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Lecture 30: Upgradation of straight run cuts from distillation unit

Hello and welcome to the 30th lecture of petroleum technology. In this lecture, we will learn about the Upgradation of Straight Run Cuts from Distillation Units. First, let us talk about the solvent dewaxing process. Many of the petroleum cuts contain wax components, which are mainly long-chain paraffinic hydrocarbons. Mostly, they are straight-chain, and a very small portion is the branched-chain paraffinic compounds. Those compounds paraffinic compounds are the wax-forming compounds that form wax when the oil is cooled. So petroleum waxes are solid hydrocarbons with melting points of 35 to 95 degrees centigrade, which are soluble in crude oils and their fractions.

So, the wax in the crude oil itself becomes part of the petroleum distillate fractions after distillation. These waxes have a wide boiling temperature range that includes distillate fuels and lubricating oils. As a result, they cannot be separated from these fuels and oils through simple distillation. In fact, these paraffinic hydrocarbon compounds that form waxes are components of both distillate fuel oils and lubricating oils. It's important to note that lubricating oil, being distinct from fuel, contains these paraffinic hydrocarbons distributed throughout its boiling range. Therefore, it is not possible to separate them by the simple distillation process.

So, solvent dewaxing is introduced to remove the wax content from all those fuels and lubricating oils. The dissolved wax is precipitated out at low temperatures, and therefore, the wax-bearing dissolved fuels and lubricating oils must be dewaxed. Actually, whenever these oils or lubricating oil is transported through the transportation line from one part of the country to another part or one country to another country, whenever this transportation line crosses some cold region or experiences cold temperatures, these waxes are precipitated out from the oil. At the same time, they form frozen oil inside the transportation line. Hence, these waxes should be removed from the oils and fuels so that there will be easy flow of the oil through the transportation line. Additionally, when these waxes are used in cold environments, they form wax crystals that can clog equipment parts, leading to various disadvantages associated with these waxes.

The most convenient and suitable dewaxing process is to use a dual solvent system, which dissolves the highly waxy viscous feedstock. In the dual solvent system, one of the solvents acts as the solvent for the oil, and another solvent acts as the solvent for the wax. This way, wax can be separated easily from the oil part. Hence, this is the advantage of a dual solvent system, and it is a very modern type of dewaxing process. One of the important dual solvent systems is the MEKT process. The MEKT process involves a methyl ethyl ketone toluene system where methyl ethyl ketone acts as the anti-solvent to the wax and solvent to the oil, while toluene acts as the solvent to the wax. Hence, toluene dissolves wax, and the anti-solvent methyl ethyl ketone dissolves oil, allowing for the separation of oil and wax.

Wax is a valuable byproduct of the dewaxing process, and it has numerous applications. Dewaxing is achieved by chilling the oil, causing the wax to crystallize out. In the very primary type of dewaxing process, the oil is chilled at a low temperature, leading to the crystallization of wax. The oil and wax can then be separated, and the wax crystals are further separated by methods such as filtration, centrifugation, or settling.

There are several processes in use for dewaxing, but they all have the same general steps, which are associated with almost all types of solvent dewaxing processes. These are mixing the feedstock with a solvent, precipitating the wax from the mixture by chilling, recovering the solvent from the wax, and dewaxing oil for recycling by distillation and steam stripping. First of all, the viscous waxy feedstock is mixed with a solvent, and after that, the temperature of the mixture should be dropped down to a temperature where the wax crystallizes out and precipitates. After that, the solvent from this system has to be recovered from the wax. The wax also contains some of the trapped solvent in it as well as the dewaxed oil by distillation and steam stripping processes, and then the recovered solvent is recycled into the system again.

This is the general step of the solvent dewaxing process. There is another method of dewaxing with urea, which is based on the fact that urea forms solid filterable complexes called adducts with large paraffins having little or no branching. Here, urea is used for the dewaxing process; although it is not a solvent dewaxing, a large amount of solvent is also used here, but not for extraction. Here, the advantage of the urea system is that urea takes some of the large paraffinic waxy compounds into its own structure, making a filterable complex. These are big solid crystals that are easily filtered compared to fine wax crystals, making it easier to separate the waxy part of the oil by forming urea adducts. Usually, this urea dewaxing process is used for lighter stocks where mostly large paraffinic hydrocarbons are present, but not very complex paraffinic hydrocarbons.

Three dewaxing processes provide the majority of the currently installed worldwide capacity. Mostly, the three major dewaxing solvent processes used in refineries worldwide are ketone dewaxing (where ketone is the solvent), propane dewaxing (where propane is used as the solvent). These two processes are physical separation processes. In contrast, the catalytic dewaxing process is hydrodewaxing, a chemical process where hydrogen is used in a catalytic reaction for the dewaxing process. Now, first coming to ketone dewaxing, ketone dewaxing units typically use a mixture of two solvents: methyl ethyl ketone (MEK) with either methyl isobutyl ketone or toluene. Methyl ethyl ketone acts as the anti-solvent to wax, and either toluene or MIBK (methyl isobutyl ketone) is used as the solvent for wax.

When running with the two-solvent mixture, optimization of solvent components is important. This is quite obvious because during this process, the nature of the feedstock is crucial. The percentage of wax content in the feedstock determines the composition of the solvent mixture. So, the optimization of solvent components, including the percentage of anti-solvent and solvent, is determined based on the nature of the feedstock. The MEK component in the solvent mixture acts as an anti-solvent for wax molecules, promoting their precipitation as crystals from the feedstock. MEK removes the oil part from the feedstock, leaving the precipitated wax after chilling. However, if MEK is used alone (as the only anti-solvent), the oil in the feed solution becomes immiscible when the feed solution temperature is reduced to the level required for filtration.

There is a fixed filtration temperature for all types of solvent dewaxing processes. If the temperature is reduced when MEK is used alone, the oil, which was supposed to go to the MEK completely, becomes immiscible as the solution temperature decreases. The solubility decreases, and two phases are formed: an oil-rich phase and a solvent-rich phase. Both phases contain solvent. The oil-rich phase contains high viscosity index oil molecules, and due to its higher viscosity, much of it remains trapped in the wax cake. Since only MEK is used, which takes only the oil, some high viscosity index oil molecules will get trapped within the wax cake. This results in a loss of both dewaxed oil yield and quality. Therefore, we are losing the dewaxed oil as well as its quality.

To avoid this problem, a second solvent is added to MEK to improve oil solubility at the filtration temperature. When we add a second solvent, which is the solvent for wax, it takes out the wax part from the feedstock, leaving the oil behind, and the oil is dissolved in MEK. So, two different components in the waxy feedstock are separated out by the two solvents. The most frequently used components are MIBK and toluene. Now, coming to another dewaxing process, propane dewaxing, where propane is used as a solvent. Propane is abundant in the refinery, obtained at various points, and is a good solvent to dissolve the long paraffinic hydrocarbons, which are wax-forming compounds. Propane dewaxing can be applied to any petroleum fraction but is particularly effective for dewaxing bright stock, light, and heavy dissolved fuel.

Bright stock, as you know, is the solvent-deasphalted vacuum residue, which is a heavy lubricating oil-based stock, and it is referred to as bright stock. Bright stock contains, as it is a very heavy cut, the vacuum residue. In fact, it contains lots of waxy molecules in it, and all the long-chain paraffinic hydrocarbons accumulate in the bright stock. So, dewaxing is very much necessary for this stock, and propane dewaxing is helpful in dewaxing light and heavy dissolved fuel. One of the most important features of the process is that it uses propane both as a diluent and as a refrigerant. So, propane can be used both as a solvent and as a refrigerant; you know that propane is a gas at room temperature.

So, to make the propane liquid, lots of pressure has to be applied to the propane, and the temperature is reduced because of the application of high pressure. At that high-pressure condition, propane becomes a liquid. So, at high pressure, the temperature is also reduced to a lower level. So, at the same time, propane acts as a solvent and as a refrigerant. It is a semi-batch process using two parallel batch chiller vessels alternately in sequence.

In this propane dewaxing process, two batch chiller vessels are used, and it is a semi-batch process. In fact, when one chiller vessel is exhausted, another vessel is put in that position. So, it is a semi-batch process. It is observed that in this propane dewaxing operation, the filtration temperature is kept at around minus 20 to minus 40 degrees Celsius. The filtration temperature is achieved by evaporating out some of the liquid propane through evaporation, which results in a lower temperature. Another important factor is that the process will not perform s

Dewaxing aids are crucial in the propane dewaxing process because wax crystals cannot form until a nucleation additive is introduced into the medium. Nucleation and grain growth occur when a dewaxing aid is added, allowing wax crystals to form, and subsequently, other crystals grow around it. Without the addition of a dewaxing aid, wax crystals cannot be separated effectively. Furthermore, the pour points of the dewaxed oil products obtained from propane dewaxing plants are limited to a lower temperature of approximately minus 15 degrees Celsius. Achieving a low pour point is, of course, desirable for any oil.atisfactorily without the use of wax crystal nucleation additives known as dewaxing aids.

So, the low-temperature characteristics are advantageous for operations in cold regions or during transportation in such conditions. However, the capital cost of the plant is significantly lower compared to that of a ketone dewaxer of similar capacity. Therefore, the operational cost of propane dewaxing is obviously lower than that of the ketone dewaxing process. Now, turning to the catalytic hydrodewaxing process. As mentioned earlier, it is a chemical process involving a reaction.

Catalytic hydrodewaxing has been an alternative to solvent dewaxing in the manufacture of lubricating oil-based products. This technology differs from solvent dewaxing, as solvent dewaxing employs the fractional crystallization process and filtration of the wax formed from the medium, followed by the recovery of oil. Catalytic hydrodewaxing, on the other hand, is a completely different chemical process technology that utilizes a fixed-bed hydroprocessing technology. In this process, a fixed-bed reactor is employed to selectively crack long-chain paraffinic wax molecules into lighter petroleum gases, naphtha, and/or kerosene. Thus, hydroprocessing involves a hydrocracking process

At high temperatures, with the use of a catalyst, this hydroprocessing technology operates by cracking long paraffinic chain molecules into shorter chains, forming lighter petroleum gases, and naphtha, or kerosene— products with lower molecular weights. Alternatively, some wax molecules can undergo isomerization to produce low pour point isoparaffins. In this alternative pathway, instead of cracking, the hydroprocessing technology may undergo a different reaction known as isomerization, where isoparaffins are formed from straight-chain normal paraffins while maintaining the same molecular weight. Isoparaffins typically have a lower pour point than their straight-chain counterparts of equivalent molecular weight, making this isomerization process beneficial. Hence, the catalytic hydrodewaxing process can operate in two modes: cracking and isomerization. Recent catalytic dewaxing processes often combine wax cracking and wax isomerization.

Both wax cracking and wax isomerization processes are conducted simultaneously in a single operation in the catalytic hydrodewaxing process, resulting in a significant increase in viscosity index and yield compared to the solvent dewaxing process. This process employs a proprietary catalyst designed to carry out both cracking and isomerization functions. The catalyst, specifically tailored for these dual purposes, facilitates the cracking of large wax molecules into lighter products and the isomerization of the remaining wax into low-pour-point isoparaffins. This dual functionality within a single catalyst leads to enhanced performance. In contrast, other dewaxing processes, such as the Edeleanu Di/Me process, utilize a solvent mixture of dichloroethane (Di) and methylene chloride (Me) for dewaxing.

So, the Edeleanu process employs dichloroethane and methylene dichloride, reflected in its name as the Di/Me process, as a dewaxing solvent. This method is utilized in lubricant base oil production to eliminate unwanted wax content from lubricating base oils and low oil content waxes. The urea dewaxing process is capable of producing oils with very low pour points and/or waxes with low oil content from paraffinic feedstock. This process is valuable in efficiently removing waxes with minimal oil content, resulting in oils with low pour points. It's important to note that while solvent is used in this process, it is not strictly a solvent dewaxing process. Instead, it is an occlusion process that leverages the hexagonal crystalline structure of urea to occlude normal paraffin hydrocarbons with six or more carbon atoms, as well as some branched hydrocarbons.

In the urea dewaxing process, urea incorporates normal paraffinic hydrocarbons with 6 or more carbon atoms, as well as some branched hydrocarbons, into its hexagonal crystalline structure. This makes the urea dewaxing process effective for dewaxing lighter hydrocarbons containing 6 or more carbon atoms. The resulting larger crystals formed by urea simplify the filtration process when percolating the feed through a bed of urea or mixing it with urea particles. An activator solvent, such as an alcohol, ketone, or chlorinated hydrocarbon, is required for the process. Following the dewaxing process, crude wax, also known as slack wax, is produced. This crude wax retains a significant quantity of oil, making the deoiling process crucial for recovering this valuable component. The oil content in the crude waxes can be as high as 50 percent if chilling is performed without any solvent. Hence, deoiling is essential, especially when chilling is conducted without a solvent.

Only the petroleum fraction is chilled without any solvent, then the wax may trap inside it almost 50 percent of the oil, which is not desired at all. Hence, de-oiling is to be introduced; a finished wax should not contain more than 0.5 percent oil. This is the specification. There are three types of de-oiling processes, namely sweating, resettling, and solvent extraction. Now, coming to the sweating process: in the sweating process, the crude wax called slack wax is melted and cast into thick sheets. In the sweating process to recover the oil trapped inside the wax, what is done is that slack wax is melted and cast into a thick sheet; a big sheet is formed. These sheets are then subjected to slow heating on pans with a perforated false bottom. So, these blocks of crude wax sheets, blocks of crude wax, are placed on a pan with a perforated false bottom, and gradually, the temperature is increased.

As the temperature is increased, the slack wax starts to sweat, meaning that the mixture of oil and low-melting wax drains out slowly from the wax sheets. These drain out from the perforation of the false bottom, and the heating is continued until the remaining wax reaches its desired melting point. So, the heating is continued until the wax reaches its desired melting point, and whatever oil and low-melting wax is drained out through the perforation are recovered. The sweating process may be repeated for the production of good-quality wax. Wax is also an important product, so to get good quality wax, the sweating process is continued.

The sweating process, as you can see, does not require any solvent for the process. Therefore, no energy is required to recover the solvent, and there is no cost for chilling in the process. So, as a whole, the operating cost is much reduced compared to other processes, and the maintenance cost is very low. It is a desirable process for deoiling. In the resettling process, the slack wax is diluted with cold naphtha and recrystallized by chilling.

Here, cold naphtha is used to dissolve the oil content in the slack wax, and then the slack wax is recrystallized by chilling. The final separation of wax crystals is done by centrifuging. Wax crystals are separated by centrifugation. Propane or a mixture of methyl ethyl ketone and aromatic solvent may be used in the solvent extraction process. These solvents are better than the cold naphtha solvent; they can work more efficiently in this process.

Now, coming to the base oil finishing process. Base oil is the lubricating base oil used to remove polar compounds for the improvement of color, color stability, and thermal stability of the base oil. Early lubricant refiners used the cold clay adsorption process using Fuller's earth or Attapulgus clay. Clay absorbs some unwanted materials from the oil, mostly color-forming materials, which are mostly aromatic compounds that form unwanted colors in the oil as well as affect thermal stability. These processes have been almost entirely replaced by the hydro-finishing process. Hydro-finishing is a more advanced process where, in the base oil hydro-finishing, the oil is contacted with hydrogen over a fixed-bed catalyst at low to medium pressures, temperatures, space velocities, and gas rates.

Then, impurities such as trace solvents from upstream processes are removed; sulfur and nitrogen are reduced, and color and color stability are improved by the use of hydrogen and a catalyst at high-moderate temperature and pressure. Hydrocracking of base oil reduces the aromatics content by saturating double bonds and by ring opening. So, it is also included in the hydrocracking of aromatics, which are the major culprits for making color. These are unwanted materials in the lubricating oil base stock because they cannot provide better low-temperature properties, as well as they hamper achieving the good viscosity index characteristics of the lubricating oil. So, hydrocracking, which is included in this hydro-finishing process, removes those aromatics by saturating their double bonds as well as by ring-opening cracking and is becoming an increasingly important process for improving the lube oil base quality.

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