Course Name: PETROLEUM TECHNOLOGY

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Lecture 25: Petroleum fractions from distillation units (Contd.)

Hello and welcome to the 25th lecture of petroleum technology. In this lecture, we will learn about some of the petroleum fractions obtained from the distillation unit. Let us first come to jute batching oil. Jute batching oil is a not very normal type of distillate fraction which is get from all the refineries. It is a specific type of straight run distillate cut obtained from the atmospheric distillation unit. It comes between kerosene and diesel, and it is a narrow range.

Jute batching oil (JBO) is a middle distillate produced by petroleum refineries. It falls between kerosene and diesel in terms of its composition. Typically, JBO and diesel have overlapping boiling ranges. JBO is obtained as a straight-run product through the distillation of crude oil in petroleum refineries.

During the twisting and weaving of jute threads, oil serves as a lubricant to facilitate the separation of jute fibers. This jute batching oil, extracted as a straight-run cut from the atmospheric distillation unit, is particularly essential in regions where there is a demand for jute batching oil due to the cultivation of jute and the presence of jute industries. Workers in the jute industry rely on this oil for its lubricating properties during the processing of jute threads. To make the oil suitable for use in jute fiber processing, it needs to be combined with an emulsifier before application. Jute batching oil finds additional applications, such as being used as wash oil by steel plants to recover aromatic products from coke oven gas. Coke oven gas produces various aromatic compounds that remain in the vapor phase; using jute batching oil, combined with an emulsifier, helps absorb these aromatic products and purify the Coke oven gas by eliminating aromatics. The specification for jute batching oil is standardized, particularly in regions like West Bengal, where there is significant jute production. Jute batching oil is obtained from refineries, particularly from the Indian Oil Refinery in West Bengal, such as the Haldia refinery. The production of jute batching oil is dependent on market demand. The properties and specifications of jute batching oil are outlined in the table below: Density at 15 degrees Celsius: Minimum 0.825 kilograms per liter Color (ASTM scale): Maximum 7 Flashpoint: Minimum 100 degrees Celsius (Penske Martin closed cup apparatus) Kinetic viscosity: Maximum 15 centistokes at 37.8 degrees Celsius Pour point: Maximum 30 degrees Celsius Distillation range: Initial boiling point minimum 265, maximum 365 degrees Celsius. The distillation range indicates that it falls within the diesel range. There are two types of jute batching oil: JBO-C (jute batching oil clear), which is a lighter cut, and JBO-P (jute batching oil pale), which is a heavier cut. Since jute batching oil is sometimes used in the food packaging industry, it is crucial to ensure that jute products used in food packaging do not contain any carcinogenic materials. Jute batching oil, particularly the heavier cut, is subjected to strict conditions to ensure that it does not contain higher molecular weight hydrocarbons. Conversely, jute batching oil clear, which may have a lighter cut resembling the boiling range of kerosene, is not accepted if it carries the smell of kerosene. The manufacturing process of jute batching oil adheres to these stringent conditions.

Another type of oil obtained from refineries is white mineral oil, also known as WMO. White mineral oil is produced from selected lubricating base oils through either severe hydrogenation or intense acid treatment with fuming sulfuric acid (oleum). The feedstock for white mineral oil is lubricating oil-based stock, and the processes of hydrogenation or acid treatment, or a combination of both, are employed to remove unwanted materials. This results in a non-reactive saturated hydrocarbon liquid. White mineral oil serves specific applications, such as being used as a plasticizer in the polymer industry, a moisturizer in cosmetics, and a lubricant in food processing and medical products. The objective of the hydrogenation or acid treatment process is to produce a non-reactive, saturated hydrocarbon liquid suitable for these applications.

In sensitive applications such as pharmaceuticals, cosmetics, and food, white mineral oil undergoes processing to eliminate all traces of reactive compounds. The stringent standards ensure that any presence of reactive compounds in white mineral oil is unacceptable for these high-end industries. For textile adhesive applications, a less restrictive technical grade of white mineral oil may be utilized. Now, concerning the manufacturing processes of white mineral oil through acid treatment, it's worth noting that severe hydrogenation and acid treatment are sometimes combined. In the severe hydrogenation process, feedstocks are subjected to high-pressure hydrogen.

High-pressure hydrogen is utilized in a high-temperature reactor for severe hydrogenation, where reactions like hydro-desulfurization and hydro-denitrification take place to eliminate sulfur and nitrogen compounds, along with saturating aromatics. This process results in the removal of reactive substances and their saturation. The feedstock can then proceed to acid treatment or be used separately as the initial step of acid treatment.

The acid treatment involves using highly concentrated sulfuric acid, either oleum or anhydrous sulfuric acid (SO_3). Specific temperature, pressure, contact time, and the acid-to-oil ratio are crucial parameters. Typically, the acid-to-oil ratio is maintained at 1:6, with a temperature range of 35 to 95 degrees Celsius and a contact time ranging from 1 to 30 minutes or more. After acidification, the acidified oil undergoes neutralization using sodium hydroxide or sodium carbonate. In this neutralization process, sodium sulfonate is produced, and it needs to be removed through solvent extraction.

The solvent used for extracting sodium sulfonate is either alcohol or an alcohol-water mixture. After sulfonate removal by extraction, some solvent may remain in the mixed oil stream. To eliminate lighter solvent products, steam stripping is employed, and the recovered solvent is purified as a byproduct. Following this, the oil undergoes treatment with activated clay to eliminate any undesirable constituents. Activated clay treatment can be done through percolation, where coarser clay particles come in contact with the acidified oil, or through a mixing process, where finer clay particles are used. This treatment removes undesirable constituents such as residual moisture, trace amounts of solvent, or any trace aromatic hydrocarbons, resulting in refined oil, known as white mineral oil. Sludges are disposed of, and the acid is recovered in this process. Now, focusing on another significant product obtained from the refinery, particularly from the vacuum distillation unit or the fractionated bottoms of various secondary processing units, we have bitumen. The term "bitumen" is used worldwide, except in the USA, where the term "asphalt" is used to describe the solid or semi-solid materials produced by processing residues obtained from refining suitable crude oil.

The properties of bitumen depend on the type of crude oil used. Light crude yields a residue with different characteristics than that obtained from heavy crude. The nature of bitumen varies based on the crude oil type. Bitumen serves primarily as a binder and waterproofing material in road construction, especially for paving and road preparation, and to a lesser extent, in some industrial applications such as roofing. The widespread use of bitumen is attributed to its unique viscoelastic behavior and cost-effectiveness as an engineering material.

Bitumen exhibits viscoelastic properties, characterized by non-Newtonian fluid behavior. It deforms under stress and strain conditions, and this deformation is influenced by temperature and time. Therefore, understanding the conditions to which bitumen is exposed is crucial to selecting the appropriate type for its intended application.

Bitumen is tailored based on its end application, and its preparation is adjusted accordingly to suit specific purposes. When subjected to high temperatures and extended loading times under the application of force, bitumen behaves as a fluid, flowing and experiencing permanent deformation. This plastic nature is akin to how wheat flour, when mixed with water to make dough, transforms into a plastic-like material that cannot revert to its original form. This exemplifies the plastic property of bitumen, where permanent deformation occurs.

Conversely, at low temperatures and during short loading times, bitumen exhibits characteristics of an elastic solid. In these conditions, it does not undergo deformation and retains its original form. Understanding these properties is crucial for selecting the appropriate type of bitumen for specific applications.

The example of pulling a spring and observing its return to the original position illustrates the elastic property, where the material retains its shape after deformation. Bitumen exhibits such elastic behavior at low temperatures and short loading times, maintaining its structure without significant deformation.

The behavior of bitumen is characterized by the stiffness modulus, a viscoelastic modulus that depends on time and temperature. Viscoelasticity means that bitumen's response is influenced by both stress and strain, and the stiffness modulus (σ/ε) is a function of time and temperature.

The elemental composition of bitumen, presented in the table, reveals a predominant carbon content of 80 to 82 percent. Hydrogen follows with a significantly lower percentage. Oxygen content ranges from 0 to 1.5 percent, nitrogen from 0 to 1 percent, and sulfur from 0 to 6 percent. The levels of nitrogen, oxygen, and sulfur are contingent on the crude oil type from which the bitumen is derived. Additionally, metals such as vanadium, sodium, iron, and nickel may be present; their presence is also linked to the crude oil source.

Petroleum wax is a crucial product from the refinery with diverse applications. Most crude oils contain some amount of wax, although the concentration can vary significantly based on the nature and weight of the crude oil. Crude oils that are paraffinic and heavy tend to have higher amounts of petroleum wax, while lighter paraffinic crude oils have lesser wax content. Crude oils with a naphthenic nature generally have a lower probability of yielding wax in their bottom products.

A significant portion of petroleum wax found in crude oils boils in the same range as lube distillate. In cases where the crude oil is lube-bearing and lube oil is obtained as a distillate product from the vacuum distillation unit, the petroleum wax components are uniformly distributed throughout the lube oil fraction. Distillation alone cannot effectively separate wax and oil, prompting the need for dewaxing processes. Within the diverse nature of petroleum wax, straight-chain normal paraffins stand out as the chemically simplest hydrocarbons. They represent a fundamental component of the multi-component composition of petroleum wax.

Normal paraffins with chain lengths ranging from 16 to 17 carbon atoms solidify at room temperature. As the chain length increases, the melting point of corresponding normal paraffins also increases. For instance, even-chain lengths may extend up to C40, and these can be separated from the distillate at room temperature.

Petroleum waxes are broadly classified into macrocrystalline and microcrystalline waxes. Low-boiling vacuum distillates are rich in normal paraffins, with slightly branched paraffins present within this boiling range. This is particularly true for low-boiling lube bases, where a simpler hydrocarbon composition, specifically normal paraffins, is expected.

As the boiling temperature increases, waxy distillates contain branched paraffins in addition to normal paraffins. The likelihood of obtaining branched paraffins, which have higher boiling points compared to normal paraffins, increases with the rise in boiling temperature. Paraffin wax with a high normal paraffin content tends to crystallize into needle-like structures. These waxes, found in spindle oil and high machine oil distillates, are termed macrocrystalline waxes. The crystals formed, primarily from normal paraffins, exhibit a well-defined needle-like structure, creating distinctive wax crystals.

The predominance of branched and cyclic structured paraffins inhibits the formation of large, well-defined crystal needles. In cases where the distillate contains a higher proportion of branched and cyclic structured paraffins (closed-structure paraffin compounds), these cannot form elongated, well-defined crystal needles. Instead, they produce smaller crystals that tend to agglomerate and trap a significant amount of oil within them. Such waxes are known as microcrystalline waxes.

This different crystallization behavior is crucial for refiners, as the filtration ability of a feedstock in either deoiling or dewaxing processes differs for feedstocks containing macrocrystalline waxes compared to those with microcrystalline waxes. Feedstocks with more macrocrystalline waxes generally exhibit easier and smoother filtration compared to those with microcrystalline waxes. Moving on to another important product of petroleum refineries, petroleum coke is a carbonaceous material obtained from the coking unit. It is a valuable solid product, and coking operations involve heating heavy oil feedstock to high temperatures, cracking the oil, and driving off lighter products. In coking, coke is the major product, with some lighter products being distilled off in the fractionating tower alongside the coking unit. Coke finds applications in various industrial processes.

The requirements for petroleum coke depend on its intended use. When used as a fuel, the desirable properties include low sulfur, ash, and metal contents. Additionally, low porosity, good conductivity, and a low coefficient of thermal expansion are essential when the coke is intended for making electrodes. Good quality petroleum coke for electrode manufacture can be obtained from high-aromatic, high-molecular-weight petroleum stocks.

Petroleum coke comes in two main types: green coke or pet coke and fuel coke. Both types are valued for their use as fuel, with pet coke often serving as a replacement for coal due to its higher calorific value. Petroleum coke typically has a calorific value of approximately 7500 kcal/kg, while coal ranges from approximately 3500 to 4500 kcal/kg.

Beyond its calorific advantages, coke offers other benefits. Unlike coal, which is hydrophilic and tends to absorb moisture in rainy conditions, coke is hydrophobic, mitigating moisture-related issues. Furthermore, the higher density of coke compared to liquid fuel makes transportation more efficient and cost-effective. Additionally, coke produces minimal ash during combustion.

The properties of petroleum coke are influenced by various factors, including the type of coking process, feedstock properties, and operating temperatures in the coker. Some of the key physical properties of petroleum coke include:

Color and Appearance: Petroleum coke is a dark grey or black infusible solid. At high temperatures, around 1500 degrees Celsius, it can go through a plastic stage.

Solubility: It is insoluble in water, indicating its hydrophobic nature.

Density: The typical density of petroleum coke is 830 kg/m^3, reflecting its high density.

Chemical Composition: Carbon is the major chemical constituent of petroleum coke. Additionally, it contains trace amounts of metals such as silicon, iron, vanadium, magnesium, manganese, sodium, and calcium.

Stability: Under normal conditions, petroleum coke is stable and non-reactive. It does not undergo polymerization and can withstand various adverse situations.

Combustion: The combustion of petroleum coke produces oxides of sulfur and carbon.

It's important to note that these properties make petroleum coke suitable for various applications, including as a fuel and in the production of electrodes. Additionally, its stability and non-reactivity contribute to its safe handling and use under normal conditions.

Incomplete combustion generates carbon monoxide also. Now, coming to some of the applications of petroleum coke. Now, application as feedstocks or as a fuel end uses in cement industries, lime kilns, gasification units, industrial boilers, etcetera. Whenever it is used as the carbon source, then the applications are in electrode manufacture for metallurgical industries to get the synthetic graphite and making aluminum anodes, TiO_2 pigments, carbon braziers, silicon carbide, boundaries, and coke ovens. All these are the application areas of petroleum coke as a carbon source.

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