuum distillation. As you've learned, the vacuum distillation unit produces light stock, medium stock, and heavy stock from the atmospheric residue obtained from crude oil suitable for lubricant production. The manufacturing route typically involves one or more of the following fundamental steps:

Vacuum Distillation: The first step involves vacuum distillation to produce distillate feedstocks.

Solvent Deasphalting: This step focuses on producing heavy lubricant-based oils from vacuum residue through the solvent deasphalting process. In essence, it recovers heavy lubricant base oil compounds from the vacuum residue. This process is also known as solvent extraction.

Solvent Extraction of Vacuum Distillates: Another form of solvent extraction is employed on vacuum distillates to enhance quality factors such as viscosity index and saturated content by removing undesirable components.

Solvent extraction is done to remove mostly the aromatics, as well as sulfur, nitrogen, and oxygen content of the heavy distillate coming out from the vacuum distillation unit. Solvent or catalytic dewaxing is carried out to remove wax and improve the low-temperature properties of base oil. Low-temperature property is obviously the pour point. So, solvent or catalytic dewaxing processes are used to remove wax. Solvent dewaxing removes the heavy paraffinic waxes, high molecular weight paraffinic waxes that freeze at a higher temperature only.

Catalytic dewaxing removes the higher paraffinic compounds, which are wax-forming, by fragmentation, cracking, as well as by forming the isoparaffins. Isoparaffins cannot produce waxes much, but normal paraffins are the major feedstock for making the wax for producing the wax in the oil. Clay or hydrogen finishing is done to improve the color and stability of the lubricant base oil products. Clay treatment is done to improve the color; clay absorbs the unwanted coloring substances in the lubricating oil-based stocks. Those are mostly high molecular weight aromatic compounds.

Hydrogen finishing is another chemical process done to saturate the aromatic content of the lubricating oil, thereby enhancing the stability of lubricating base oil products. Severe hydrotreating processes, such as hydrocracking and hydrotreating, are employed to improve the viscosity index and saturate content. These steps can be executed individually or in combination as needed to achieve the desired properties for the end lubricating base oil.

Now, let's discuss the lube oil deasphalting process. The heaviest lubricant base oils are found in vacuum residue and cannot be economically recovered through distillation. To extract valuable heavy lubricant base oil components from the vacuum residue, especially those contained within semi-solid asphaltenes and resins, the most commonly employed process is propane deasphalting. This process utilizes propane as a solvent for deasphalting to separate and recover the heavy lube oil molecules from the asphaltene-rich vacuum residue. Propane deasphalting is an extractive precipitation process.

Extraction involves removing the oil part from the vacuum residue, while precipitation entails separating the asphaltenes and resinous materials. In the propane deasphalting process, the density difference and inverse stability characteristics of light liquid hydrocarbon solvents, such as propane, are utilized to selectively precipitate undesired components like asphalt resins, metals, and other hydrocarbons from the vacuum residue. Propane dissolves the oil part while separating or precipitating the undesirable asphalt resins, metals, and other hydrocarbons. The resulting deasphalted oil is suitable for further refinement into heavy lubricant base stock. Another method that can be used to obtain lubricating oil base stock is the solvent extraction process.

The purpose of solvent extraction is to prevent corrosion, protect catalysts in subsequent processes, and improve finished products by removing unsaturated aromatic hydrocarbons from lubricant stocks. Lubricating oil should not contain many aromatics because aromatic compounds do not contribute to improvements in viscosity index and pour point. The solvent extraction process effectively removes unsaturated aromatic hydrocarbons from lubricant stocks.

In the solvent extraction process, aromatics, naphthenes, and impurities are separated from the product stream through dissolution or precipitation. The feedstock is first dried since most extraction solvents cannot tolerate moisture. It is then treated using continuous counter-current solvent treatment operations. The solvent is separated from the product stream through methods such as heating, evaporation, or fractionation. Residual solvent amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing. In the extraction process, the extractant contains the oil part, while the raffinate contains the undesired components. Most of the solvent goes to the extract phase, from which it is recovered using various processes like heating, evaporation, or fractionation. The solvent in the raffinate, which primarily contains asphaltenes, resins, aromatics, and other undesirable components, is recovered through steam stripping or vacuum flashing.

The qualities required in a lubricating oil-based stock are usually determined by measuring either the product's viscosity index or saturate content. Viscosity index and saturated content are the primary measurements used to assess the quality of a lubricating oil-based stock. High olefinic or aromatic content is undesirable in lubricating oil-based stock. To achieve the required viscosity index or saturates level, it is necessary to remove aromatic compounds. The solvent used for this purpose must be selective in removing predominantly aromatics and undesirable sulfur, nitrogen, and oxygen compounds. Therefore, the solvent should be capable of accepting aromatics and other undesirable compounds.

Three of the most widely used solvents worldwide are furfural, phenol, and N-methyl-2-pyrrolidone (NMP). Less frequently used solvents include liquid sulfur dioxide, nitrobenzene, and 2,2-dichloro ether. The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the requirements of the finished product. The choice of solvent and process parameters for the solvent extraction process is determined by the type of feedstock, the nature of contaminants present, their quantity, and the specifications of the finished product.

Now, let's delve into the furfural extraction process. Furfural extraction is one of the efficient extraction processes employed in refineries. It has been widely adopted as the primary method for lubricant-based oil production on a global scale. The primary variables in the extraction process include temperature, treat ratio (solvent to feed ratio), and the amount of extracted material recycled back into the feed. Recycling is an essential aspect of the furfural extraction process, as it enhances the efficiency of separation and extraction.

Typically, the operating temperature and solvent dosage fall within the range of 40 to 120 degrees Celsius for temperature and 100 to 250 percent concerning the feed, respectively. Various extraction devices are used, including rotating disk contactors, packed or tray towers, and centrifuges. Among these, the rotating disk contactor (RDC) stands out as the most popular and efficient choice. Feedstocks are contacted in a counter-current fashion using essentially anhydrous (moisture-free) solvent to ensure the solvent's optimal performance. Furfural preferentially extracts aromatics and compounds containing sulfur, oxygen and nitrogen.

Now, let's explore phenol extraction. Phenol is a highly effective solvent with good selectivity when it comes to lube oil extraction. In the phenol extraction process, water plays a crucial role as the treating solvent. Phenol acts as a solubility modifier or anti-solvent in this context. Water is used to balance the solvent treatment rate, which typically falls within the range of 100 to 250 percent, while also adjusting the treater operating temperature. The addition of water enhances phenol's solubility and overall effectiveness.

The extractor used in phenol extraction can be a mixer-settler. However, it's important to note that using phenol as an extraction solvent comes with significant disadvantages.

Phenol is toxic in nature, and proper safety precautions must be taken during operation, plant shutdowns, and maintenance. Operators should always wear appropriate protective clothing and gloves when working with phenol, as it is a corrosive and toxic substance.

Another drawback of phenol is its high melting point, around 41 degrees Celsius, which can lead to the plugging of some equipment components. Additionally, the yield of refined oil obtained with phenol is usually somewhat lower compared to that achieved with either furfural or NMP (N-methyl-2-pyrrolidone). NMP is the most effective solvent used in the process so far. It has a non-toxic nature, high solvent power, and good selectivity, making NMP an attractive alternative to phenol.

This process excels in various aspects, particularly in solvent circulation, and it requires less corrosion protection. As a result, it has the lowest requirements for energy investment and operating costs. Thanks to the numerous advantages of NMP (N-methyl-2-pyrrolidone), it contributes to lowering the overall costs.

The operation is carried out in a mixer-settler with 15 to 20 trays. NMP's higher boiling point facilitates more efficient heat integration, allowing for extraction at higher temperatures and highly efficient extraction processes. The lower viscosity of the solvent leads to faster settling and coalescing, enhancing the treater's capacity significantly. Due to its low viscosity, solvent losses are minimized, resulting in reduced expenses for makeup solvent purchases, thus lowering production costs.

These are the references. Thank you for your attention.