

Effect of Sodium Salts on Demercaptanization Process

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Abstract- Demercaptanization is an appropriate process for sweetening of LPG. Where, mercaptanic components of LPG are converted to alkyl disulfides. Based on Sulfrex liquid-liquid process and during mercaptans extraction process, some side reactions such as sodium carbonate and sulphate were produced. In order to provide the detailed technical guidance for the industrial operation in LPG sweetening, the effects of carbonate and sulphate salts content on the caustic regeneration and LPG sweetening were studied.

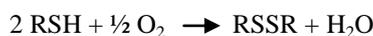
Keywords- carbonate; regeneration; caustic.

I. INTRODUCTION

The SULFREX process used in Propane and Butane sweetening units employs a caustic soda solution to extract the mercaptans from the C3 cut and the C4 cut respectively. After extraction of mercaptans and separation from the organic phase, the exhaust caustic solution streams coming from the two units are collected and fed to caustic regeneration unit, where they are regenerated by a catalytic oxidation using air. The oxidation, with use of a liquid catalyst dispersed in the caustic solution changes the mercaptans to disulphides plus water. Spent air is routed to steam generation unit, while the organic liquid phase, containing disulphides, is separated from the caustic solution and routed to storage. Regenerated caustic solution is split and fed both to the Propane extractor and Butane extractor.

II. PROCESS DESCRIPTION

The Sulfrex process, in all of its applications, is based on the ability of catalyst to accelerate the oxidation of mercaptans into disulfides using atmospheric oxygen:



Due to the presence of the Sulfonated Cobalt Phthalocyanine catalyst, this reaction proceeds quickly at or near ambient temperatures. However, this reaction will only

proceed in alkaline environment. The low molecular weight mercaptans in the LPG cut are very soluble in the caustic solution. When the hydrocarbon and caustic phase are intimately contacted, the mercaptans are absorbed into the caustic solution.

The caustic is then regenerated by bringing it into contact with oxygen and catalyst to oxidize the mercaptans into disulfides.

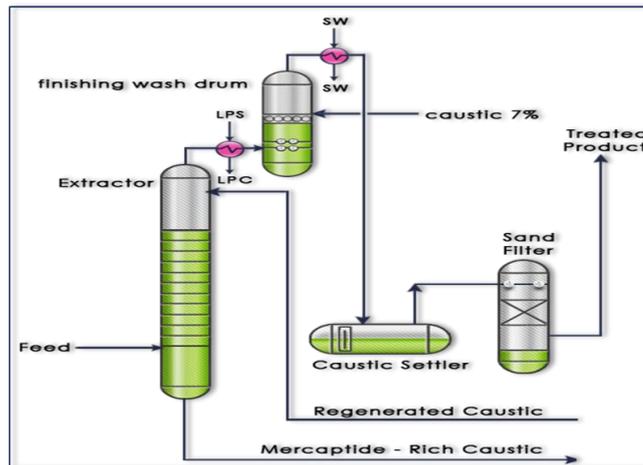


Fig. 1. Process Flow Diagram of Extraction Section

Finally, the disulfides, which are not soluble in the caustic, are separated by gravity in the Disulfides separator. COS, when it is present in LPG cuts, hydrolyses to H₂S and CO₂ during this phase.

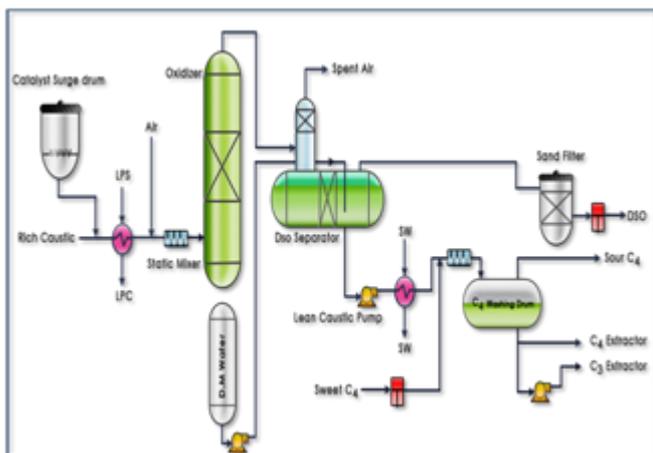


Fig. 2. Process Flow Diagram of Extraction Section

Hydrogen sulfide (H₂S) and Carbonyl sulfide (COS), consume caustic and oxygen and will eventually form sodium salts (Na₂S, Na₂CO₃) which are detrimental to the process.

A. Oxidation

Rich caustic solution containing mercaptides salts coming from C3 extractor is mixed with rich caustic containing mercaptides salts coming from C4 extractor. This rich caustic is routed to the oxidizer heater. This heater is used in order to obtain a temperature of 45 Deg. C at the oxidizer inlet (optimum conditions). Then, the rich caustic solution is mixed with air. The resulting blend (rich caustic + air + catalyst) crosses the Oxidizer static mixer and enters the Oxidizer. The Oxidizer, loaded with packing rings, ensures the homogeneous distribution of the three phases (rich caustic + catalyst + air) requested for the caustic regeneration. The mercaptides RSNa contained in the rich caustic solution are oxidized to disulfides oil (DSO) R-S-S-R by the means of LCPS 30 catalyst dispersed into the caustic solution. The resulting oxidizer top effluent, made of disulfides oil + excess air + lean regenerated caustic, flows to the disulfides separator. Three phases are obtained from the Disulfides separator.

B. Air injection

Oxygen is supplied to the oxidizer from Process Air. The amount of necessary oxygen corresponds to about 0.25 kg per kg of mercaptans sulfur. Air injection to the Oxidizer should be about 180 % of the theoretical requirement to oxidize all the mercaptans. Normally, the oxygen content should range from 8 to 12 vol. % O₂ at Disulfides separator vapor outlet. While a low mercaptans concentration is desirable, the caustic should never be completely regenerated by excessive air rates for the following reasons:

a) In the absence of mercaptans, traces of oxygen can dissolve in the circulating caustic and cause sweetening to occur in the extractors. The disulfides will then return to the LPG phase and increase the product total sulfur content.

b) A small amount of mercaptides in the caustic helps to keep the catalyst dispersed in it. Complete regenerated caustic might result in the catalyst accumulating at the rich disulfide/caustic interface in the Disulfides separator and, therefore, the catalyst will not be circulated.

c) The spent air will have a higher oxygen concentration leading to increased corrosion and potential hazards.

C. Caustic concentration

The caustic concentration for sulfur compound removal from LPG is set between 12 and 15 wt %. The absolute maximum caustic concentration of the circulating solution should not go over significantly 20 wt % (25 °Bé).

Above this level, competition from the hydroxide ions already in solution hinders any increase in mercaptans solubility. Also caustic viscosity at high concentration may affect the contact between LPG and caustic solution in the extractors and caustic entrainment might be accentuated. Emulsification problems may also occur.

Low caustic concentration in extractors (below 12 wt %) is to be avoided as the efficiency of sulfur component extraction will be reduced drastically. When the caustic concentration in the caustic loop reaches 12 wt %, a portion of it is drawn off and replaced with fresh caustic to recover the needed alkalinity.

D. Extraction temperature

Mercaptans extraction is favored by lower temperatures. The lowest practical hydrocarbon feed temperature for extraction is about 20 Deg. C. below this temperature, caustic entrainment may become a problem. Above 45 Deg. C, mercaptans extraction will become increasingly poorer. High temperatures (~ 80 Deg. C) favor COS elimination by caustic solution. Consequently, with regard to the impurities levels presented in the LPG feed and cooling water constraint, an operating temperature of 40 Deg. C has been chosen and should be respected.

E. Caustic regeneration temperature

The oxidizer temperature is set in function of catalyst solution activity and of the mercaptans content in the LPG feed. The caustic regeneration reaction is favored by higher temperatures. The minimum caustic temperature at the oxidizer outlet would normally be 45 Deg. C for LPG treatment.

Occasionally, it may be necessary to increase the oxidizer temperature to 50 Deg. C. However, the Oxidizer temperature should always be run as low as possible while still maintaining the desired degree of mercaptans regeneration.

In any event, 55 Deg. C would be considered as an absolute maximum temperature because of metallurgical considerations (i.e. stress corrosion embrittlement), and also due to the possibility of decomposing disulfide oils to sulfonic acids. Furthermore at this temperature, the catalyst LCPS 30 would start to be decomposed.

III. RESULT AND DISCUSSION

Effect of Sodium Salts on Demercaptanization Process:

The caustic solution can react with non mercaptans acidic compounds in the feed, which will reduce its strength. Two parameters are therefore taken into account in order to adjust the caustic solution strength to the optimum range.

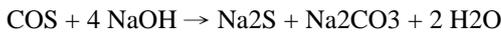
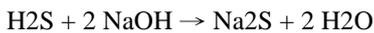
- The total alkalinity will be in the range 180-240g/l.
- The reactive soda (2free alkalinity - Total alkalinity) will be greater than 70g/l.

Therefore,

- If the total alkalinity falls below 180g/l, some caustic is drawn off and fresh 40% caustic added, as described earlier.
- If the total alkalinity rises above 240g/l with the reactive soda greater than 70g/l, then cold condensate is added at the lean caustic circulating pumps suction to reduce the total alkalinity below 240g/l.
- If the reactive soda falls below 70g/l while the total

alkalinity in the range 180- 240g/l, then some caustic is removed from the separator and replaced by caustic, plus cold condensate if necessary, in order to keep the total alkalinity and reactive soda within their required ranges.

As previously described, Hydrogen sulfide (H₂S) and carbon dioxide (CO₂) react with caustic by competing reactions.



These competing reactions create several problems:

- Caustic is irreversibly consumed and must be replaced.
- The production of sodium salts uses 8 times more oxygen than mercaptans oxidation. Thus, inadequate facilities for air injection can become the limiting factor in caustic regeneration, leading to salts build up in regenerated caustic.

The presence of sodium salts in caustic will reduce its power to absorb the mercaptans. As sodium salts

- Accumulate in the process, they will precipitate out of solution and cause plugging problems.

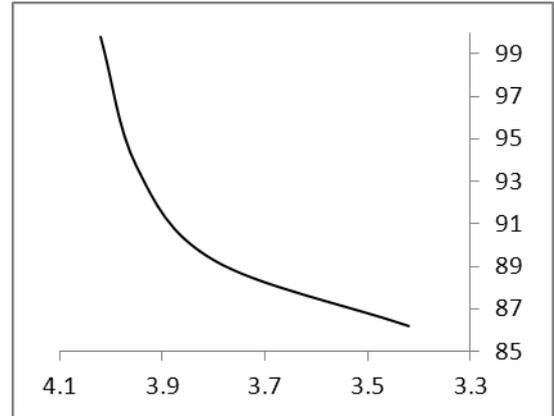


Fig. 3. Relative content of Sodium Mercaptide with Sodium Carbonate concentration in caustic solution (January 2012)

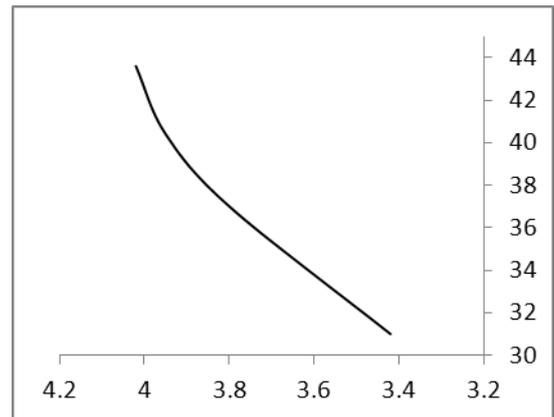


Fig. 4. Relative content of Total Sulphur with Sodium Carbonate concentration in caustic solution (January 2012)

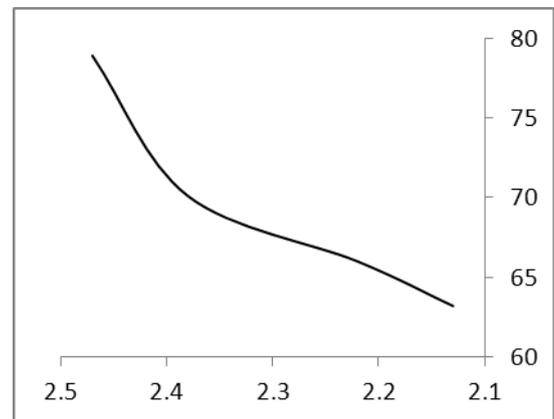


Fig. 5. Relative content of Sodium Mercaptide with Sodium Carbonate concentration in caustic solution (February 2012)

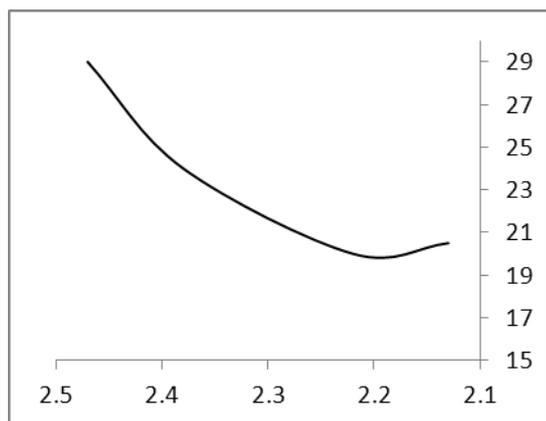


Fig. 6. Relative content of Total Sulphur with Sodium Carbonate concentration in caustic solution (February 2012)

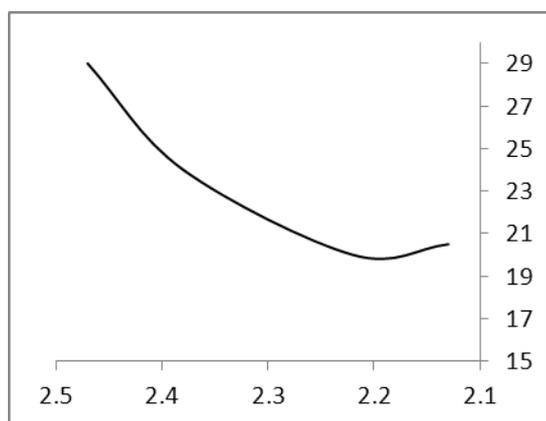


Fig. 7. Relative content of Sodium Mercaptide with Sodium Carbonate concentration in caustic solution (March 2012)

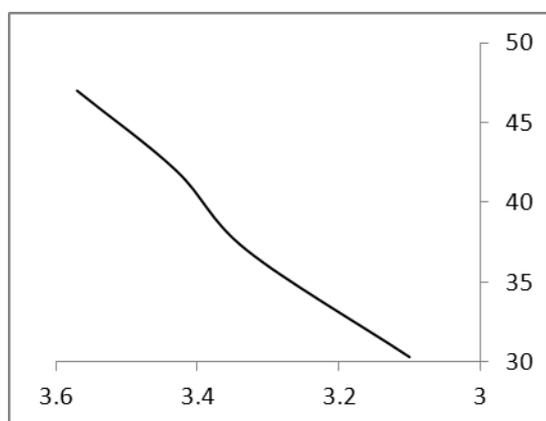


Fig. 8. Relative content of Total Sulphur with Sodium Carbonate concentration in caustic solution (March 2012)

The results from Figures 3-5, express that mercaptans extraction is weaker in the higher concentration of salts, especially sodium carbonate salt. Thus, the presence of sodium salts in caustic solution will reduce its property to adsorbed mercaptans. Also, due to presence salts and its reaction with oxygen during oxidation, some sodium mercaptides remain as unreacted salts in caustic solution and at result, caustic regeneration was not completed. So, according to experimental results, salts contents (Na_2CO_3 and Na_2S) have to be maintained less than about 2.2 wt% in order to prevent above problems and precipitate. On the other hand, the lean regenerated caustic solution should have a mercaptide sulphur content of 30-50 ppm wt. To avoid salt (Na_2CO_3 and Na_2S) increasing in the circulating caustic solution, because they can't be removed by the regeneration procedure, the caustic circuit must be partially purged. Purging is done from disulfides separator bottom on a frequency basis before the fresh caustic make up injection to restore the right concentration of NaOH.

IV. CONCLUSION

Due to the extraction of non-mercaptans acidic compounds (like COS) from the LPG feed, the sodium salts content is becoming higher. So caustic is irreversibly consumed and must be replaced by fresh 40% wt soda. On the other hand, the productions of sodium salts use more oxygen than mercaptans oxidation and reduce absorption of mercaptans. In order to provide the detailed technical guidance for the industrial operation in LPG sweetening, it is recommended that add prewash drum by 7% wt caustic before propane and butane extractors in order to get rid of all COS.

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