Course Name: PETROLEUM TECHNOLOGY

Professor Name: Dr. Sonali Sengupta

Department Name: Chemical Engineering

Institute Name: Indian Institute of Technology Kharagpur

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Lecture 33: Bitumen preparation processes

Hello and welcome to the thirty third lecture of Petroleum Technology. In this lecture, we will learn about the bitumen preparation processes. We have already learned about bitumen, the introductory part of bitumen, in our previous lectures. So, I think you are all acquainted with bitumen. So, today, we will talk about the composition and constitution of bitumen.

The properties and performance of bitumen are determined by its chemical composition and the way in which molecules interact. In fact, it is impossible or impractical to predict the properties of bitumen due to its very complex nature and complex molecular structure. Bitumen originates from various types of crude oil, each with versatile or different properties, and undergoes various refinery processes. So, the properties can be described in a broader way, and bitumen can be described in terms of its performance. There are various components of bitumen, and these components are divided into different types of compounds.

First is asphaltenes. Asphaltenes are high molecular weight complex aromatic structures with aliphatic side chains. Among all types of component groups of bitumen, asphaltenes are the heaviest compounds with molecular weights reaching up to around 10 to the power of 6. The molecular weight may go up to 10 to the power of 6, indicating that these are very high molecular weight compounds.

Mostly, these asphaltenes have aromatic structures with shorter aliphatic side chains. These aromatic structures are highly condensed, forming poly-nuclear aromatic structures where many aromatic rings are joined together in a composed structure, and they have a shorter aliphatic side chain. The aromatic part of asphaltene is much more compared to the aliphatic or paraffinic component. Asphaltenes can be considered as natural polymeric structures that form the backbone of bitumen. They are the major component of bitumen and form the main structure, earning them the title "backbone of bitumen."

Asphaltenes are the most complex-natured component compared to the other components of bitumen. Due to the poly-nuclear structure formed by these aromatic compounds, they can be considered as a polymeric structure. Higher asphaltene content leads to a higher penetration index, as we have discussed previously.

Now, another component is resin. Resins are complex aromatic structures with aliphatic side chains. Compared to asphaltenes, resins have a lower percentage of aromatic content and a higher percentage of aliphatic content. They contain string structures of aromatics with longer aliphatic side chains. Resins are soluble in normal heptanes, unlike asphaltenes, and have molecular weights ranging from 500 to 50,000. The molecular weight is obviously lesser than that of asphaltenes. Resins form a stabilizing solvating layer around the asphaltenes. In fact, resins make the asphaltenes peptized and dispersed throughout the matrix of bitumen. They impart ductility to the bitumen, contributing to its ductile nature.

Another component is aromatics. Aromatics are simpler aromatic naphthenic ring structures with aliphatic side chains. Compared to asphaltenes and resins, aromatics have a much simpler structure with several aromatic rings or naphthenic rings along with the aliphatic side chains. Their molecular weight ranges from 300 to 2000. Aromatics are polar in nature and act as solvents to high molecular weight aromatic hydrocarbons, similar to resins and particularly asphaltenes.

Another component is saturates. Saturates contain straight and branched aliphatic hydrocarbons as well as non-aromatic ring structures like naphthenes. This part of bitumen consists of straight and branched aliphatic hydrocarbons that are not very complex in nature. It also contains non-aromatic ring structures, possibly naphthenes, which are saturated aromatics without any double bonds. These are saturated molecules, and they may be joined together.

Wax or paraffin are composed of aliphatic hydrocarbons and aromatic and naphthenic structures, with the aliphatic side chains being dominant. In the saturated part, the dominating components are the aliphatic structures, such as straight-chain or somewhat branched-chain paraffinic hydrocarbons. They may be attached to some aromatic or naphthenic rings, but these aromatic or naphthenic rings are not very complex. A saturate fraction can be non-waxy, meaning it does not have a paraffinic structure, or very waxy, meaning it is highly paraffinic in structure. Saturates are nonpolar and act as the anti-solvent to resins and asphaltenes.

Now, coming to the manufacture of bitumen, we cannot use bitumen as-is from various units in the refinery; the straight run bitumen has to be manufactured to make it suitable for various applications. Bitumens are manufactured from high molecular residual components present in petroleum crude oils. Heavy petroleum crude oils mostly contain asphaltenes, and these asphaltenes, along with resins, accumulate in the residue part of crude oils after processing in distillation units. If the petroleum crude is very heavy, viscous, and thick, after atmospheric distillation, the atmospheric residue obtained contains a significant amount of asphaltene.

In cases where the petroleum crude is very heavy and viscous, after atmospheric distillation, the atmospheric residue obtained may contain a substantial amount of asphaltene. When this atmospheric residue is sent to the vacuum distillation unit to recover valuable oils, the vacuum residue obtained is very thick, highly viscous, and semi-solid in nature. All the asphaltene, resin components, and aromatic components accumulate there as bitumen. The bitumen obtained from the vacuum distillation column is called straight-run bitumen. The residual components used for bitumen have atmospheric cut points above approximately 450 degrees Celsius, which is a cracking temperature at atmospheric pressure.

So, no petroleum product can exist at this temperature at atmospheric pressure without cracking. This 450 degrees Celsius is mentioned in terms of the atmospheric unit because when the vacuum distillation column operates, it is under a vacuum, and the temperature is much lower compared to the atmospheric column. When the temperature of the vacuum distillation column is converted to atmospheric conditions, it will be significantly higher. Therefore, this temperature is referred to as the 450-degree Celsius atmospheric cut point of bitumen.

Bitumens are divided into two broad classes: road or paving grade bitumen and industrial grade bitumen, each with different applications. The processes used for bitumen production include vacuum distillation, oxidation (air blowing process), and blending. In the refinery, plants that operate oxidation or air blowing, as well as blending processes, are entirely dedicated to the manufacture of bitumen. However, the vacuum distillation column is also used to extract various valuable cuts, such as lubricating oil, heavy distillates, or residual fuel oil.

Now, coming to the vacuum distillation, this is one of the processes.

The vacuum distillation process is crucial for obtaining the required consistency of bitumen and controlling its volatility. Consistency refers to the softness or stiffness of bitumen, and controlling volatility involves managing the release of volatile components during bitumen applications. The front-end volatility of bitumen is a critical aspect of this process.

Front-end volatility is the temperature at which bitumen feedstock starts to evolve volatile components as it is heated. To meet standard specifications, it is essential to reduce front-end volatility by setting up a bitumen cut point. During bitumen applications, volatile or low molecular weight materials can evaporate, leading to a hardening effect. Additionally, the evaporation of these components poses health, safety, and environmental (HSE) concerns, as some of them are heavy molecular weight aromatic compounds, often carcinogenic in nature. Minimizing these components is crucial, and defining the minimum distillation conditions for feedstocks is an important factor in achieving this goal. Countries often have specific specifications governing these processes to ensure the quality and safety of bitumen production.

The minimum cut point value for bitumen during vacuum distillation is typically set at 450 degrees Celsius at 1-atmosphere pressure. This parameter helps define the starting temperature at which bitumen feedstock begins to release volatile components during heating. On the other hand, the maximum vacuum distillation conditions are determined by plant design and the consistency specifications required for the final bitumen product. Plant design dictates the highest vacuum level attainable, and the consistency specifications address whether the bitumen should be soft or hard. These conditions are established based on the desired properties of the final bitumen product.

Air blowing is a unique oxidation process specific to bitumen, not applied to any other petroleum product. This process involves the introduction of air to achieve the required viscoelastic properties and temperature susceptibility of bitumen. The goal of air blowing is to control the viscoelastic nature of bitumen, ensuring it exhibits both elastic and plastic behavior at appropriate temperatures. The blowing process is conducted at elevated temperatures, typically ranging from 200 to 325 degrees Celsius.

The standard temperature for air blowing of bitumen is typically around 275 degrees Celsius. During this process, the air is bubbled through bitumen using a spider fitted at the bottom of the reactor or bitumen-blowing unit (BBU). This spider, resembling a sparger, facilitates the introduction of air into the bitumen.

At higher blowing temperatures, especially above 250 degrees Celsius, the predominant oxidation reactions involve the dehydrogenation of aromatic structures, followed by polycondensation. Dehydrogenation leads to the removal of hydrogen from aromatic structures, resulting in highly condensed and unsaturated structures. This process increases the molecular weight of asphaltenes. As a consequence, the asphaltene content rises, contributing to the development of viscoelastic properties and temperature susceptibility in bitumen.

The increased asphaltene content is crucial for providing the desired viscoelasticity and temperature susceptibility to bitumen. Asphaltenes play a key role in imparting these properties to bitumen, making it suitable for various applications. Conversely, at lower blowing temperatures, the reactions primarily involve direct oxidation to alcohols and carboxylates. This milder operation results in less severe chemical transformations, mainly leading to the formation of alcohols and carboxylate molecules. Overall, air blowing is a critical process for producing industrial bitumen with specific requirements for high viscoelasticity. The temperature conditions during this process significantly impact the final properties of the bitumen product.

In the context of industrial bitumen production, blowing is particularly crucial when bitumen obtained from vacuum distillation lacks the required viscoelasticity properties. When the straight run bitumen from the vacuum distillation column is too soft and lacks sufficient viscoelasticity, blowing is employed to enhance its suitability for paving grade bitumen. This process is often termed semi-blowing (SB) or the SB process for paving grade bitumen, which is also referred to as semi-blown bitumen. For paving-grade bitumen, the degree of oxidation is relatively mild, distinguishing it from the more severe oxidation applied to industrial-grade bitumen. The resulting bitumen from this mild oxidation is known as semi-blown bitumen. On the other hand, the industrial grade bitumen undergoes more severe oxidation, leading to fully oxidized bitumen or fully blown bitumen.

Bitumen blowing can be conducted in either batch or continuous mode, depending on the preference and suitability of the refiner. The continuous blowing operation involves preheating bitumen, feeding it into the blowing column, and introducing air from the top of the column. The air is bubbled through the bitumen using an air sparger or air spider, with air being introduced at the bottom through a spider sparger that also serves for agitation. The size of the air bubble plays a crucial role in determining the efficiency of the reaction during blowing.

The exothermic nature of the oxidation reaction in bitumen blowing demands careful temperature control. To manage this, heat generated during the highly exothermic oxidation reaction needs to be efficiently removed from the reactor to maintain a specific temperature. Once the air-blowing process is complete, the oxidized bitumen exits the bottom of the unit and is directed to a surge drum. In the surge drum, the blown bitumen undergoes heat exchange with the feedstock and is subsequently cooled before storage. Steam is introduced from the top of the drum to control the foaming of bitumen, thereby preventing undesirable foaming in the bitumen-blowing unit.

Comparatively, batch blowing is a simpler and more cost-effective operation than continuous blowing. In this process, a vessel is filled with bitumen feedstock, and the temperature is raised to the blowing temperature. Air is then blown through the feedstock, initiating exothermic reactions starting at around 200 degrees Celsius. Notably, batch-blowing operates in a discontinuous manner, with no continuous flow of feedstock. The reactions occur within a batch reactor and are driven by the presence of oxygen and the bitumen feedstock.

In batch blowing, it's crucial to control the temperature effectively to prevent the risk of fire or decomposition of the product, given the discontinuous nature of the operation. Continuous monitoring and control are necessary as the temperature gradually increases during the process. Off gases generated during the batch blowing process also require careful control, particularly in managing oxygen content to avoid the potential for combustion.Batch units typically have a limited capacity compared to continuous blowing units, which is a natural consequence of their operating mode.

Catalytic blowing is another approach where chemicals like iron chloride ($FeCl_3$), phosphoric acid (H_3PO_4), or potassium hydroxide (KOH) are employed to accelerate the blowing reaction. While these chemicals enhance the blowing process and improve bitumen properties, it's important to note that this is not strictly catalytic blowing since the substances remain within the bitumen after the process.One drawback of catalytic blowing is the high corrosivity of the catalyst toward the metals used in plant construction. This corrosion occurs due to the nature of the chemicals used in the process.During the blowing process, gases are evolved, and the off gases leaving the reactor primarily contain nitrogen, unreacted oxygen, and other components in small amounts. Some of these components may include hydrocarbon gases that are both highly corrosive and environmentally unfriendly.

The presence of sulfur-containing molecules in the blowing gases can contribute to an unpleasant odor, and these gases typically need to be treated, often by burning in an incinerator. Given that blowing gases are often acidic, the selection of materials for the gas-handling components needs to be carefully considered to withstand the corrosive nature.

The oxidation process, being a high-temperature reaction, induces various changes in the composition of bitumen. During oxidation, there is a transformation of resins into asphaltenes. The severity of the operation and the oxidation conditions lead to the conversion of lower molecular weight compounds, including resins, into higher molecular weight asphaltenes. Consequently, the percentage of asphaltenes in the bitumen increases. Similarly, resins are formed from the aromatic fraction during oxidation. The lower-grade aromatic compounds are converted into higher-grade resins. However, saturates, being saturated molecules, are minimally affected by the oxidation process. This process alters the molecular composition of bitumen, influencing its properties and performance.

These are not susceptible to attack by oxygen during the oxidation process. This limitation in the blowing process is essential for the manufacture of certain types of bitumen. The extent of oxidation is determined by the desired properties of the bitumen.However, an increase in asphaltene content and a reduction in the aromatics or resin fraction can render bitumen unstable, leading to the separation of asphaltenes. Excessive oxidation, which results in a high amount of asphaltenes, is not preferable as it can destabilize bitumen. Despite its challenges during processing, bitumen finds widespread application due to its unique polymer-like properties, relative chemical inertness, and cost-effectiveness. As the residue from the bottom of the atmospheric or vacuum distillation unit, or the last fraction in the crude oil processing unit, bitumen serves a variety of purposes in different industries.

So, they are low-cost, but at the same time, they possess many other important properties like unique polymer-like properties and relative chemical inertness. They are almost inert to various acids, alkalis, etc., making them applicable in various contexts. Its functions include acting as a binder in road-making processes, an adhesive, a coating, a sealant, and it is commonly used in roofing and preservation. On average, 80 percent of bitumen is used in paving applications for road-making, while the other 20 percent is utilized in the building and construction industry for various purposes. Paving grade bitumens have a service temperature range between about minus 50 to 80 degrees Celsius, depending on the climate. Therefore, paving grade bitumens are manufactured to be suitable for their intended end-use and temperature conditions.

Temperature is a very important factor for paving grade bitumen or any type of bitumen. Industrial bitumens have a service temperature range of minus 50 to 120 degrees Celsius.

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