

Cost Effective Technology for Organic Sulfur Removal from Refinery Fuel Gas

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Abstract

Presently, sulfur removal from refinery fuel gas is focused primarily on hydrogen sulfide (H₂S). H₂S can be effectively absorbed from gas stream with an amine system and converted to elemental sulfur in a Claus plant. However refinery gas streams, especially those derived from cokers, contain other sulfur compounds such as mercaptans, thiophenes and sulfides which are not effectively treated by an amine system. Praxair has developed a new technology based on a short contact time catalyst that can reliably convert organic sulfur to H₂S which can then removed in a conventional amine treater.

Introduction

Refinery gas fuel has been recognized as one of the two major sources of sulfur emissions from refineries (the other being the Fluid Catalytic Cracking Unit or FCCU). Since refinery gas usually represents the majority of fuel that is used in refinery heaters and boilers any sulfur in refinery gas will convert to SO_x during the combustion process and end up as emissions from the refinery stacks. Refinery gas is amine treated to remove H₂S but refinery gas streams, especially those derived from cokers contain other sulfur compounds such as mercaptans, thiophenes and sulfides which are not effectively treated by an amine system.

Additional processing steps are needed to take out these sulfur compounds. One approach is to add caustic treatment such UOP MEROX process¹ after the amine unit. This solution is effective but can be expensive and generates waste in the form of spent caustic that must be regenerated or treated for disposal.

A second option to address non-H₂S sulfur is the installation of scrubbers to remove SO_x at the combustion emission point. This approach is both logistically complex and cost prohibitive since multiple stack-specific units are needed as opposed to a single centrally located sulfur removal system.

A third option employs a conventional hydrotreater to convert non-H₂S sulfur species to H₂S which is subsequently removed by the amine system. The use of a hydrotreater better integrates with existing refinery operations but has a few shortcomings. For one, a large, expensive reactor is needed due to the low pressure operation, the presence of sulfur species that are difficult to convert to H₂S and low activity of traditional hydrotreater catalysts.

¹ MEROX is a registered trademark of UOP

Furthermore, multiple reactors may be needed to convert diolefins, oxygen and COS (carbonyl sulfide). Conventional hydrotreater technology is using a CoMo or NiMo catalyst and is very effective in natural gas pretreatment technologies for the production of hydrogen in steam methane reformers. Natural gas however contains less than 10 ppm mercaptan and H₂S. In addition plenty of waste heat is available from the hydrogen plant to preheat the natural gas for effective treatment in the hydrotreater. Refinery gas typically has variable olefin content, high content of C₂₊ hydrocarbons and, particularly if derived from coker gas, a high content of non-H₂S sulfur components. High olefins present significant problems for conventional hydrotreater, which operates within a narrow temperature window from about 550 to 750 °F. Olefin hydrogenation reactions are exothermic and each percent of olefins in the feed results in about 40-50 °F temperature rise in the hydrotreater. A refinery stream must contain less than 5% olefins to be fed to a conventional hydrotreater. Higher olefin concentrations can lead to temperatures that can cause catalyst deactivation. In order to control the exotherm the refinery stream must be diluted with some of the treated gas from the hydrotreater which must be cooled and recycled to the feed. This necessitates the use of a high temperature blower or booster compressor. Recycle compressors have been used but they introduce reliability concerns and increase capital and maintenance costs. If the refinery gas contains less than 3% olefins then heat must be supplied from an external source like a fired heater which creates additional complexity, expense and emissions.

Praxair Concept Description

Praxair has developed an alternative solution that retains many of the positive attributes of the conventional hydrotreater but remedies its shortcomings. The Praxair technology can be applied to any type of refinery gas. The key to this concept is the development of a cost effective short contact time reactor (Refinery Gas Processor or RGP). RGP has been developed for conditioning refinery gas to be used as a feed for a steam methane reformer for hydrogen production or a gas turbine for electricity production². As is described below RGP operation can be adapted to convert non-H₂S sulfur to H₂S which can be then efficiently removed in an amine system.

RGP contains a precious metal catalyst that can operate over a wide temperature range to respond to olefin variation (no recycle gas compressor is required). Non-H₂S sulfur conversion occurs optimally around 700 °F but the reactor can operate as high as 1100 °F with no need for feed dilution. No external energy source is required. The energy demand is satisfied with either olefin hydrogenation or addition of oxygen if olefin levels in the refinery gas are low. RGP can operate with high olefin levels and in that case the heat required to convert organic sulfur components to H₂S is easily provided by the olefin hydrogenation reactions. However, if the olefin concentration in the feed is low, some oxygen can be added to the RGP reactor to provide make-up heat. The oxygen can be in the form of pure oxygen or air if dilution of nitrogen is acceptable. The oxygen will react selectively with hydrogen to

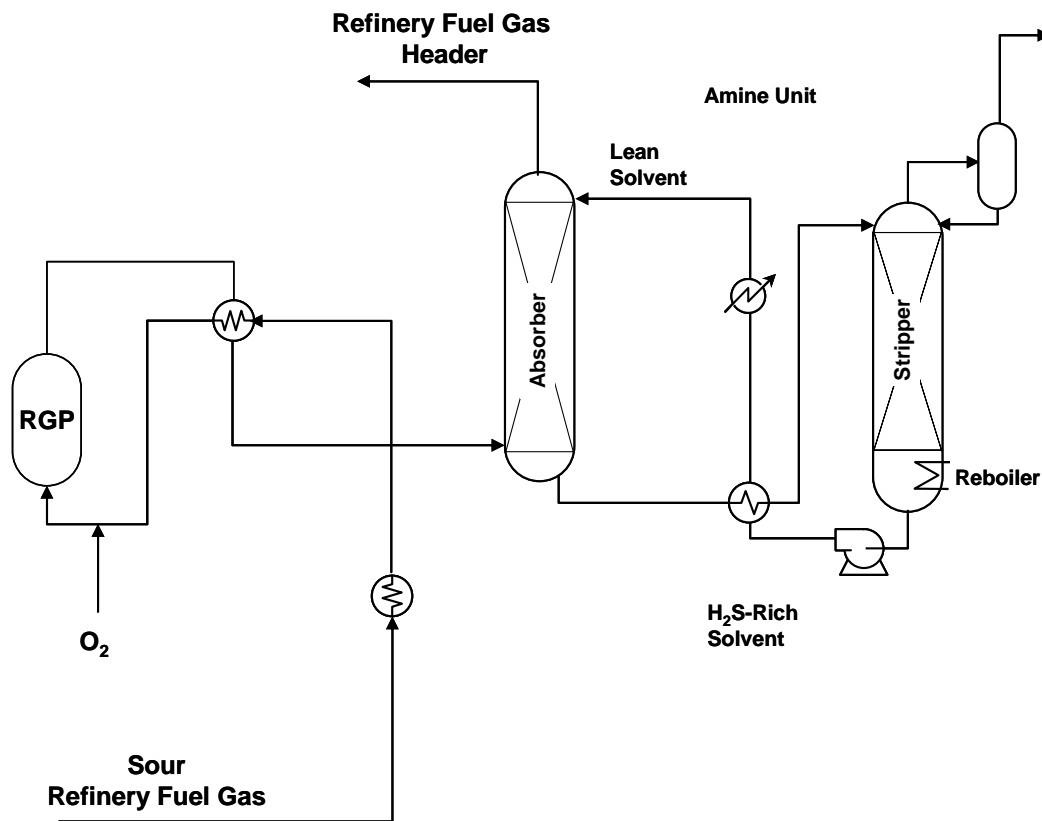
² Ramona Dragomir, Raymond F. Drnevich, Jeffrey Morrow, Vasilis Papavassiliou, Gregory Panuccio, Ramchandra Watwe, TECHNOLOGIES FOR IMPROVED REFINERY GAS UTILIZATION, NPRA 2010 MEETING PHOENIX AZ, AM-10-178.

produce water and heat, which will enable the conversion of organic sulfur to H₂S. No other oxygen side reactions occur.

RGP with or without oxygen can convert all other sulfur species to H₂S which can be then removed by a conventional amine system. A single reactor is used in both operational modes. More importantly the same reactor can operate with variable oxygen addition to respond to changing levels of olefins in the refinery gas and maintain reactor operating temperature in optimum range for sulfur conversion to H₂S. Composition variation is common characteristic of refinery gas that is derived from complex refinery processes and a major attribute of RGP is its ability to respond to composition variation without the need of external heating of recycle compressor.

A simplified process flow diagram with RGP is presented in Figure 1. The refinery gas flows to the RGP unit after removal of bulk sulfur (H₂S). The cold refinery gas feed is heat exchanged with hot reactor product to preheat it to the desired temperature. Oxygen is added as needed. The amount of oxygen required is dependant on the olefin content of the refinery gas. When required, oxygen addition is generally less than 3% of the refinery gas flow on a molar basis; however if olefin content is sufficiently high, no oxygen is added. The cost of the oxygen is an insignificant component of the total removal cost.

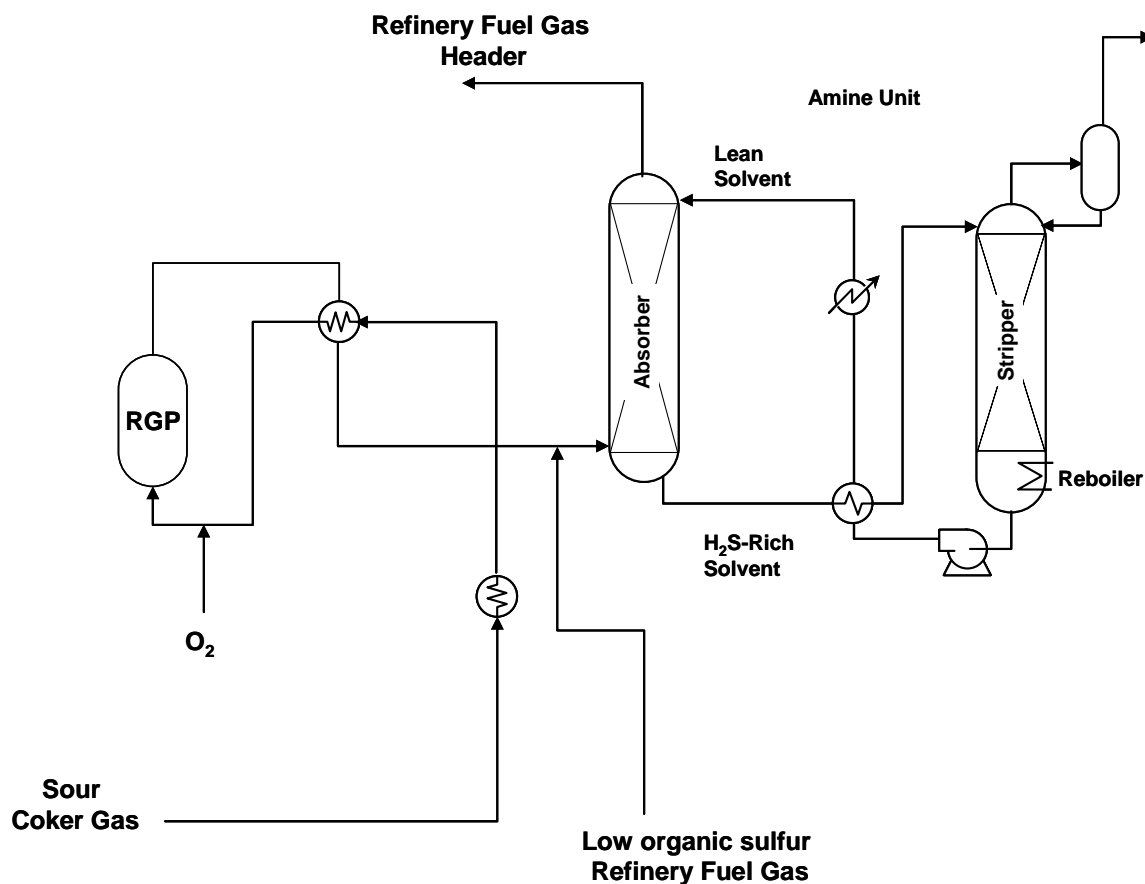
Figure 1. RGP process for organic sulfur removal from refinery fuel gas.



Refinery gas typically contains enough hydrogen to completely hydrogenate olefins, convert organic sulfur to H₂S and react with oxygen. In cases where the feed stream is hydrogen deficient, hydrogen can be added from any convenient source with high hydrogen content such as hydrotreater purge gas or hydrogen plant product.

An alternative process option using RGP is presented in Figure 2, where only the coker gas is treated to convert organic sulfur to H₂S. Since the coker gas is the primary source of organic sulfur, it may be less costly to treat it separately. The balance of the RGP configuration and operation remains substantially the same as in Figure 1. The applicability of this solution will likely depend on whether the coker gas is amine treated to remove H₂S separately from the rest of the refinery gas.

Figure 2. RGP process for organic sulfur removal from coker gas.



Cost competitiveness

Emission control technology for refinery gas can be classified as post-combustion and pre-combustion. Post combustion technologies include dry and wet scrubbers and pre-combustion includes wet scrubbers, conventional hydrotreaters/amine systems and RGP/amine systems. Both pre and post combustion technologies can achieve similar removal efficiencies. Post combustion is unlikely to be cost effective due to the large number and diverse location of refinery process heaters and boilers. Pre-combustion has the additional

benefit that can target the gas stream that contains the majority of organic sulfur which can reduce cost and increase effectiveness. Pre-combustion technologies can be in the form of retrofit of existing amine system by replacing the amine with one that is more selective to organic sulfur or can be in the form of new system such as caustic treatment (MEROX). Cost effectiveness for a caustic system (ISBL) was estimated³ to be \$46,500 per ton SO_x for a system treating 17.3 MMSCFD of coker off-gas containing 85 ppm sulfur (with non-H₂S sulfur compounds 90 percent of the total).

Praxair estimates that RPG/amine cost (ISBL) for a similar stream as the one referenced above is in the range of \$12,000 per ton SO_x (both capital and operating cost). The estimate for RGP assumes that only a new amine contactor will be needed and an existing amine regenerator can be utilized. These numbers should be regarded as guidelines since it is not possible to calculate exact cost without a specific location and refinery gas stream definition. Since amine systems are common to refineries today it is expected that the RGP system will be easier to integrate into refinery operations.

Technology Status

RGP technology is ready for commercial deployment. Praxair has completed a three year test campaign using a sub-scale demonstration unit (RGP alpha) located at a US Gulf Coast refinery treating actual refinery gas. The RGP alpha unit demonstrated greater than 95% conversion of organic sulfur to H₂S for reactor exit temperatures of 650-700 °F. It has operated successfully with olefin levels as high as 17% in the feed. Safe oxygen addition with a mixer designed by Praxair was also demonstrated. Currently, discussions are underway with a refinery to site the first commercial RGP unit for organic sulfur removal.

Figure 3 depicts the composition of the sulfur species during a three-month span of plant operation. The species analysis was done by collecting gas samples in Tedlar bags and analyzing them with gas chromatography within twenty four hours. The analysis was performed by a certified laboratory. From Figure 3 it can be observed that the majority of the sulfur species in RFG were mercaptans. The low level of H₂S is due to the fact that the RFG was already amine treated.

Figure 4 depicts the feed and product olefin composition for a period of two months with significant olefin variations in the feed (4-17%) but with product composition that remained below 1% for the majority of time. Only when the unit was operated with very high propylene in the feed did the exit olefin composition approach 2% at the high reactor exit temperature (1100 °F), where propylene conversion was limited by thermodynamic equilibrium. The ability of RGP to respond to a range of olefin concentrations (typical of refinery gas) with no additional equipment and no effect on performance is a critical advantage of the technology because it permits high on-stream factors and high reliability.

³ ETS, 2008-1. SO_x RECLAIM Study - Final Report – Module 2: Refinery Fuel Gas Treatment and Sulfur Recovery/Tail Gas Units. AEC Engineering Inc./ETS, Inc. April 20, 2009

Figure 3; Refinery fuel gas feed sulfur species analysis from demonstration plant (sulfides include COS)

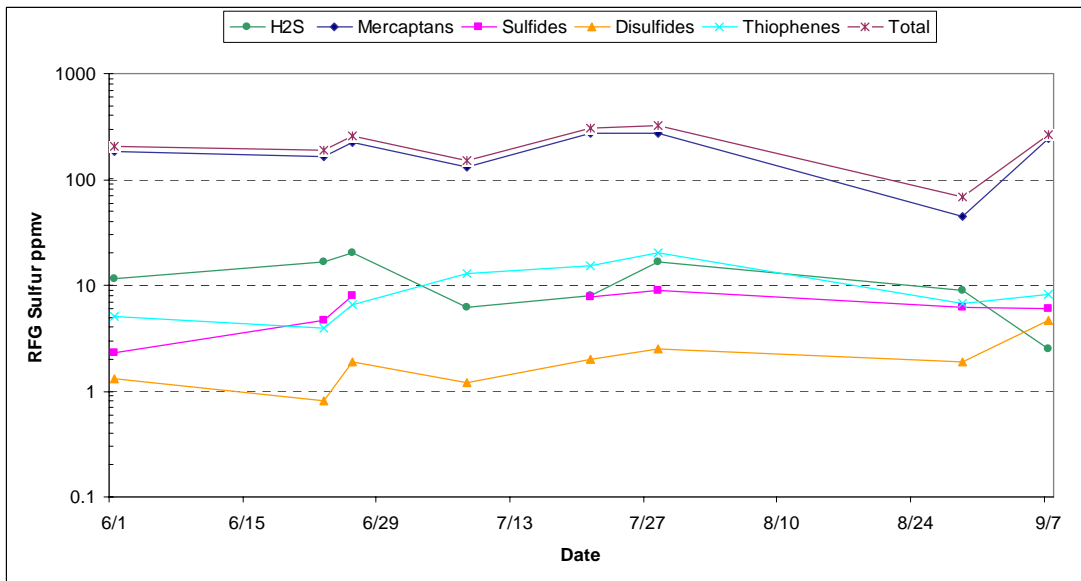
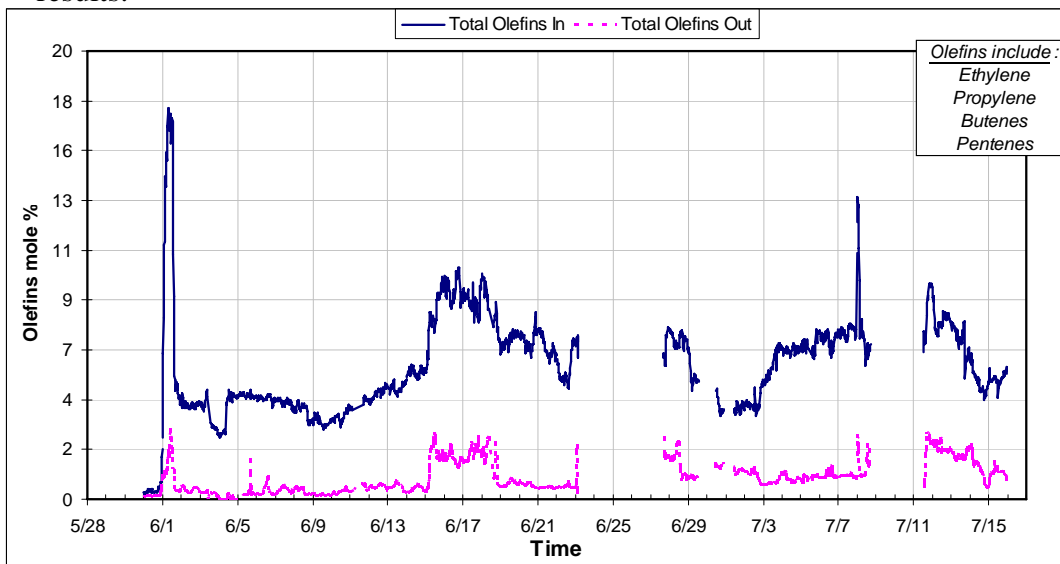


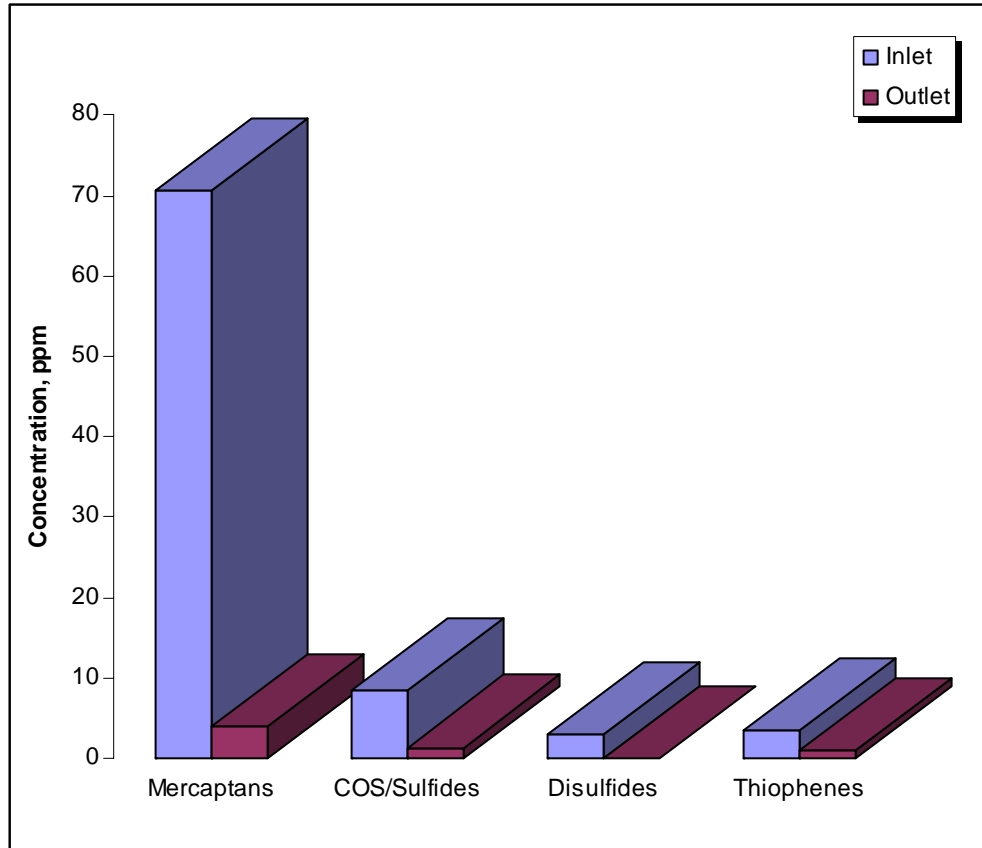
Figure 4: RGP feed and product olefin composition from demonstration plant results.



The refinery gas treated in the pilot plant contained significant amount of sulfur in the refinery gas stream that was not in the form of H₂S. Samples were taken at points before and after the RGP reactor and analyzed by outside laboratory to monitor conversion of mercaptans and other sulfur compounds into H₂S. The results are summarized in Figure 5 where the non-H₂S sulfur species conversion to H₂S is plotted as a function of the average reactor temperature (600-800 °F). In general, organic sulfur conversion increased with increasing reactor temperature and increasing molecular weight for given family of sulfur compounds.

Overall a 90-95% conversion to H₂S was achieved at temperatures above 650 °F. The RGP sulfur conversion performance is more than adequate for refinery gas which contains mostly mercaptans in the non-H₂S sulfur component.

Figure 5: Non H₂S sulfur species conversion to H₂S from demonstration plant results



Conclusions

A new technology (RGP) that can effectively convert organic sulfur to H₂S in refinery fuel gas has been developed by Praxair. Once the sulfur is converted to H₂S it can be removed by conventional amine systems. This technology is flexible in operating with high or low olefin content, generating energy in-situ either by olefin hydrogenation or oxygen/air addition, it can be operated at high or low pressure and can be easily integrated with the rest of refinery operations. The RGP system can be skid mounted for easy delivery and installation.