WASTE WATER TREATMENT

REFINERIES
Introduction
REFINING PROCESS

Crude oil → Fractionation units

- Liquefied petroleum gas
- Naphtha
- Kerosene
- Aviation turbine fuel
- Diesel oil
- Residual fuel

Secondary process
- Catalytic cracking and reforming
- Thermal cracking
- Others

Desired product specifications
- Feedstocks
- Lubricating oils
- Bitumens
- Coke
Petroleum industry, have had considerable role in generation and release of waste materials into the environment.

A variety of waste products are produced in refineries in gaseous, liquid and solid phases, which must be treated and disposed in an environmentally friendly manner.

Production, refining and conversion of crude oil to useful chemicals are associated with direct or indirect release of waste materials and pollutants into the environment.

Water consumption in oil refineries is huge and so is the wastewater generation.
Crude oil contains small amount of water soluble compounds, but **Water and hydrocarbons** are basically **immiscible** which makes wastewater treatment operations a challenge.

Oil refineries are under immense pressure to comply with the new rules and regulations related to environment protection and operation safety.

Despite **regular generation of wastes**, there are inevitable release of pollutants in refineries due to malfunctioning of the units, **pump leakage, erosion, corrosion, pipeline failure**, etc.
- These contaminants are highly mobile and can easily travel distances by different mechanisms through air, soil and underground water.

- Contamination may be in the form of free phase product (e.g. liquid or vapor), dissolved products, or emulsified phase.

- On the other hand physical, chemical properties of water and soil will be affected, which results in shifting ecological equilibrium in damaged areas.
Ultimate fate of refinery wastes

- The primary processes determining the fate of waste materials in an oil refinery may be summarized as:
  - Dispersion in air and water
  - Dissolution in water
  - Emulsification
  - Sedimentation
  - Adsorption/absorption
  - Spreading

- The waste materials may undergo some of these processes simultaneously.
TYPE OF WASTES
Utility wastes

- Refineries usually own their own power plant to be independent of the grid, which generates gaseous emissions and ash.

- Refineries also need high pressure steam for different operations. **Steam production** also generate waste gaseous stream in boiler house.

- Cooling towers, heat exchangers and activities associated with cleaning and maintenance also generate mostly **dilute aqueous waste** streams.

- These wastes are **usually non-toxic**.
Processing wastes

- Desalting process waste: Depending on the crude oil, the wastewater stream may contain chlorides, sulfides, bicarbonates, ammonia, hydrocarbons, phenol, and suspended solids.

- Some dissolved gases such as hydrogen sulfide, ammonia, and volatile hydrocarbons may be desorbed during the desalting process depending on the type of crude oil.
Hydro-cracking wastes

- Addition of water, which partially absorbs ammonia and H2S from the reactor effluent is the major waste stream in Hydrocracking.

- Absorption of H2S from the hydrogen recycle streams also generates gaseous and liquid waste streams which are small in quantity.

- Spent catalyst and metallic compounds are the solid waste in this process.

- Furnace for feed preheating is a source of toxic gases waste due to low quality fuel usage.
FCC wastes

- Similar to Hydrocracking wastes plus fine catalyst particles discharge from stripping and regenerator.

- Large amount of catalyst are withdrawn as solid wastes from the regenerator.

- Fine catalyst particles from electrostatic separator.

- Recent advances in FCC technology have resulted in energy saving and thus less gaseous and solid waste generation.
Coking wastes

- **Furnace** stack gaseous emissions including Sox, Nox and CO and unburned fuel.

- **Thick slurry** containing water and coke and water soluble hydrocarbons,

- **Coke dust and hydrocarbons**

- **Fugitive emissions**
Alkylation and polymerization wastes

- Waste acidic solution containing acid, sulfated compounds and dissolved hydrocarbons

- **Sludge** from product neutralization (sodium hydroxide scrubber).

- Gaseous emissions from the reactor or settling tank (mostly light hydrocarbons)

- Emissions associated with heater and refrigeration units.
Catalytic reforming wastes

- Toxic volatile aromatic chemicals which are formed during catalytic reforming process.

- Fugitive emission of these highly volatile compounds during the reforming process, and the volatile components of the feed are the major source of their release into the environment.

- Due to Catalyst attrition, some particulate matter and dust can be generated during the reforming process.

- Small amount of liquid waste is produced in the scrubber.
Wastewater treatment

- Waste waters from petroleum refining consist of cooling water, process water, storm water, and sanitary sewage water.

- A large portion of water used in petroleum refining is used for cooling (may contain hydrocarbons due to leakage).

- Process wastewater is usually highly contaminated depending on the process.

- Storm water (i.e., surface water runoff) is intermittent and will contain constituents from spills to the surface, leaks in the equipment and any materials that may have collected in drains.

- Runoff surface water also includes water coming from crude and product storage tank roof drains.
Wastewater treatment

- Waste waters are treated in onsite wastewater treatment facilities and then discharged to publicly owned treatment works (POTWs) or discharged to surfaces waters under National Pollution Discharge Elimination System (NPDES) permits.

- It is essential not to mix wastewaters from different processes as it may complicate the treatment process, unless they have similar properties.

- Petroleum refineries typically utilize primary and secondary wastewater treatment.

- Wastewater treatment plants are a significant source of refinery air emissions and solid wastes.
WASTE WATER TREATMENT SCHEME

Combined wastewater from refinery

- Slop Oil Tanks (Two stages) → Oil & Grease
- Mixing
- Oil & Grease Traps (3-4 Hrs. RT) → Oil & Grease
- Equalisation
- Dissolved Air Floatation → Oil & Grease
- Flash mixer
- Primary settling
  - Sludge to SDB
- Septic Tank
- Aeration Tank
  - Return Sludge
  - Excess sludge To SDB
- Secondary Clarifier → Treated wastewater
OIL SKIMMERS

• Pieces of equipment that remove oil floating on the surface of a fluid. In general, oil skimmers work because they are made of materials to which oil is more likely to stick than the fluid it is floating on.

• Pre-treating the fluid with oil skimmers reduces the overall cost of cleaning the liquid.

• All designs depend on the laws of gravity and on surface tension in order to function. The six primary types of oil skimmers are belt, disk, drum or barrel style, mop, large tube or mini tube, and floating suction oil skimmers.
EQUALIZATION TANKS

- They are provided (i) to balance fluctuating flows or concentrations, (ii) to assist self neutralization, or (iii) to even out the effect of a periodic "slug" discharge from a batch process.

Types of Equalization Tanks

- Flow through type - useful in assisting self neutralization. A flow through type tank once filled, gives output equal to input.

- Intermittent flow type - Flow balancing and self-neutralization are both achieved by using two tanks, intermittently one after another.

- Variable inflow/constant discharge type - When flows are large an equalization tank of such a size may have to be provided that inflow can be variable while outflow is at a constant rate.
TRICKLING FILTERS

- Also called trickle filter, trickling biofilter, biological filter and biological trickling filter roughing filters, intermittent filters, packed media bed filters, alternative septic systems, percolating filters, attached growth processes, and fixed film processes.

- Consists of a fixed bed of rocks, lava, coke, gravel, slag, polyurethane foam, peat moss, ceramic, or plastic media over which sewage flows downward and causes a layer of microbial slime (biofilm) to grow, covering the bed of media.

- Aerobic conditions are maintained by splashing, diffusion, and either by forced air flowing through the bed or natural convection of air if the filter medium is porous.
AERATION TANK

• An aeration tank is a place where a liquid is held in order to increase the amount of air within it.
• There are two main methods of aerating liquid: forcing air through the liquid or forcing liquid through the air.
• The water is mixed with biological agents and then aerated. The increased oxygen promotes the growth of the beneficial biological material. That material will consume unwanted waste products held in the water. The beneficial material will grow due to the increased oxygen and food, which makes it easier to filter from the clean water.
LAGOONS

- Sometimes refineries have lagoons or final polishing ponds.

**Types of aerated lagoons or basins**

- Suspension mixed lagoons, where there is sufficient energy provided by the aeration equipment to keep the sludge in suspension. 
  
- Faculative lagoons, where there is insufficient energy provided by the aeration equipment to keep the sludge in suspension and solids settle to the lagoon floor. The biodegradable solids in the settled sludge then degrade anaerobically.
MINIMUM NATIONAL STANDARDS

- The treated water should have the maximum limits of the following

  - **BOD (Biological Oxygen Demand)**
    - 25 mg/l (30 day average)
    - 45 mg/l (7 day average)

  - **TSS (Total Suspended Solids)**
    - 30 mg/l (30 day average)
    - 45 mg/l (7 day average)

- **pH** shall remain between 6.0 and 9.0

- In addition, there shall be no visible solids and/or visible oil or greases in the discharge.
Pollution reduction/prevention in refineries

- There are three options for pollution reduction in a refinery:
  - Reduce or eliminate waste generation at sources
  - Recycling back or use for other purposes
  - Waste Treatment

- Compared to liquid and solid wastes, air emissions are the largest source of untreated wastes released to the environment as they are more difficult to capture.
Pollution reduction/prevention in refineries

- **Segregate** process waste streams

- **Control solids content of water** as solid particles and oil make thick sludges, which adhere to the wall of the treatment units and results in efficiency reduction as well as increase in maintenance cost.

- **Train personnel** to prevent soil contamination

- **Install vapor recovery** for barge loading
Pollution reduction/prevention in refineries

- Install high pressure power washer - Chlorinated solvent vapor degreasers can be replaced with high pressure power washers which do not generate spent solvent hazardous wastes.

- Refurbish or eliminate underground piping - Underground piping can be a source of undetected releases to the soil and groundwater.

- Replace old boilers, It is possible to replace a large number of old boilers with a single new cogeneration plant with emissions controls.
Pollution reduction/prevention in refineries

- Eliminate use of open ponds

- **Remove unnecessary storage tanks** from service - Since storage tanks are one of the largest sources of VOC emissions, a reduction in the number of these tanks can have a significant impact.

- Place secondary seals on storage tanks, especially when volatile compounds are stored (e.g. gasoline)

- Establish leak detection and repair program

- **Install rupture discs and plugs** - Rupture discs on pressure relieve valves and plugs in open ended valves can reduce fugitive emissions.
Pollution reduction/prevention in refineries

- The primary barrier to most pollution reduction projects is cost as many pollution reduction options simply do not pay for themselves.

- The equipment used in the petroleum refining industry are very capital intensive and have very long lifetimes, which reduces the incentive to make process modifications to (expensive) installed equipment that is still useful.

- It is a complicated situation influenced by many factors some of which are out of the control of the industry.
THANK YOU