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Lecture 35: Emission control and effluent treatment in refinery

Hello and welcome to the 35th lecture of Petroleum Technology. In this lecture today we will learn about the Emission Control and Effluent Treatment in the Refinery. All industries are very careful about environmental protection, where the emissions or effluent that they produce are strictly controlled by several regulatory bodies and their concerned countries. The industries have to follow all those regulations before they produce the pollutants that are very harmful to the environment. So, environmental management has become a major factor for refineries, and it is important that refiners at least meet the standards set by the regulatory authorities, if not more. So, the refinery is one of the largest industries worldwide, and it produces refinery produces lots of various kinds of emissions as well as pollutants and effluents that are generated from various refinery processes practiced in the refinery.

Environmental management poses a significant challenge for refineries, considering the vast differences in processes, oil types, sizes, throughputs, locations, and ages among them. Refineries worldwide vary in terms of the crude oil they process, the scale of their operations (particularly in the atmospheric distillation unit), throughput capacity, and the types and quantities of distillates and products they generate through secondary processing units. The location and age of a refinery also contribute to these variations.

Given these diversities, there is no universal "best" environmental practice that can be applied to all refineries. Each refinery has its unique set of effluents, emissions, and pollutant generation based on its specific characteristics. Achieving complete elimination of all pollution is an unattainable goal and is not practically feasible across all refineries. Environmental management strategies need to be tailored to the individual circumstances and profiles of each facility.

Complete elimination of every type of pollution emanating from the refinery is an unattainable goal and not feasible. However, efforts can be directed towards minimizing environmental impact through pollution reduction strategies. These strategies include Pollution Reduction at Source: Implementing measures at the initial stages of processing, such as careful handling and processing of feedstock, to minimize the generation of pollutants.

Recycling: Rather than discarding leftover reaction substances into the environment, explore recycling options wherever possible. Emission Control: Implement measures to control emissions, reducing the release of pollutant materials into the environment after they are generated. Responsible Waste Disposal: If waste is inevitably produced, ensure that disposal is conducted responsibly and in an environmentally friendly manner. The preferred approach is pollution reduction at the source, emphasizing both good practices and good housekeeping to curtail the generation of pollutants before they enter subsequent processing stages.

Controlling pollution in a refinery involves adhering to specific rules, leading to good operating practices and effective housekeeping. Addressing atmospheric emissions is a critical aspect, as these emissions are a prominent form of pollution and have been a primary focus for regulation in many countries. While it may be challenging to prevent the generation of certain atmospheric emissions, their control becomes essential.

Numerous comprehensive regulations worldwide are designed to manage atmospheric emissions, highlighting its paramount importance. Despite the availability of various emission control processes, their implementation may face challenges, whether due to economic constraints or impracticality within the refinery's operational context. The quantity and nature of emissions from refineries vary significantly based on factors such as crude oil capacity, crude oil quality, specific refinery processes, adopted air pollution control measures, and overall maintenance and housekeeping practices.

The quantity and type of emissions from refineries depend on factors such as crude oil capacity, the quality of crude oil processed (including sour crude), specific refinery processes, air pollution control measures, and the overall level of maintenance and housekeeping practices. Careful management of these aspects can help reduce atmospheric emissions associated with various refinery processes.

Key emission sources in refineries include combustion processes in furnaces, which generate flue gases. Sulfur recovery units produce hydrogen sulfide gases, while catalytic cracking units generate carbon dioxide, carbon monoxide, sulfur oxide gases, and undesirable hydrocarbon gases during the regeneration of catalysts. Flares, utilized for burning gases in the refinery, also contribute to the emission of combustible gases. Addressing these emission sources through effective control measures and maintaining high standards of maintenance and housekeeping practices can help mitigate atmospheric emissions.

Flares also produce carbon dioxide and carbon monoxide gases. Major atmospheric pollutants emitted from refineries include sulfur oxides (SOX), nitrogen oxides (NOX), particulate matter (PM), volatile organic compounds (VOC), and carbon dioxide. These pollutants result from the combustion process of oil and various refinery processes at different stages.

Combustion-related emissions account for approximately 4 to 9 percent of crude oil usage in refineries, serving as fuel in processes such as furnaces. The generated flue gas is then discharged into the air. Initially, air quality regulations specified minimum discharge stack heights to facilitate the proper dispersion of flue gases. This practice ensures that the stack or flare reaches a sufficient height to prevent the mixing or dispersion of carbon dioxide, carbon monoxide, and sulfur oxide gases near ground level where human activities occur. Stack height is, therefore, a crucial factor in emission control.

In a refinery, the majority of sulfur oxides, nitrogen oxides, and particulate matter emissions are directly related to the type of fuel used. If the fuel contains a significant amount of sulfur or nitrogen compounds, they produce sulfur oxide and nitrogen oxide gases upon burning. Particulate matters are generated when the fuel contains heavy aromatic or high molecular weight carbonaceous compounds. Therefore, efficient energy use is an essential first step in air pollution control, and energy conservation is also necessary.

Now, focusing on sulfur oxide control, sulfur dioxide is a major pollutant in refineries. Sulfur oxide is a key contributor to acid rain. Acid rain occurs when sulfur oxide gases come into contact with rainwater, forming acidic rain that, when it reaches the ground, makes lakes, rivers, and soil acidic. This phenomenon negatively impacts the quality of life systems, especially short-life organisms like fish, plants, and algae.

So, sulfur oxide emissions arise from burnt fuels containing a significant amount of sulfur compounds. The catalytic cracking process, where the catalyst is burned in the regenerator, releases sulfur oxide gases. Additionally, if the feedstock of the catalytic cracking process contains sulfur, it also produces sulfur oxide gases. Sulfur removal and recovery operations involve the absorption of sulfur oxide gases, and when these gases are stripped off from the absorbed solution, sulfur oxide gas is emitted.

Reducing sulfur emissions can be achieved by using lower sulfur fuels and feedstocks for the catalytic cracker. Cracking units are major contributors to these pollutants due to their high-temperature operation. Therefore, controlling sulfur emissions involves using lower sulfur fuels and feedstocks, which can be obtained from low sulfur crudes, known as sweet crude. Another option is to desulfurize both fuel oils and feedstocks using hydrodesulfurization before feeding them into the process. In this method, hydrogen sulfide formed in the processing of crude oil and other feedstock is treated in an amine treater, where H_2S is absorbed from the refinery gases.

Refinery gas produces a significant amount of hydrogen sulfide gas due to the presence of sulfur in the feedstock. This hydrogen sulfide is absorbed in the amine treater, typically using solvents like monoethanolamine or diethanolamine. The amine treater absorbs H_2S gas. Sour gases containing H_2S and ammonia are removed from the refinery's sour waters in a sour water stripper. Sour water, produced at various points such as in the atmospheric distillation column, vacuum distillation column, or any fractionator, contains H_2S and ammonia gases dissolved in it. These sour waters are collected and sent to a sour water stripper to remove H_2S and ammonia gases through a steam stripping process, leaving less sour water or nearly pollution-free water.

The streams containing H_2S and ammonia from the feedstock for the refinery are then sent to the refinery sulfur removal plant, where the Claus process is commonly used to recover elemental sulfur. Elemental sulfur can be observed in heaps around the refinery, appearing as yellow-colored sulfur. For NOx control, nitrogen oxides are generated in combustion processes in refineries. They originate from the oxidation of atmospheric nitrogen, known as thermal NOx, and indigenous nitrogen in the fuel, known as fuel NOx. NOx can be generated by burning fuel containing nitrogen.

So, there are two sources of generating NOx. One is the nitrogen compounds present in the fuel oil. After burning the fuel oil, these nitrogen compounds react with atmospheric oxygen during the combustion process to produce NOx. Another source is the good combustion of fuel, where high heat (around 2000 to 3000 degrees Celsius) is generated. At this high temperature, atmospheric nitrogen reacts with atmospheric oxygen to produce NOx, known as thermal NOx. Nitrogen compounds are removed by the hydrotreating process before combustion. Hydrodenitrogenation is a useful process used to eliminate nitrogen compounds from the fuel.

Additionally, remedial technologies such as catalytic and non-catalytic flue gas treatments are available. After the flue gas is formed, it may undergo treatment using catalytic or non-catalytic processes. However, these processes are not always economically feasible, and only very large plants might consider implementing them. Various methods can be adopted to reduce NOx emissions, including reducing nitrogen in the feed (reduction at the source), reducing oxygen supply to lower the combustion temperature, and reducing the combustion temperature itself. The most common method involves reducing residence time, which is a design feature of the burner. Reducing residence time means less time for fuel and oxygen to interact, resulting in controlled NOx formation. However, it's important to note that controlling NOx formation may lead to an increase in particulate matter formation as a potential drawback.

Now, turning to particulate control, particulate matter is formed when fuel combustion ash and unburned hydrocarbons agglomerate. Occasionally, flares can also contribute to particulate matter when fuel is combusted, leading to the formation of ash and unburned heavier hydrocarbons that agglomerate to create light, fluffy materials known as particulates. These particulates float in the air, contributing to airborne particulate matter. Flares, where refinery gases are burned, can also be a source of particulate matter.

It is observed that with certain burners, the combination firing of oil and gas can reduce overall particulate emissions compared to burning in separate burners. Some burners are designed to accept oil and gas together as fuel, and this combined firing reduces overall particulate emissions compared to processes where oil and gas are burned in separate burners. Similarly, the atomization of fuel oil can increase the carbon burnout rate. In burners or furnaces, fuel oil is sprayed by an atomizer. If atomization is highly efficient, meaning oil globules or droplets are uniformly dispersed within the furnace, they can interact effectively with air, resulting in efficient combustion and lower particle emissions. However, efficient combustion at high temperatures may lead to the formation of thermal NOx. Improved air-fuel mixing enhances combustion and reduces particulates. The formation of particulate matter is closely linked to combustion intensity and the quality of fuel oil.

In low-quality fuel oil, unburned carbon in the form of asphaltenes and sulfur undergoes slow burning, resulting in the production of particulate matter. Catalytic cracking units and cokers, being high-temperature processes, are major sources of particulate emissions. The use of cyclones and electrostatic precipitators, which capture and arrest particulate matter, along with careful catalyst selection, contributes to reducing overall process temperatures and burning unburned carbonaceous material, thus minimizing particulate emissions from these sources.

Now, addressing aqueous emissions, in refineries, significant aqueous emissions occur in the form of effluents. Refinery effluents are discharged into receiving streams, introducing contaminants that are toxic and diminish the natural oxygen content of the stream, making it unsuitable. Potential water contaminants in refinery effluents include oil, organic materials (such as acids and alkalis), sulfides, ammonia, cyanides, and heavy metals. These contaminants pollute water bodies. Various analytical processes, such as measuring total dissolved solids, total dissolved salts, total suspended solids, total organic carbon, total organic nitrogen, chemical oxygen demand (COD), biochemical oxygen demand (BOD), etc., can effectively quantify these pollutants. Source control, being the most efficient method, focuses on minimizing the generation of pollutants at their origin.

Effluent treatment plants are often classified as treatments where all wastewater streams are collected and treated downstream of the process units and other sources. Therefore, the effluent treatment plant operates on a system that, after collecting wastewater streams from various refinery processes, takes them to the ETP (Effluent Treatment Plant) and treats them. Effluent treatment is much easier and more effective if the contaminant loading can be controlled or limited at the source. If the contaminant loading is not limited at the source, meaning that if it is not controlled from the beginning, a sub-treatment plant can be operated in between, preventing overburdening of the effluent treatment plant and enabling the handling of minimum contaminants.

In sour water strippers, H_2S and ammonia are selectively stripped by steam, which is then cooled and condensed. After this sour water stripper, H_2S and ammonia are removed by the stripping process using steam, and the off-gases containing H_2S and ammonia are routed to the sulfur plant, where elemental sulfur is produced. For the cooling water system, a closed cooling water network can be employed, where water is cooled either in a cooling tower or cooling exchangers and used to cool process streams. In the refinery, it is often necessary to cool process streams, such as different oil streams, using cooling water. The cooling water network includes cooling towers and heat exchangers. The advantages of a closed cooling water network include a lower water consumption rate and minimum heat pollution at the final discharge.

This closed cooling water network recycles the water used in the process several times, lowering the water consumption rate and minimizing heat pollution at the final discharge. As the water is used multiple times, additives should be introduced to reduce scale formation, corrosion, and bacterial and fungal growth inside the equipment. Now, turning to process operations, desalter operations generate oily wastewater with a high salt content, representing a substantial treatment load. The desalter is employed to reduce the salt content in the crude oil before it proceeds to the atmospheric distillation unit. Crude oil carries water in the form of emulsion, and this water is dissolved with various types of salts. These salts are corrosive in nature, and if the salty water, along with the crude oil, advances to the next stage of processes, it could lead to corrosion issues. Hence, the desalter is positioned before the crude oil enters the atmospheric distillation unit. Desalters produce a significant amount of wastewater containing oil in the form of an oil-water emulsion, along with a high salt content, imposing a substantial treatment load on the effluent treatment plant.

So, the load on the effluent treatment plant can be minimized by directing this water to a break tank. In this intermediate step, the desalter sour water is taken to a break tank where, with the use of a de-emulsifier and sufficient residence time, oil and water are separated through decantation. The salty water and the oil in emulsion form can be efficiently separated using a de-emulsifier within a specified time frame. After separation, the oil is recovered and sent for reprocessing in the refinery, while the water containing salts is directed to the effluent treatment plant, thus reducing the load on the effluent treatment plant.

Now, turning to the effluent treatment process, a typical refinery effluent treatment plant consists of three main stages: primary treatment, secondary treatment, and tertiary treatment. In the primary treatment stage, the focus is on gross oil and solids removal. Refinery effluent, as it emerges from the refinery, contains some amount of oil and solids.

The first stage involves passing the effluent through gravity separators or corrugated plate interceptors, where gravity facilitates the separation of solids, and oil can float on the surface of the wastewater, allowing for efficient removal of these components. Corrugated plate interceptors utilize the principle of gravity separation for the removal of free oil and suspended solids, providing a higher surface area due to the corrugated nature of the plates.

So, passing through these corrugated plate interceptors, the oil is separated and rises to the surface, while the suspended solids come down to the bottom. The free oil is then separated or skimmed off and scraped from the surface of the water. Substantial quantities of sludge can also be collected in these separators as the solids descend to the bottom of the tank. Sludge is thus produced, containing solids as well as some liquid substances and watery substances.

Secondary treatment, as a second-stage treatment, involves the use of air flotation or filtration units for the removal of fine oil droplets from the water. If any oil still remains in the water, it needs to be removed to obtain properly purified water. For this purpose, air flotation or filtration units are employed. Flotation units operate on the principle that oil droplets are carried to the surface by small air bubbles, which attach themselves to the oil globules or suspended particles, floating them to the surface where they are removed for further processing. The process involves bubbling air into the tank, and the air bubbles interact with the oil globules so that they rise to the water's surface. This separation mechanism effectively separates the oil, and suspended particles are detached from the oil globules in this manner.

So, chemicals such as coagulants, acids, and alkalis are often added ahead of the system to promote more complete removal. To enhance this removal, some chemicals such as coagulants, acids, and alkalis are added before starting the flotation process. In the filtration system, the oil is filtered from the aqueous stream using a filter media such as sand or anthracite. Either sand or anthracite coal, very fine particles of anthracite coal, and the sand bed—any one of them or a combination of both—can be used as a filter media to filter out the remaining oil in the water. These media are then backwashed to recover the oil collected there. This primary and secondary treatment has no effect on the soluble contaminants.

Now, coming to tertiary treatment, once the majority of the free oil has been removed, biological treatment is used to remove the water-soluble constituents of the effluent. The biological treatment employs bacteria to degrade pollutants. The process relies on the use of biological activity of various types of bacteria. Once the effluent is discharged into the natural water body, the bacteria already present in the system start to digest these organic pollutants while using the natural oxygen dissolved in the water. For most wastewater, the destruction of organic material takes place under aerobic conditions, in the presence of water, air, or oxygen.

So, this destruction of organic material, which is the digestion of the organic material by the bacteria, takes place under aerobic conditions. For certain concentrated organic waste, anaerobic treatment in the absence of oxygen can be used, although its applicability is relatively limited. Anaerobic bacterial treatment is employed for some specialized cases. The most widely used biological process for industrial wastewater is the activated sludge process. The activated sludge process involves a collection of various types of bacteria for the destruction of organic pollutants.

In the activated sludge process, the sludge consists of a mixed blend of microorganisms, 95 percent of which are a variety of mostly aerobic species of bacteria. This process operates in an aeration tank where the effluent is introduced, and air or oxygen is bubbled through the tank. A large amount of bacteria, known as activated sludge, is added to the system to digest the contaminants using the supplied oxygen. This process results in the production of purified water. The wastes and bacteria are held in contact long enough to stabilize the organic material and achieve the desired effluent quality, which is purified effluent water. Now, coming to the control of solid wastes, we have discussed gaseous emissions, and we have discussed wastewater treatment.

Now, coming to the control of solid waste, solid wastes have no further primary use. So, waste is defined as any solid or semi-solid material that remains as an unwanted byproduct of refining, which is not required at all and disturbs the system; that is the waste which has to be disposed of. Segregation of different waste is the first priority, segregating bigger solid particles from the smaller ones is the segregation method. The most cost-effective way to minimize waste is to control it at the source. It is often said that control at the source is the most important, most cost-effective method because sometimes waste may contain some valuable raw materials, valuable intermediates, or products.

Since some waste generation is unavoidable, we cannot escape generating waste. So, treatment of wastes, particularly sludges, is required to minimize the quantity before final disposal; as much as possible, the final disposal of waste should be minimized. Some of the most common techniques used by refineries are to dewater or deoil sludges. The sludge, which contains water as well as oil, first requires dewatering so that the water can be separated from the solid waste or deoiled, and oil can be separated from the solid waste to decrease its quantity and recover oil from them. Oil is an important, valuable material.

To recover the oil from sludge, dewatering processes such as gravity thickening, filtration, centrifuging, and drying by heating are employed. The resulting waste is usually an easily handled solid with low leachability. The waste that is disposed of into the atmosphere should have low leachability, and no pollutants should get leached into the soil. This should be carefully handled.

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