SWEETENING

PROCESSES

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Introduction

- Alkyl and aromatic Mercaptans are among important sulphuric compounds distributed in petroleum products.
- These Mercaptans cause foul odour and are corrosive towards metals.
- Mercaptans may cause oxidative deterioration as well as inhibit the performance of various aditives in finished products.
- It is necessary to remove them ,either by extraction processes or by converting them into harmless disulphides.

Commercially viable processes

- The processes which remove mercaptans but do not affect materially other sulphur compounds include caustic scrubbing, Merox extraction, Solutizer, Atlantic Unisol.
 - The processes which convert mercaptans to disulphides include Doctor sweetening, PbS sweetening, Merox sweetening, Copper chloride sweetening, inhibitor sweetening.
 - The processes which remove some or all of the different types of sulphur compounds include acid treating, clay treating, sodafining, catalytic processes. Acid treating and clay treating also removes gums, these are also used for cracked gasoline stocks.

Caustic treatment

- Caustic treatment of petroleum products is as old as the industry itself.
- Hydrogen sulphide in low concentration, napthenic acids, aryl mercaptans, alkyl phenol are normally removed by a nonregenerative caustic treatment.
- Naphthenic acids or alkyl phenols are removed by simple one stage caustic wash in a mixer/settler unit, because of their effects on some sweetening catalysts.
- Recovery of the acids for by product sale is a common practice.

Solutizer process

- Caustic washing removes some of the lighter mercaptans, to remove the heavier ones solutizer process is used.
- This process utilizes suitable organic solvents or salt in the aqueous phase with improved solubility of mercaptans.
- The solutizer process can treat most cracked or straight-run napthas to a doctor sweet product below 0.0003 percent mercaptans.
- Octane number and susceptibility show a slight improvement.
- Mercaptan removal gives this process a big advantage on high mercaptan content stocks.

Doctor treating process

- This process was the first treating process to be employed commercially for conversion of mercaptans.
- The operation can be either batch or continuous, regenerative or non-regenerative.
- Sour naptha is mixed with the doctor solution, this doctor solution reacts with mercaptans to form lead mercaptides.
- A stream of lead mercaptides is mixed with the stream of the naptha containing dissolved sulphur. On reacting it gives disulphides and lead sulphides.
- As a disadvantage of this process is the formation of polysulphide which increases the corrosion and reduce the thermal stability.

$$PbO + 2 \text{ NaOH} \longrightarrow Na_2PbO_2 + H_2O$$

$$Sodium$$

$$plumbite$$

$$2RSH + Na_2PbO_2 \longrightarrow (RS)_2Pb + 2 \text{ NaOH}$$

$$Alkyl$$

$$mercaptan$$

$$(RS)_2Pb + S \longrightarrow R_2S_2 + PbS$$

$$PbS + 2 \text{ NaOH} + \frac{1}{2}O_2 \longrightarrow Na_2PbO_2 + S + H_2O$$

Copper chloride sweetening

- This process is used for sweetening of gasolines and kerosines by the direct oxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent.
- There is a net production of water which must be removed continuously to maintain correct reaction conditions.
- There are many advantages of this process like:a. no loss in octane number.
 - b. Product is more responsive.
 - c. Good thermal stabilities

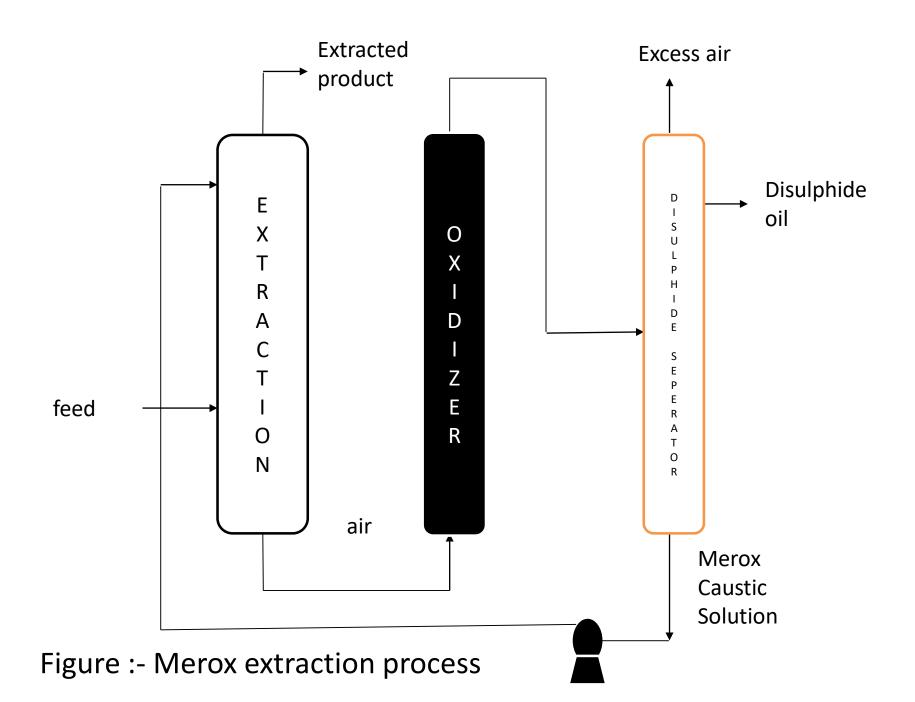
Merox process

- This is an efficient and economical catalytic process developed for the chemical treatment of petroleum distillates to remove mercaptans.
- This process is based on the ability of a catalyst to catalyze the oxidation of mercaptans to disulphides in alkaline medium at ambient temperature using air as the source of oxygen.
- It is used for liquid-phase treating of LPG, napthas , kerosines, jet fuels , diesel fuels and heating oils.

$$2RSH + \frac{1}{2}O_{2} \rightarrow RSSR + H_{2}O$$

MEROX EXTRACTION & SWEETENING

- The merox extraction process are used to extract low molecular weight mercaptans from gases , LPG and light napthas fractions.
- This reduces the total sulphur content in the finished product.
- The merox sweetening process is achieved by blowing caustic/hydrocarbon mixture with the air in the presence of merox catalyst.
- Mercaptans are oxidized into disulphides which remain dissolved in the product. There is no reduction in the total sulphur content of the finished product.



Sulphuric acid treatment

- One of the oldest processes udes for the removal of sulphur, aromatics, olefins. is the sulphuric acids treatment.
- This treatment is usually applied to light petroleum distillates.
- The process is applicable to the pretreatment of straight-run napthas that are to be reformed and for the removal of thiophene from aromatic streams.
- But two major drawbakcs of this process are appreciable material loss resulting from the formation of acid sludge and the problem of sludge disposal.

Clay treatment

- This treatment is generally applied for removal of olefins and diolefins from cracked gas/liquid streams.
- This process improves colour , odour , and oxidation stability of the lubricating oil base stocks and waxes.
- The feed enters at the top of the tower and the treated product leaves from the bottom. While treating lubricating oils and waxes ,the slurry of oil and clay is heated at about 120-150 °C.
- The clay used in the process is generally activated.

Thanks