# Lecture 23: Petroleum fractions from distillation units (Contd.)

Hello and welcome to the 23rd lecture of Petroleum Technology. In this lecture, we will learn about various petroleum fractions coming from distillation units. Today, we will talk about fuel oil. Fuel oil is a heavy oil that is made from the residues obtained from either atmospheric or vacuum distillation columns as well as the fractionating column bottoms of various conversion processes after the removal of light hydrocarbons. This residue is one of the components of fuel oil, but the residue is very thick in nature and its density is very high viscosity is also very high. So, that residues cannot be directly used in different applications.

Residual fuel oils, used for various purposes, are made suitable by blending heavy cuts such as vacuum or visbreaker residues, catalytic cracker slurry oils, or asphalt with lighter cuts like gas oil or light cycle oil. Gas oil is obtained as a straight-run product from the atmospheric distillation unit just before drawing the atmospheric residue from the bottom. Light cycle oil is also a side-draw cut from the vacuum distillation tower. These are lighter cuts compared to the heavier fuel residues. These oils are blended with the residues to create residual fuel oils, and in the refinery, these lighter cuts are referred to as cutter stocks, which act as blending agents.

Typically, residues are blended with lighter stocks in a ratio of around 70:30. There are two general uses for fuel oils: burners and engines. Burners can range from stoves to thermal power stations, while engines can range from small gardening equipment to the largest ships.

Now, there are several important physical and chemical properties of fuel oils that need to be considered. The first is viscosity and its relationship with temperature. Viscosity is a key property of fuel oil, as it affects how the fuel oil is handled, stored, and preheated. The higher the viscosity of the fuel oil, the higher the preheating temperature required for atomizing the oil in burners or for other purposes, such as in engines. Therefore, understanding viscosity and its temperature relationship is crucial for fuel oil characterization.

Now, let's discuss the whole point. The pour point is an important characteristic of heavy oils. The pour point for fuel oil is significantly higher compared to lighter oils due to the presence of long straight-chain paraffin hydrocarbons in fuel oil. These compounds are responsible for forming wax crystals, which cause the oil to freeze at a relatively lower temperature, known as the pour point. If the fuel loses its mobility due to the crystallization of these long-chain paraffin compounds and the formation of wax, it becomes a matter of concern. Therefore, monitoring the pour point is crucial for assessing fuel oil quality.

Particulate emissions are another important consideration. After the burning of fuel oil, where the fuel is atomized into small droplets, these droplets transform into hollow coke spheres. These hollow coke spheres, known as cenospheres, typically have diameters in the range of a few to tens of micrometers. Additionally, fuel oil combustion produces soot, which contributes to particulate emissions.

The carbon-hydrogen ratio is another essential parameter for fuel oil. Fuel oil is a heavy oil, and it contains objectionable compounds and heavy hydrocarbon components. Its composition primarily consists of paraffin, naphthenes, and light aromatics, with molecular weights ranging up to 800. Apart from that, fuel oil contains resins, which are condensed aromatic hydrocarbons with long alkyl side chains and molecular weights ranging from 800 to 1000. Another component of fuel oil is called asphaltenes.

Asphaltenes are highly bulky condensed aromatic hydrocarbons with shorter alkyl chains, and their molecular weight can range beyond 1000, possibly up to 2000. This composition results in a high carbon-to-hydrogen ratio in fuel oil. Consequently, there is a significant risk of coke deposition in engine or burner parts when using fuel oil. When coke deposits on the burner, it creates a sooty flame that degrades combustion quality.

Moving on to sulfur content, since fuel oil is a residual oil, we can expect the accumulation of sulfur compounds in it, as it represents the last part of crude oil. Any objectionable sulfur compounds present in the crude oil may also be present in the fuel oil. After burning fuel oil in a burner or boiler, if this equipment lacks provisions for flue gas washing, scrubbing, or treatment, the resulting flue gas will contain sulfur oxide gases, contributing to environmental pollution. Therefore, it is essential to consider the sulfur content of fuel oil and impose restrictions on it.

Regarding the flash point, fuel oil has a high flash point due to its heavy nature and low volatility. The flash point for fuel oil is typically above 66 degrees Celsius, making it a safer fuel. Hence, the flash point is also an important consideration, even though its volatility is low.

Now, let's discuss the storage of fuel oil. Storage tanks for residual fuel oils are typically constructed from mild steel, which is a cost-effective material. These tanks can be in the form of vertical or horizontal cylinders. Safety regulations for this type of fuel are generally relaxed because of its high flash point and low volatility, making it less flammable due to its low volatility. Therefore, there are not many stringent regulations imposed on the storage of fuel oil.

Due to the high viscosity of fuel oil, it is essential to control the storage temperature to maintain low viscosity for easy pumping. As fuel oil is a heavy compound with high density and viscosity, it can be challenging to move the oil after storage if the container is not maintained at a specific temperature that allows for easy pumping. The bulk temperature is typically kept around 10 degrees Celsius above the pour point of the fuel oil. The pour point of fuel oil is relatively high, typically around 20 degrees or more, depending on the type of crude oil from which the fuel oil is derived. The bulk storage temperature should be maintained more than 10 degrees higher than the pour point of the fuel oil.

This restriction is imposed to prevent freezing at the pour point, as reaching the pour point can hinder the efficient operation of strainers and filters at the pump. In the pump, there are strainers and filters that remove impurities from the oil before it enters the pump. Highly viscous fuel oil with wax crystals cannot be easily pumped through these strainers and filters, so maintaining an appropriate temperature is crucial for efficient pumping.

Now, let's turn our attention to another important oil known as lubricating oil. Lubricating oil is typically obtained as a straight-run cut from the vacuum distillation unit. However, the oil obtained directly as a side-draw cut from the vacuum distillation unit is not suitable for use directly as a lubricant. Lubricating oil can be obtained from the vacuum distillation column if the crude oil being handled contains a significant amount of lubricating oil.

Petroleum fractions with an average volatility lower than that of gas oil serve as the foundation for various lubricating oils. Gas oil is the last liquid product obtained from the atmospheric distillation unit, and the atmospheric residue is sent to the vacuum distillation column for further processing to obtain lubricating oil. In the sequence of distillate fractions obtained from crude oil, lubricating oil follows gas oil in the atmospheric distillation column, making it less volatile than gas oil.

Lubricating oils are blends of lubricating oil base stock and chemical additives. The straight-run products directly obtained from the vacuum distillation column cannot function as lubricants until they are modified for specific applications. For this reason, various chemical additives are mixed with the lubricating oil to make it suitable as a marketable or finished product. So that it imparts enhanced desired properties. There are four most important functions that a lubricant must fulfill. The first is lubrication. Lubricating oil is specifically designed for this purpose, to introduce a thin liquid film on the metal surfaces of two moving parts. This thin lubricating film reduces friction between the two moving parts, helping to avoid excess friction, control energy loss, and extend the equipment's life by reducing wear and tear.

Next is cooling. Lubricating oil also acts as a coolant at the point of application. If any heat is generated due to friction, the lubricating oil dissipates and absorbs that heat, serving as a cooling medium.

Another function is cleaning and suspending. During the movement between friction or due to the motion of two moving parts where lubricating oil is applied, undesirable contaminants may form. These contaminants, which can include carbon, acid sludge, or varnish, are either removed or suspended by the lubricating oil, preventing them from depositing on the metallic surfaces and compromising the lubrication properties of the oil.

Lastly, lubricating oil should protect metal surfaces from rust and corrosion. In moist environments, rust may form on ferrous materials. The different process sequences involved in the manufacture of lube oil base stocks determine how we obtain these base stocks to which additives will be added. We obtain raw lube oil fractions directly from the beginning of the vacuum distillation process according to the desired properties.

Three types of lube oil base stocks can typically be observed as side cuts from the vacuum distillation column: low viscosity index, medium viscosity index, and high viscosity index, which can also be referred to as light base stock, medium base stock, and heavy base stock. These base stocks, which are not precisely lubricating oils, can also be deasphalted, or the vacuum residue can undergo deasphalting to produce a feedstock for a very heavy lube oil known as bright stock. Even after removing the lubricating oil fractions, the vacuum residue produced at the bottom of the vacuum distillation column can be subjected to deasphalting, which involves the removal of asphaltenes through extraction. The heavy oil obtained after deasphalting, referred to as deasphalted oil, serves as a lube oil base stock known as bright stock. The extraction process can again be employed to improve the viscosity-temperature characteristics. In this process, objectionable compounds can be extracted to properly maintain viscosity and the relationship between temperature and viscosity.

Dewaxing is a process that removes wax and improves the pour point. It involves the removal of long straight-chain paraffinic hydrocarbons, which are responsible for the high pour point. However, it's important to note that these waxes also contribute to a high viscosity index. Therefore, removing all the long-chain paraffinic hydrocarbons can reduce the viscosity index. To strike a balance between viscosity index and pour point, dewaxing should be carried out at an optimum level.

Another type of dewaxing process is catalytic dewaxing, where long straight-chain paraffinic hydrocarbons are converted into iso compounds, meaning branched-chain paraffinic hydrocarbons. Branched-chain paraffinic hydrocarbons do not produce wax. This approach allows for the retention of a high viscosity index while improving the pour point.

The final stage may involve finishing, which enhances color, color stability, and oxidation stability. Oxidation stability is crucial for maintaining the grade of lube oil, ensuring it doesn't degrade easily. Color and color stability also play a significant role in meeting specifications.

Lubricating oil base stocks are typically obtained from petroleum sources, specifically mineral oil sources. Lubricating oil is not consumed; it is used for the purpose of lubrication. After use, the used lubricating oil can be refined and reused. However, after several reuses, the lubricating oil may no longer retain its properties. At this point, there may be no other option but to dispose of it, which can lead to atmospheric pollution.

In recent times, there has been a shift towards newer thoughts and the use of synthesized base stocks. Base oils can also be obtained from synthetic or biological sources, which is highly preferable because biological sources offer biodegradability. Mineral oil, on the other hand, is not biodegradable. Therefore, base oils can be derived from synthetic or biological sources.

Synthetic-based stocks are manufactured through the chemical transformation of petroleum-derived organic chemicals, such as poly alpha olefin, polyalkaline glycol, and so on. Now, let's turn our attention to another important point: synthetic-based stock.

Petrochemical-derived organic chemicals can be synthesized through chemical transformation to produce synthetic-based stocks. These base stocks, while expensive, become the only choice for extremely demanding applications where mineral oil may not perform well due to limitations such as thermal stability, low viscosity index, and volatility. In such cases, synthetic-based stocks excel. However, the production of these base stocks requires additional steps, increasing the overall cost.

To balance cost and performance, blended base stocks, which are mixtures of synthetic-based stocks and mineral oils, are often used. This allows for the utilization of superior low-temperature properties, high flash points, and high viscosity index at a lower cost. By blending mineral oil with synthetic-based stocks, the overall cost can be reduced, while the mixture retains excellent properties. Base stocks of biological origin include vegetable oils obtained from seeds and fruits, making them highly preferable due to their natural source, ease of acquisition, biodegradability, and non-petroleum origin. These oils are becoming increasingly important. The table below presents the characteristics of various lube oil base stocks.

The first one is low viscosity index lubricating oil (LVI). In this case, the viscosity index is very poor, below 30, and these oils are rich in aromatics. It's important to note that lubricating oil requires a high paraffin content for a high viscosity index, and aromatics cannot provide a high viscosity index; they are low viscosity index compounds. Consequently, due to the high aromatic content, the viscosity index is lower. LVI is used in applications where viscosity index and oxidation stability are not critical.

Now, let's consider medium viscosity lubricating oil. Here, the viscosity index falls within a medium range of 30 to 85. The viscosity index scale starts from 0 and ends at 100, so 30 to 85 is the medium range. It contains a mixture of aromatics and paraffin and is used in situations where low viscosity index lubricating oil is a disadvantage. This is particularly useful where low viscosity index lubricating oil cannot be applied.

For high viscosity index lubricating oil, the viscosity index exceeds 85. This type of lubricating oil contains paraffin. If it exclusively contains paraffin, it is expected to have a higher viscosity index. High viscosity index lubricating oil is used in applications where good oxidation stability and a high viscosity index are required, such as in motor oils and turbine oils. It is typically extracted from paraffinic crude distillates, as this oil is obtained from paraffinic crude. All the high-end, high molecular weight paraffins are collected in the lube oil base stocks.

Now, there are several purposes for adding lubricating oil additives.

The first one is to improve the viscosity index. This is important because the viscosity index determines the high-temperature characteristics of the lubricating oil. It determines whether the lubricating oil can retain its viscosity at high temperatures, similar to its low-temperature viscosity. When lubricating oil additives are added, they should improve the viscosity to such a degree that engine parts or moving components can operate easily at high temperatures. Confidence should exist that the lubricating oil can perform consistently at both high and low temperatures.

Another purpose is to enhance oxidation stability. Oxidation stability is improved by these additives because they prevent the formation of hydroperoxide radicals. Hydroperoxide radicals are responsible for the degradation of lubricating oil through oxidation. By reducing the rate of oxidation, these additives help maintain oxidation stability.

Additives also help keep contaminants in suspension within the lubricating oil. They are added to ensure that contaminants generated during operation can remain suspended within the lubricating oil. Additionally, these additives aim to reduce friction. Friction can be reduced if a continuous thin film of lubricating oil is maintained on the surface of moving parts. Additives act to sustain this thin, continuous film of lubrication. Furthermore, lubricating oil additives are used to neutralize acids derived from fuel combustion in engines or equipment where fuel oil is burned. Sulfur oxide gases formed during combustion, in combination with moisture, can produce sulfurous acids that may react with metallic surfaces, causing wear. Lubricating oil additives prevent this wear by neutralizing these acids.

Pour point depressants are also crucial because they maintain low-temperature characteristics. At low temperatures, wax formation should be inhibited. Pour point depressants prevent the growth of wax crystals, ensuring that the oil does not freeze and lose its mobility due to the network structure formed by wax crystals.

Anti-rust additives are included to prevent rusting on metallic surfaces.

Anti-foaming agents are added to improve the anti-foaming characteristics of the lubricating oil, facilitating the efficient collapse of foams and reducing foam formation.

The physical composition of a formulated lubricant typically consists of:

Base fluid: Comprising 70 to 90 percent of the lubricating oil.

Performance package: Comprising 2 to 30 percent, depending on the application.

Viscosity modifiers: Used at 0 to 15 percent.

Pour point depressants: Used at 0 to 2 percent.

The performance package contains various classes of additives to enhance the properties of the lubricating oil. These include Emulsifiers and demulsifiers, Foam inhibitors, Friction modifiers, Pour point depressants, Viscosity modifiers, Oxidation inhibitors, Corrosion and rust inhibitors, Emulsifiers, demulsifiers, foam inhibitors, friction modifiers, pour point depressants, and viscosity modifiers, pour point depressants, and are chemically inert additives, meaning they do not react with the oil or metallic surfaces.

Rather, oxidation inhibitors and corrosion and rust inhibitors are chemically active additives. They work by some reaction. This table shows the different types of additives, their purpose of application, and their mode of action. Emulsifiers, which are added, are used to promote the mixing of water and oil properly in the form of either water-in-oil emulsion or oil-in-water emulsion. The typical compounds added under this class are non-ionic and ionic surfactants, and the mechanism of performance is that they facilitate emulsion formation by lowering the surface tension of water and allowing its thorough mixing with the oil.

Sometimes, water-based lubricating oils are used for those cases; emulsifiers can be added. Demulsifiers enhance water separation from oil contaminated with water. If it is a fully oil-based lubricant and it comes in contact with water, then that water should be removed by the use of demulsifiers. Those may be the block polymers of ethylene oxide or propylene oxides with glycerol, siloxanes, etcetera; there are many. They facilitate the water separation from a water-contaminated lubricant.

The next one is foam inhibitors. Foam inhibitors prevent lubricant from forming a persistent foam. Foam should be qualities and can be subsided. These inhibitors act like silicon polymers, such as polydimethyl siloxane; it is one of the examples. These inhibitors reduce the surface tension of air or gas bubbles, facilitating their collapse.

Easily, they collapse by reducing their surface tension. Friction modifiers alter the coefficient of friction. These are organic fatty alcohols, acids, and amides. These modifiers form a durable lubricant film of desired frictional characteristics. It maintains a lubricant film, and this film is durable so that it can act as the lubricant film all the time throughout the operation of the process.

The next one is pour point depressants. These are used to enable the lubricant to flow at low temperatures, which means they maintain the low-temperature properties for smooth operation as well as at high temperatures. Several compounds, such as alkylated naphthalene and phenolic polymers, are used for this purpose. Here's how they work: they adsorb onto the wax crystals and prevent the formation of undesirable wax crystals, thus inhibiting the growth of wax crystal formation.

Viscosity modifiers are used to minimize the rate of viscosity change with temperature. Their purpose is to maintain viscosity at almost all temperatures, from low to high. Some examples of compounds used for this are polyalkyl methacrylates, polyolefins, etc. This results in a lower loss in viscosity at high temperatures by associating with the lubricant. Viscosity modifiers can maintain viscosity at all temperatures, improving the viscosity index characteristics as well.

Oxidation inhibitors inhibit the oxidative decomposition of lubricants and additives by the formation of free radicals. They reduce the rate of oxidation, thus reducing the degradation characteristics of lubricating oil. Examples include zinc dialkyl dithiophosphate, organic sulfides, and polysulphides, which are able to decompose hydroperoxides that promote oxidation. These are the references. Thank you for your attention.