

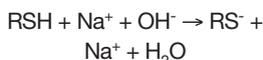
CAPTURE *and* **CONVERT**

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LOOK AT HANDLING
MERCAPTANS IN
HYDROCARBON STREAMS.*

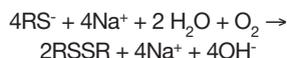
With the development of increasingly difficult hydrocarbon streams, mercaptans emerge as a major nuisance. The removal and conversion of mercaptans is becoming a challenge under the ever increasing restraints on emissions. This article gives a summary of available technologies to capture and convert mercaptans.

Capturing mercaptans in refineries

In refineries, mercaptans can be found in both gaseous streams (fuel gas) and liquid streams (LPG). Raw fuel gas typically contains substantial amounts of H_2S , sometimes some CO_2 , and often organic sulfur compounds such as COS and mercaptans. Usually, the fuel gas is treated with amine based solvents (MEA, DEA, DIPA or MDEA) to remove the H_2S . If the gas does not contain CO_2 (or the CO_2 was absorbed by the amine solvent), the gas can be further processed in a caustic scrubber process such as the Merox process. Here, the mercaptans which are by their nature very weak acids, react with the strong base in the caustic, forming a salt according to the reaction:



The caustic solution containing the mercaptides can be regenerated by contacting it with air. With the aid of the Merox catalyst in the caustic solution, the mercaptides are oxidised and a disulfide oil (DSO) is formed:



The DSO is decanted for further processing. Typically, this stream is routed to the inlet of a hydrotreating process in which the disulfides are hydrogenated to form H_2S and hydrocarbons. The H_2S is subsequently absorbed in the amine system, and further processed in the sulfur plant.

Usually, the removal of CO_2 is not targeted, so the gas from the amine section

can still contain substantial amounts of CO_2 . In that case, the Merox process will be less economical since the CO_2 reacts with the caustic and results in high chemicals consumption. In such a situation, a caustic prewash system is commonly applied to remove the CO_2 before feeding the gas to the Merox system.

For liquid hydrocarbon streams (LPG) a similar strategy is usually applied, with an amine extraction step to remove the H_2S followed by a mercaptan extraction system based on the Merox process. In cases where the LPG contains high levels of

COS, the amine extraction system can be expanded with one or more mixer/settler combinations in order to reduce the COS to low levels and to off load the Merox unit.

Moderate mercaptan removal in natural gas

The process line up that is used to treat gases containing mercaptans depends strongly on the required removal efficiency. If only a moderate degree of removal is required (typically up to 95% removal), a mixed physical/chemical solvent such as Sulfinol or Flexsorb SE can be a good choice. Sulfolane, used as the physical component in these solvents, has a certain affinity for mercaptans and can thus act as an absorbent. The solvent can be tailored by varying the sulfolane content and selecting the amine (Flexsorb for high CO_2 selectivity, MDEA for moderate CO_2 selectivity, DIPA for deep CO_2 removal) to achieve an optimised removal of H_2S , COS, CO_2 as well as mercaptans.

Deep mercaptan removal in natural gas

Sometimes deep removal of mercaptans is required, e.g. in liquefied natural gas (LNG) production, and additional treating steps are needed. For this purpose, molecular sieves are usually the technology

Example of a mercaptans removal route (Figure 1)

For a sour gas containing typically 5% H_2S , 5% CO_2 and 1000 ppm mercaptans, the following process line up is proposed. With a combination of a Sulfinol unit and mole sieves the gas is treated to specification (5 ppm H_2S and 5 ppm organic sulfur).

- *A big main absorber, using Sulfinol, to absorb all the H_2S to sales gas spec (< 5 ppm). With Sulfinol already some 80 - 90 % of the mercaptans will be absorbed.*
- *To remove the remainder of the mercaptans, a mole sieve unit is used. The mole sieves can be regenerated using hot treated gas from the main absorber. The regeneration gas is subsequently cooled and passed through a small side absorber using Sulfinol as well to capture the mercaptans and route them to the regenerator. The treated regeneration gas is routed to upstream the mole sieves, and finally flows with the sales gas.*
- *The loaded Sulfinol solvent from the main absorber is flashed in two stages. In the first stage mainly the absorbed and entrained hydrocarbons are flashed off. After passing through a small recontactor, the hydrocarbons can be used as fuel gas inside the complex, e.g. as fuel gas in the incinerator.*
- *In the second flash stage substantial amounts of CO_2 are released from the solvent. After recontacting with Sulfinol solvent, the CO_2 rich stream can be vented to the incinerator, since it still contains traces of H_2S . As a consequence of this flash stage the ratio H_2S to CO_2 in the rich solvent improves, such that the acid gas to the SRU contains more than 70% H_2S .*
- *Finally, the loaded solvent is routed to a regeneration section, where all the acid components (including mercaptans and COS) are released. This gas is then routed to the sulfur recovery unit (SRU). The lean Sulfinol from the regenerator is cooled and recycled to the absorbers.*
- *The acid gas can be processed in a conventional SRU.*

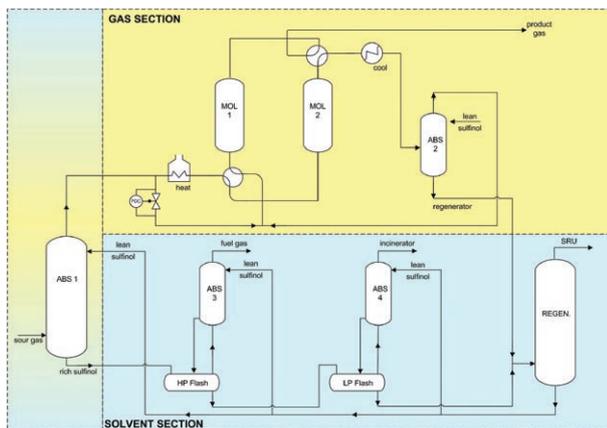


Figure 1. Process line up for mercaptans removal.

to look at. Preferably, the raw gas is pretreated as described earlier to minimise the load on the molecular sieve. Molecular sieves achieve a very low concentration of mercaptans in the treated gas, typically as low as 5 ppmv.

The mole sieve unit is a swing type adsorption process in which the organic sulfur is adsorbed at low temperatures. Once the mole sieve bed is (almost) saturated, it is taken offline and stripped with hot gas from a furnace to release the sulfur species. The resulting small gas stream contains the concentrated organic sulfur compounds. After cooling this gas, the bulk of the sulfur species are absorbed in a small contactor applying the same solvent as in the main contactor. The resulting gas is fed back to the front end of the mole sieve to re-adsorb the remaining mercaptans and will be treated to sales gas specification. The absorbed mercaptans will ultimately be released in the solvent regenerator, from where they are routed along with the acid gas to the sulfur plant. Considering the batchwise nature of the mole sieve process, it is evident that the mercaptans will be released in peaks that can have a very negative effect on the operation of the sulfur plant.

Although mole sieve systems are quite often the technology of choice because of their excellent adsorption characteristics, other regenerative adsorption processes such as the Sorbead process can be used as well, providing an attractive combination of sulfur removal and hydrocarbon/water dewpointing.

An alternative route consists of a physical solvent system followed by a Merox type caustic wash. The solvent (e.g. Selexol) removes the H_2S and CO_2 from raw natural gas to bring it to treated gas specification. It will also remove the bulk of the mercaptans, thereby reducing the size and chemicals consumption of the downstream Merox system. The disulfide oil formed in the Merox oxidiser has to be handled in the gas plant, so cannot be hydrotreated. Therefore it will be combusted separately and thereafter routed to the thermal stage of the sulfur plant as an additional feed.

Converting mercaptans in a rich acid gas

Once the mercaptans are absorbed and released in the regenerator together with H_2S , the resulting acid gas has to be processed further to recover the sulfur. If the acid gas is of a good quality (containing more than 35 % H_2S), it can be processed directly in a Claus type unit. However, if the gas originates from a mole sieve type unit, the mercaptans are released in peaks that substantially influence the performance of the sulfur plant.

Simply relying on the tail gas analyser to handle the peaks is not an advised option, because the disturbances are too large for a feed back system. In those situations, the improved burner control system using a feed forward analyser (known as ABC⁺) is an excellent option.¹ With this system the sulfur plant air demand is calculated as a function of the acid gas composition and flow, resulting in more accurate control and improved sulfur recovery. Also, because of the better control, the downstream part of the sulfur plant will be offloaded, potentially releasing capacity in existing plants. The ABC⁺ control system can be applied to all types of Claus plants, whether it is in a subdewpoint plant, a direct oxidation plant (SUPERCLAUS[®] technology) or a plant with a reducing stage and an amine absorber (such as SCOT type units).

Converting mercaptans in a lean acid gas

Sometimes the H_2S content in the acid gas is too low to process it directly in the thermal stage of a Claus unit. In such cases an additional enrichment step may be required, using a selective solvent like MDEA or Flexsorb. However, this step only concentrates the H_2S and cannot concentrate the mercaptans because they are not absorbed in the aqueous solvent, and neither are most of the CO_2 and the sometimes substantial amounts of benzene, toluene and xylene (BTX). All these components remain in the off gas that is not easy to process. The mercaptans content precludes routing the off gas to an incinerator, since burning the mercaptans would result in excessive SO_2 emissions. Direct processing in a conventional SCOT unit is also not possible: at the relatively high temperatures that are encountered in a conventional SCOT unit, the BTX start to crack, and will soot the catalyst bed in relatively short time.

This is where a low temperature SCOT unit using TG-107 catalyst may fill the gap²: laboratory tests showed that the conversion of mercaptans to H_2S is very high at the typical operating temperatures of the catalyst (below 240 °C). At the same time, the reduced operating temperature strongly suppresses the cracking of BTX, allowing for acceptable run lengths. The off gas containing mercaptans, CO_2 and BTX are directly processed in the LT SCOT reactor. Once the mercaptans are converted to H_2S , this is processed in the SCOT absorber and routed to the front end of the sulfur plant. Calculations show that the overall sulfur recovery for this system, including sulfur in the mercaptans, can be in the range of 99.3 - 99.8%, depending on the CO_2 concentration in the feed to the enrichment unit.

Conclusion

The ever increasing environmental legislation makes the removal of mercaptans more and more important. Various technologies are available in the market to capture mercaptans from gaseous or liquid hydrocarbon streams, and similarly various process routes are available to process the captured mercaptans. The complete processing route has to be evaluated on a case to case basis to determine which combination of technologies best fits an application and is the most cost effective solution. 

References

1. MOLENAAR, G., HENNING, A. and KOBUSSEN, S., 'Next generation SRU control', *Hydrocarbon Engineering*, August 2008.
2. BLOEMENDAL, G., SCHEEL, F., HOETMER, D., 'How low can it go?', *Hydrocarbon Engineering*, May 2008.