Course Name: PETROLEUM TECHNOLOGY

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Lecture 31: Purification processes

Hello and welcome to the 31st lecture of Petroleum Technology. In this lecture we will learn about various types of purification process which are practiced in the refinery. Purification processes petroleum products are required to reach the consumer in a certain degree of purity and quality. You know that all the petroleum products has to maintain its own specifications which are set by a particular country. So, before the petroleum products are marketed they have to maintain the certain degree of purity and quality. The impurities and undesired components may come from the original crude or may be developed during various stages of processing the crude and its fractions.

So, you know that the petroleum compounds contain many objectionable compounds and impurities, which directly come from the original crude. These may include sulfur, nitrogen, oxygen compounds, and metal compounds, which are components of the original crude. They come and accumulate in the petroleum distillates or may be developed during various stages of processing. One example is the gum; gum is formed during storage, and also different impurities may arise during other stages of processing of the crude and its fractions. Depending upon the nature of the crude and the ultimate use of the product, the required purification may involve simple treatment or quite an elaborate processing.

So, depending on the type of impurities that need to be removed from the petroleum fraction to achieve the desired quality and purity, the after-treatment may range from a simple process, such as solvent de-waxing or solvent extraction, to a more elaborate processing method, such as some hydro-treatment processes involving fixed-bed reactors operating at high temperatures and pressures. Even feedstocks for catalytic processes require purification to minimize catalyst deactivation. Let's take the example of the catalytic reforming process or the FCC process, where there is always a risk of catalyst deactivation if the feedstock contains unwanted substances such as sulfur, nitrogen, or oxygen, which can deposit on the catalyst and lead to deactivation. Therefore, feedstocks should be purified before undergoing further secondary processing steps.

The specific aims of purification processes are to minimize various factors. For instance, acidity in petroleum fractions should be minimized to prevent corrosion. Carbon residue in the fraction should be minimized to avoid coke deposition and the tendency for coke formation. Catalyst deactivation should be minimized, necessitating feedstock processing before it enters the operation. Corrosivity and gum formation should be minimized, meaning that compounds responsible for gum formation should be removed from the petroleum distillate. Additionally, the formation of noxious combustion products, such as foul-smelling gases, can be minimized through certain operations before they are released into the environment.

To improve certain characteristics, various measures can be taken. For instance, to enhance the burning quality of kerosene and diesel fuel, the aromatics content of these petroleum products needs to be reduced. Improving gasoline properties, such as lead susceptibility and octane rating, involves adding alkyl lead compounds to raise the octane number. Therefore, gasoline properties can be enhanced by improving both the lead susceptibility and octane number. Color and color stability are standard specifications for any petroleum distillate products.

So, color should be maintained and improved, and color stability should be enhanced to ensure stability. Odor should be improved, ensuring a pleasant smell in petroleum distillate products. The pour point of diesel fuel should be lowered to improve its pour point, preventing freezing in cold regions. During these purification processes, several byproducts are formed, which can be recovered for sale or further processing. Byproducts such as alkyl phenol, hydrogen sulfide gas, mercaptans, naphthenic acid, and sulphonates can be processed in other units, like Claus-type sulfur recovery units, to obtain elemental sulfur. This elemental sulfur can then be sold in the market as feedstock for sulfuric acid production.

As hydrogen sulfide (H_2S) is an abundant and environmentally unfriendly gas in refinery gases, it needs to be removed before further processing. There are two main methods for H_2S removal: absorption by regenerative solvent and adsorption on a solid bed. Absorption by regenerative solvent involves counter-current contact of the gas stream with a solvent. In the absorption tower, the solvent is introduced from the top, while the gas is introduced from the bottom.

During the counter-current contact in the absorption tower, the solvent absorbs the H_2S gas from the gas stream. The H_2S-rich solution is then taken out from the bottom of the absorber and sent to a regenerator. In the regenerator, H_2S is removed by heating, and the resulting H_2S-lean solution is cooled and recycled back to the top of the absorber. This process continues in a continuous cycle. The H_2S-rich solution, after stripping off H_2S in the regenerator, is usually fed to a Claus-type sulfur recovery unit. In this unit, H_2S is converted to elemental sulfur. Elemental sulfur is a valuable byproduct with various industrial applications. Two commonly used chemical solvents for H_2S absorption are amines (such as monoethanolamine, diethanolamine, diisopropanolamine) and hot carbonates. In hot carbonate solvents, aqueous potassium carbonate is often used. These solvents play a crucial role in efficiently removing H_2S from the refinery gases.

Adsorption on a solid bed involves the use of a porous solid material as an adsorbent bed to remove H_2S from the gas stream. This method relies on the adsorptive properties of certain porous solids to selectively capture low to medium concentrations of H_2S. The porous nature of the solid material is essential because it provides a larger surface area for effective adsorption. The choice of the solid material is crucial, and it should possess high adsorptive properties. The porous structure allows for efficient adsorption of H_2S, particularly from gas streams with low to medium concentrations of the gas. This process can be categorized based on the types of adsorbents used.

Non-regenerative adsorbents, such as zinc oxide and iron oxides, are materials that do not undergo a regeneration process. On the other hand, regenerative adsorbents, including molecular sieves and zinc titanate, can be rejuvenated and used again after the adsorption process. Molecular sieves are porous sodium aluminosilicates known for their adsorption capabilities. Zinc titanate is another regenerative adsorbent used for removing H_2S gas. Gasoline sweetening is a process aimed at eliminating foul-smelling sulfur compounds, mainly mercaptans, from petroleum products. Mercaptans contribute to the unpleasant odor of the product. The sweetening process transforms the foul-smelling petroleum cut into a more pleasant-smelling product. Straight run naphtha, obtained from both sweet crude and sour crude, generally has low sulfur content.

Regardless of whether the crude is sweet or sour, naphtha, being the initial liquid product from the atmospheric distillation unit's overhead, typically has low sulfur content. In contemporary scenarios, gasoline sulfur content is mandated to be at lower levels, with a maximum specification of 10 ppm, as per the Bharat Stage 6 standard. This stringent standard is in place to ensure that the sulfur content in gasoline remains below or at a maximum of 10 ppm. Adhering to such standards is crucial to mitigate adverse effects on the effectiveness of catalytic converters in processes like catalytic reforming or FCC (Fluid Catalytic Cracking). This regulation helps in reducing exhaust emissions, particularly sulfur dioxide, which is more environmentally friendly. Gasoline sweetening plays a role in converting mercaptans to disulfide, contributing to improved exhaust quality without necessarily reducing the absolute sulfur content.

If gasoline contains mercaptans, which are malodorous compounds, the sweetening process is employed to convert these mercaptans to disulfide—a sweet-smelling compound. However, it's important to note that this process doesn't lead to a net reduction in the sulfur content. The mercaptans, with a specific number of sulfur atoms, are transformed into disulfide with an equivalent number of sulfur atoms, maintaining the overall sulfur content in the gasoline. While the sulfur content remains constant, the odor is enhanced. The success of this treatment depends on the balance within the gasoline pool, where components with very low sulfur levels, like catalytic reformate, light straight run naphtha, alkylate isomerates, etc., can absorb sweetened gasoline to achieve a satisfactory sulfur level. The gasoline pool comprises products obtained from various points in both primary and secondary processing units in the refinery.

In the gasoline pool, the major components include catalytic reformate from the catalytic reforming unit, light straight-run naphtha from the atmospheric distillation column, alkylate from the alkylation unit, and isomerates from the isomerization unit. These components generally have low sulfur levels. Sweetened gasoline is allowed to mix or blend with this gasoline pool only when its sulfur level is still low after the sweetening process. Now, let's talk about the UOP Merox process. Universal Oil Products (UOP) developed the Merox process, which is a sweetening process. The Merox process is designed to control the mercaptan sulfur content in a wide range of hydrocarbon streams, from fuel gas to distillates with endpoints up to 345 degrees Celsius. This means that the Merox process can be applied to various petroleum distillates, including those in the diesel range.

The UOP Merox process is utilized from the refinery's fuel gas to the diesel cut. The process chemistry involves the oxidation of mercaptans to disulfides in an alkaline environment using oxygen from the atmosphere and a suitable organometallic catalyst. The general reaction can be expressed as:

$RSH+1/2O_2 \longrightarrow RSSR + H2O$

Here, R represents any alkyl radical, which can be a straight chain, branched chain, or cyclic saturated or unsaturated. The same R is present in the resulting disulfide, and there is no net reduction of sulfur content in the feedstock.

In Merox extraction, applicable to gases and straight-run and thermal naphthas up to about 100 degrees Celsius, and to some extent to FCC-derived naphthas, mercaptans are extracted with caustic soda, oxidized to disulfides, and then removed from the system. This extraction process is distinct from the regular Merox process. Merox extraction is suitable for feedstocks boiling up to about 100 degrees Celsius, including gases, straight-run naphthas, and thermal naphthas. Mercaptans within this boiling range are sufficiently soluble in caustic soda for extraction, and the extracted mercaptans are oxidized to disulfides, leading to a net reduction in sulfur content in the product. However, Merox extraction has limitations. Mercaptans with boiling points above 100 degrees Celsius are insufficiently soluble in caustic soda, requiring the use of the Merox sweetening process for these larger mercaptan molecules.

In the fixed bed Merox sweetening process, the catalyst is supported on a bed of activated charcoal, and the bed is kept wetted by intermittent circulation of caustic solution. The process takes place in a Merox reactor, where feed, along with air, is introduced from the top, and mercaptans are converted into disulfides. Sodium hydroxide (NaOH) is intermittently injected into the reactor to maintain the catalyst's activity. After sweetening, the treated feed, along with caustic, is sent to a caustic settler, where caustic is recovered from the settler bottom. The oil is directed to a sand filter, and the treated products are recovered. The recycled NaOH is then reintroduced into the reactor for injection. The typical caustic strength is 10 degrees Baume', equivalent to 6.6 weight percent NaOH, and the consumption ranges from 5 to 20 pounds of NaOH per 1000 barrels of gasoline.

Another process, called minimum alkali fixed bed sweetening, is introduced to address the increasing difficulty and cost of spent caustic disposal. This process significantly reduces caustic consumption to approximately 1 pound of NaOH per 1000 barrels of feed. This reduction is achieved to minimize the environmental impact and costs associated with caustic dispos In the Minalk process, caustic consumption is significantly reduced to one-fifth of the standard fixed bed sweetening process, with only 1 pound of NaOH per 1000 barrels of feed. The key difference lies in the use of a high selectivity catalyst with higher activity. Unlike the intermittent circulation of highly concentrated NaOH in the standard process, Minalk employs continuous injection and disposal of a small amount of weak caustic at 1.9 weight percent NaOH.

The process flow in Minalk involves introducing gasoline, along with air, into the reactor, where continuous injection of weak concentrated alkali occurs. Sweetened gasoline is recovered from the reactor's bottom, and the spent alkali is circulated, with some being extracted from the regenerator's bottom. This approach allows for the use of a much lower concentration of alkali for injection, and the spent alkali, along with water, is easily recovered and sent to the sour water processing plant. The caustic-free Merox system is introduced in response to environmental concerns related to spent caustic disposal. In this version, ammonia is used instead of NaOH to maintain alkalinity and facilitate the sweetening reaction. The mineral catalyst is replaced with a more active catalyst, which remains in the active state through continuous injection of a liquid activator. This caustic-free version aims to address environmental pressures associated with spent caustic disposal.al.

In the caustic-free Merox process, gasoline, along with ammonia, water, and air, is directed to the reactor where the sweetening reaction takes place. The sweetened gasoline is then recovered from the reactor. The ammonia-water mixture is recirculated within the system, and a portion of the drained ammonia water can be utilized for other purposes, such as fertilizer production. This approach eliminates the need for caustic soda (NaOH) and addresses environmental concerns associated with spent caustic disposal.

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