Course Name: Industrial Wastewater Treatment

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Week – 10

Lecture 50: Treatment of wastewater produced from Refineries and Iron & Steel (Coke Ovens)

So, welcome you all. Today I am going to deliver lecture 5 of module 10 which is on treatment of wastewater produced from refineries from iron and steel industries especially the coke ovens and the coal washy wastewater. So, under this we are going to cover about the basic operations that undergoes in the refinery industries where crude oil is processed for production of gasoline, diesel and many other byproducts along with the flow diagram of these processes. Then we will also discuss about the fractional distillation process which are used for separating various byproducts from the crude oil. Then we will be looking about the major waste steams which are generated from the refinery industry along with the characteristics of the wastewater generated from different sources. And then we will be looking finally on the treatment process which are used in the refinery industries for the management of wastewater produced from different sources.

So this if we see about the refineries so as of now there are 23 oil refineries all over India with a total refining capacity of around 250 metric million ton per annum and if we see most of these refineries they are basically located near to the sea shores, like if we see in this diagram these are the refineries most of the refineries like these refineries they are basically located onto the sea shores, while the new ones they are also coming up and located far away from the sea shores. The production refining and the conversion of crude oil to the useful chemicals that are associated with the direct and indirect release of the wastewater and many other pollutants that goes into the environment and can have adverse impacts. So those wastewaters, that pollutants we have to collect characterize and then accordingly we have to plan for their treatment so as to avoid any adverse impact onto the environment.

So let us see what are the basic raw materials which are used in the refinery industries. So, if we see that is the crude oil which is the major raw material which is basically the complex mixture of hydrocarbons of varying molecular weight and structure and from this crude oil we try to recover out these many byproducts like LPG, gasoline, diesel, kerosene, oil and then we have lubricating oil, asphalt, bitumen, coke so many other byproducts they are generated during the refining of the crude oil which is obtained as a raw material in this industry.

So let us talk about what are the basic operations through which the crude oil is processed so this is the first operation that we say that is the topping. In this process the crude oil is subjected to the fractional distillation to obtain the raw products including raw gasoline, naphtha, which is basically the flammable oil, gas oil and the fuel oil. So, this operation basically comprises of fractional distillation of crude oil when heated the mixtures of different hydrocarbon having

different boiling points they are vaporized at different temperature and then they are collected separately. So, there are number of byproducts they will be separated from the crude oil and then these byproducts like which are having high molecular weight and high boiling points they are further goes for the cracking process, so this cracking process again if we see that is two types of cracking process that is thermal cracking process and the catalytic cracking process. So, this thermal cracking process basically that is done at a very high temperature and pressure. So, this process basically is used for thermal cracking of the high molecular weight of hydrocarbons which may yield into naphtha, gas oils and other byproducts like solid residue, which we say that is the coke. So, these are the process where thermochemically the hydrocarbons they are separated into lighter products and like this gas oils, naphtha and coke they are produced out of this cracking process. So later on, it was perceived that thermal cracking process requires very high temperature pressure and also a lot of residence time for cracking. So, to reduce this residence time for cracking and this catalytic cracking has been initiated. So, this process is carried out like the similar process of separation of lighter fractions of the hydrocarbon from the higher molecular weight of hydrocarbons. So, that is done catalytically in presence of the catalyst where this high molecular weight of hydrocarbons they are decomposed like into gas oils and the fuel oil. So, in catalytic cracking process like the decomposition of high boiling petrol distillates like gas oils and fuel oils they are converted into the lighter products like gasoline, so these are basically the major products which are formed after this catalytic cracking process. So, this reduces the overall temperature and the requirement of high pressure and residence time so this process again it is used for producing the gasoline. And then there is a process called catalytic reforming that is also carried out for transformation of naphtha into high octane gasolines. So, these are the basic process which are carried out where the crude oil is processed using various refining operations and a number of byproducts including LPG, gasolines, diesel, naphtha, kerosene oils, gas oils, fuel oil they all are generated as a byproduct and they are purified and then they are sold in the market.

So, this is basically the process diagram of the crude oil to final products. So, here if we see that is the crude oil that is the raw material which goes in a distillation process where the fractional distillation of this crude oil is carried out so as this crude oil contains the mixture of various hydrocarbons having different boiling points. So, they are fractionated at different temperatures so first of all this liquid petroleum gas that LPG is generated, then naphtha is generated kerosene is generated then aviation turbine fuels they are generated out of this fractional destination and then finally the diesel oil and the residual fuels they are generated and then these byproducts they go for secondary process where catalytic cracking and reforming is done. So as to further refine these products from rod to final product form so this is done using catalytic cracking process thermal cracking process and then catalytic reforming process. So many other processes nowadays are so they are developed to produce the desired product specification as a product we are able to generate the LPG, gasoline, diesel oils, lubricating oils, bitumen, coke, asphalt and many other products which are sold by these industries.

So, this is basically the flow diagram of the basic refinery process. So, if we see this is the crude oil so this first of all this crude oil goes for this topping operation, this is also called as the skimming process where this fractional distillation of the crude oil takes place and as a result of this fractional distillation if we see there are production of state-run products like this you can see

these are the products like gasoline, naphtha, kerosene diesel and then burner fuel oils they are generated out of this fractional distillation process and the heavy molecular weight of hydrocarbons which and does not undergo this fractional distillation. So, that is taken out that is what we call a topped crude oil and then this goes for further cracking process. So, here if we see this is the thermal cracking process and here this goes for vacuum distillation process, so in the vacuum distillation process whatever the topped crude oil that is basically again heated under vacuum distillation process under vacuum they are the gas oils, lube stocks they are separated from this topped crude oil and here from the bottom the solid residue which is obtained from this operation that is collected separately here from the bottom and then if we see this gas oils and this lubricant oils they goes to the catalytic cracking process along with the light oil which are generated out of this topping that are also mixed here in a catalytic cracking and then this entire hydrocarbon, mixture of hydrocarbon again goes for this catalytic cracking under the presence of catalyst. This hydrocarbon further they are decomposed into the lighter fractions of hydrocarbon as a result this LPG that will be generated here and then here this gasoline will be generated and finally this will generate the distillate which does not undergoes this catalytic cracking. So, again this is a recycled back for this thermal cracking process and this LPG whatever is generated here that is again goes for polymerization where this gets converted into high octane gasolines and as a product, we will also be generating the fuel and liquefied gases after this polymerization process so this is like the products from polymerization process. And again, if we see if this top oil/crude oil goes for this thermal cracking process and this distillate which is coming out after this catalytic cracking process that is mixed together in a thermal cracking process and then it basically generates the gasoline as a byproduct. So, convert this hydrocarbon into gasoline and then if we see the total operation, so this is finally catalytic reforming of this distillate the distillates which are obtained from fractional distillation, so that basically also produce this high-octane gasoline process. So, these are basically the products are this side and this is the single crude oil that is the raw material which is used and from this raw material when it undergoes through different process of refining like fractional distillation, cracking, thermal cracking, vacuum distillation, catalytic cracking and then catalytic refining process. So, at the end we are able to generate the LPG which is the liquid petroleum gas and then we are able to generate the gasoline including the high octane gasolines then we are also able to generate the diesels, then we are also having the lubricant oils and the waxes they are basically generated from this de-waxing process that is carried out of this lubricant stocks, so and then finally the residue materials like coke, bitumen, asphalt they will be also generated. So, this is like the overall process diagram which are used in the basic refinery industries to produce different types of petroleum products from the crude oils.

So then let us talk about the what is the total water demand and how much water that is generated. So, if we see the water demand that is basically three-meter cube per ton of the petroleum products that is process this is the US, EPA that is the Environmental Protection Agency. So, out of this if we see the overall consumption of this total water which is required in refining process so we can see that most of the water more than 56 % that is used in the cooling operations rest 16 % that goes into the boiler section, where this is used in the cooling water and then this is around 19 % of the water that goes into the production process and used as a process water and rest 9 % that goes into auxiliary operations used in the cleaning and washing of the

reactors and the area so this is like the total water consumption that takes place in a refinery industries and as a result of this utilization. So, there are various waste streams they are generated like cooling water then it will generate the process water it will also generate a lot of surface runoff along with the industrial wastewater, so it will also have sanitary wastewater so these all-different types of waste streams they are generated and if we see this refining process mostly generates wastewater in the tune of 0.4 to 1.6 m^3/m^3 of crude oil processed.

Then let us talk about the various waste streams which are generated from the refinery operations. So, these are basically the waste streams if we see that is desalted water, so this water basically that is produced from the washing of the raw crude oil prior to it goes for topping operation and then there is a sour water so this is the wastewater produced from the stripping process, steam stripping and fractionation operations where it comes in contact with the crude. And then if we see another type of wastewater what we say that is the process water which is used for the product washing catalyst regeneration and dehydrogenation process. So, this is the process water and then if we see there are also the waste stream which we say that is the spent caustic which is formed in the extraction of acidic compounds from the productive streams and then if we see there are tank bottoms. So, they are basically the bottom sediments and the water which settles to the bottom of the tank and they are collected periodically and removed from the bottoms and then if we see there are cooling water that is basically the cooling water blow down that will be generated as a waste water which is this water is used to prevent basically the buildup of the dissolved solids in the closed loop cooling system. And then if we see like this condensate blow down that is also generated in the boiling and steam generation process and again this is used for maintaining dissolved solid levels in the closed loop cooling system. And then there are storm water so this is basically the surface runoff which is generated after the precipitation from the process area and non-process area as a storm runoff and then if we see these are another terminology that is used for the waste water which is generated mostly from the product tankers and is termed as ballast water.

So before going into these various waste streams and their treatment let us talk about the characteristic of the waste water which are produced from oil refineries waste so here if we see that is the refinery waste and these are the characteristics and all the values if we see here that is given in milligram per liter. So, if we see mostly this basically this type of waste water which is generated from refinery industry that mostly contains oil and grease having a lot of free oil content up from 2000 to 3000 mg/L and then there are also another form of oil which get emulsified with the water and its concentration if we see that also ranges from 90 to 120 mg/L then it will have also the H_2S and other sulfur compounds which are generated during this distillation process. So, their concentration that varies from 10 to 220 mg/L then it also have some phenolic compounds to the tune of 12 to 30 mg/L then if we see in terms of BOD_5 days at 20 °C. So, this also contains the organic matter to the tune of 100 to 300 mg/L and then in terms of suspended solids also this is 200 to 400 mg/L. So, overall if we see the characteristic of the refinery wastewater.

So, we can see most of the major impurity that is basically the oil and grease this has to be removed from the waste water before it goes for secondary treatment process. So, there are a lot of geochemical process which are used for removal of these oils and then there are biological

treatment process like activated process which are used for removal of these suspended solids and organic matter present in the oil refineries so if we see the talk about the treatment. So, as I said there are physiochemical treatment, physical treatment, chemical treatment and then biological treatment. So, physical treatment mostly targets for separation of the free oil which is present in the tune of 2000 to 3000 mg/L. So, this is basically done by gravity separation methods using this gravity separators or we have dissolved air flotation systems and then specially designed oil separators that is referred to as American petroleum institute (API) type of oil and grease separators that are used. And then in chemical process if we see they are coagulation process flocculation process, where this coagulants are added with emulsified oils to break their emulsions so this consists of coagulation flocculation and sedimentation unit operation to remove this emulsified oil and other suspended impurities present into this wastewater and then in the biological treatment process basically this aims for removal of the organic matter, BOD, phenols and other toxic compounds which are present in the refinery wastewater and this is done basically by biological treatment system where this stabilization ponds, aerated lagoon, oxidation ditch, tickling filter, activated sludge process, these are mostly the aerobic treatment process because the BOD-COD that is not very high, so this aerobic treatment system are mostly preferred for the treatment of this refinery wastewater.

So, this is basically the wastewater treatment schemes which are the conventional system which are used in the refinery industries for the treatment of their wastewater. So, here if we see whatever the wastewater generated from desalter and stripping operations and then spent caustic operation then contaminated process wastewater contaminated process runoff, cooling tower blow down they all together they are mixed and this mixed stream is taken here to the first unit operations as I said that is the API separators which basically uses the oil and grease separators where this oil is required as a slop oil and then the sludge whatever is generated at the bottom which contains mostly the inorganic impurities they are separated and then disposed-off. So, next after this all free oils they are removed then it goes for equalization tanks so this equalization tank is basically for equalizing the flow and equalizing the strength of wastewater to avoid the shock loads during the excess flow conditions. So, this is again for this a separate facility is provided to avoid the shock loading during excess flow conditions so excess flow condition most the wastewater the when it comes in excess than the average flow so they are sent to this shock load divergent tanks and during the lean flow the wastewater from this shock load divergent tank diverted to this to the average flow, so as to meet the constant flow to the downstream process. In the downstream process if we see that is the DNF process, that is dissolved nitrogen flotation process. So, here then the nitrogen is purged into the wastewater which breaks out the emulsified oils and then these oils they float onto the surface and from there they are removed from rest of the wastewater and then it goes for biological treatment process and this biological treatment process they require also some nutrients, so here this nutrients like phosphorus and nitrogen they are added before it goes for aerobic treatment process, so this proper a C:N:P ratio is to be maintained before the wastewater goes for this aerobic biological treatment system and in this system this entire wastewater that is aerated and during this process whatever this organic matter they are present in the wastewater that undergoes aerobic decomposition and finally this organic matter they are decomposed in the form of carbon dioxide. So, this basically helps the reduction of BOD and COD present in the wastewater and then this activated sludge process has a lot of

sludge yield so it generates a lot of biomass so this biomass that is separated from the tank and then this is stored in the bio sludge storage tank from there this sludge is taken for further treatment process where this sludge is thickened then it is digested and finally this sludge dewatering has to be done out so as to remove whatever the sludge biomass that is generated from the process and finally this separated sludge that contains a lot of nutrients so they can be used as a manual for gardening and agricultural activities. And here after this aerobic treatment process because this is a CSTR system where the sludge they are mixed with the wastewater, so this sludge will be separated and then it will come to the storage tank where this treated wastewater that will be stored here and then following to this there are policing treatment which is carried out through the filter media by passing the wastewater through the filter so here these filters are provided, so as to remove any kind of biomass that left out in the treated effluent and then finally this treated effluent that is taken out for the discharge or recycle within the operations for its reuse.

So, this is American Petroleum Institute (API) based Separator. So, this basically helps in separation of this free oil present in the wastewater. So, here this is the diagram of this separator so this API separators basically consist of this influent well so where this wastewater which is coming out from the plant, so that will be taken into tank and from here it enters into the API separator tanks where through the diffusion valve, so this basically a valve is provided so that inlet wastewater enters into the API tank and in this if we see this API separator consist of a conveyor belt which moves on this pulleys so and these are basically the sludge scrapers or the oil and grease remove scrappers, so they are provided here all over the surface on onto the this conveyor belt, so when they move in a clockwise direction when they move onto the top because of this oil and grease they remain in a floating state so they will float onto the surface and using this scrappers they will be removed out using this pipe skimmers or there are the surface skimmers they are provided where from this the floating oil which is scrapped out by these scrapper blades so they reaches onto the surface skimmers or to the pipe skimmers provided in the API separators from where these free oils they are taken out and when this moves down and then again it moves at the bottom so it again takes out all the free oil and grease materials present in the wastewater and separates it from rest of the water and the comparatively clarified water that goes here and then this is basically the divider wall or the underflow baffles which are provided for treated water to go in this way from here these are the overflow vias they are provided from here they are the clarified water that is taken out of the separators so this clarified water that will be separated out and from the free oil and grease materials which are present in the wastewater and this free oil and grease which are scrapped out from the top they are taken and collected and then finally the sludge which is generated oil and grease sludge that is to be treated as a hazardous waste and this hazardous waste has to be disposed as per the guidelines. And from the bottom here if we see in the influent well whatever the solid impurities which are present in the wastewater, they used to get settled down at the bottom so this sludge outlet pipes are provided here from where this the inorganic sludge containing oil and grease that will be separated mixed with that mix and will be disposed as a hazardous sludge. So, these are the schematic diagram and the process that are used for removal of free oil and grease materials present in the refinery wastewater using these API separators.

So, these are basically the references that one can refer for more details on to the process and the wastewater treatment system.

Thank you