SOUR GAS CONDENSATE CORROSION OF REFINERY BOILER HEATER TUBES

P. Rostron*, M. W. H. Gawargy

Arts and Sciences Program, The Petroleum Institute, Abu Dhabi, U.A.E. prostron@pi.ac.ae

Abstract

Gas condensate is formed during the production of petroleum gas. Upon cooling the higher molecular weight fractions condense to a liquid. When the gas field is sour (contains H_2S), the gas condensate also contains organic sulfur and dissolved H_2S. The presence of these types of sulfur compounds causes sulfide corrosion in the refinery reboiler heater tubes, occasionally resulting in refinery fires due to penetration of the heater wall. We show in this paper that at low temperatures, dissolved H_2S can come out of solution and attack the steel, and at higher temperatures, the organic sulfur compounds decompose to produce H_2S resulting in a double attack.

Keywords :Hydrogen sulfide, organic sulfur, sour gas condensate

Introduction

At a sour gas production facility in the Gulf region, the daily production rate of gas condensate after separation from the gas is approximately 300K bbl day^{-1}. This condensate is then piped to a refinery facility where it is used as a petrochemicals feedstock. The condensate requires extensive refining via plate distillation tower. Since there is a wide range of mainly hydrocarbons present (greater than 300 different compounds), covering a wide boiling range, the condensate is processed in a two step heating process. Initially, the condensate is heated to 175 °C to separate the lighter fractions in a flash distillation column. The residue is then piped to a second heater circuit and heated to 315 °C before injection into a large plate distillation column for fractional distillation. Both of the heater coils have suffered through wall corrosion failures. The heater tubes are carbon steel with a wall thickness of 8 mm. The same corrosion failure of wall thinning and penetration via formation of iron sulfides was the mode of failure in both cases. The penetration rate was in excess of 4 mm yr^{-1}. In both cases the greatest extent of wall thinning occurred on the high temperature side of the heater coils. Apart from this difference, the corrosion was uniform, with no evidence of pitting, commensurate with iron sulfide formation as the mechanism of corrosion. The same corrosion failure type was unusual since hydrogen sulfide dissolved in the condensate cannot explain the second coil failure. This report is not concerned with the identification of sulfide scaling corrosion, descriptions of which can be found in the literature[1-3].

Investigation

An Agilent model 6890 gas chromatogtaph coupled to Agilent 5973 quadropole mass spectrometer was used to record a fragmentation spectrum for each component of the condensate using carbowax capillary column and a heating rate of 20 ° min^{-1}, Fig 1. This failed to produce a good separation due to the structural similarity of the large number of compounds present in the condensate. Fragment searching for characteristic thiol decomposition products in the mass spectrum did not yield any traces of organic sulfur compounds being present in the condensate.

In order to understand the thermal properties of the condensate, the heating process was modeled in the lab. The condensate was slowly distilled under an inert gas blanket via dry nitrogen supplied at a constant rate. The inert gas was used as a carrier to move any H_2S produced during decomposition to a H_2S detector, whereby the production of H_2S could be followed as a function of temperature. H_2S levels and pot temperature were recorded every minute. This generated two graphs, one showing the evolution of H_2S over time and one showing the evolution of H_2S as a function of temperature. For the time –ppm H_2S graph, the area under the curve, assuming a constant gas flowrate (which was achieved) corresponds to the total amount of H_2S evolved. The temperature- ppm H_2S graph shows the temperature at which H_2S evolution occurs (figure 2).

Discussion of results

The graph in figure 2 shows very clearly there are two distinct evolutions of H_2S. The long time interval between evolutions shows this is not a kinetic difference, but there must be clearly different causative mechanisms for the evolution of the Hydrogen sulfide. It is proposed that the bimodal nature of the H_2S production as a function of temperature can be explained as follows.

The low temperature production of H_2S can be most easily explained as simply physically dissolved H_2S. the fact that there is no clear starting temperature at which evolution occurs, coupled with the broad range of temperatures over which evolution occurs strongly indicates a physical dissolution model. As the condensate is heated, physically dissolved H_2S outgases from solution. When no heating is applied, H_2S can be detected, indicating that the H_2S evolves according to its partial pressure in the gas phase. With sustained carrier gas flow and moderate heating, eventually all of the dissolved H_2S outgases and the concentration of H_2S in the gas phase returns to zero. This out gassing of H_2S is most likely responsible for the sulfide corrosion occurring in the low temperature heater coil. The hydrogen sulfide reacts with the metal in the cool heater column producing iron sulfide. The scaling reaction will consume all available hydrogen sulfide. There is evidence from the operator that dissolved hydrogen sulfide is causing this corrosion as there has been reports of sulfide scaling corrosion in the pipeline leading to the refinery.

The second evolution of hydrogen sulfide is more challenging to explain. There is a clear temperature at which evolution of hydrogen sulfide is observed. The sharp initiation temperature is strongly indicative of the overcoming of an energy barrier, to the evolution of hydrogen sulfide, such as the thermal decomposition of organic sulfur compounds, such as thiols. Thiols are known in the literature to undergo thermal decomposition, resulting in the evolution of hydrogen sulfide[4].

To test this hypothesis, we tried a simple method of sulfur removal in the condensate oil. Both hydrogen sulfide and thiols, being slightly acidic compounds, will dissolve into an alkaline aqueous layer[5]. To test this, samples of the gas condensate were washed with dilute aqueous sodium hydroxide (1.0 M) and the aqueous layer separated. The aqueous layer was acidified with hydrochloric acid and extracted with dichloromethane. The dichloromethane extract was dried over magnesium sulfate and the solvent removed by rotary evaporator. The resulting residue had the characteristic stench of thiols. The extract containing thiols was subject to headspace GC-MS analysis using Shimadzu GC 2010 with QP2010 MS column used was a 30 mSLB 5NS column with temperature profiling from 70°C – 220°C. Headspace is a sampling approach where heat sensitive chemicals are to be investigated[6].

A sample of the extract was added to a sealed bottle and the bottle heated to 70°C. 5.0 mL of the vapour in the bottle was collected and injected directly in to the GC column. In this way, there is no possibility of damaging the column as the sample is gasified and the temperature is low enough that no thermal degradation occurs. After analysis by this method, a range of thiols were identified as being present in the gas condensate, as produced in table 1.

As a final check, the sweetened condensate was subject to the same analysis and during the heating there was no hydrogen sulfide detected. This indicates that the source of the hydrogen sulfide is indeed the gas condensate, and also indicates that an aqueous wash with dilute sodium hydroxide is a viable method to remove both hydrogen sulfide and thiols responsible for thermally produced hydrogen sulfide as well.

The H_2S produced by the thermal decomposition of thiol compounds explains why sulfidation corrosion can occur in the higher temperature boiler tubing. The thiols do not decompose until at least 240 °C. The high temperature boiler is held at 315 °C, whereas the low temperature heater tube, at 175 °C is not hot enough to cause decomposition. In addition, this rapid thermal decomposition of thiols explains why thiols are not present in the chromatogram. In a GC, the sample is preheated to 350 °C in the injection port to volatilize all of the sample. Thermal decomposition of the thiols occurs at this point.

Conclusions

We have been able to demonstrate why both heater coils suffer the same type of corrosive attack. In order to control sulfide corrosion it is important to remove both the dissolved H_2S through a sweetening process, as well as any organic sulfur compounds present which are capable of thermal decomposition to produce H_2S.

There are several advantages to this, firstly, the condensate itself is less corrosive to production facilities, and secondly the fuels produced are extremely low in sulfur, and can therefore be sold at the ultra low sulfur premium price. Desulfurization processes therefore have a double advantage, reducing corrosion in the plant equipment as reducing sulfur emissions from combustion of the resulting fuel.

Acknowledgements

References

1. "A mechanistic model of H₂S corrosion of mild steel", Wei Sun and Srdjan Nesic, paper 07655, NACE Corrosion 2007 Conference and Expo, NACE International, Houston Tx 2007.

2. F. H. MEYER, O. L. RIGGS, R. L. McGLASSON, and J. D. SUDBURY (*1958*) Corrosion Products of Mild Steel In Hydrogen Sulfide Environments. Corrosion: February 1958, Vol. 14, No. 2, pp. 69-75

3. R. L PIEHL (*1960*) Correlation of Corrosion In a Crude Distillation Unit With Chemistry of the Crudes. Corrosion: June 1960, Vol. 16, No. 6, pp. 305t-307t.

4. The Thermal Decomposition of Mercaptans", A. H. Sehon , B. deB. Darwent, *J. Am.Chem. Soc.*, **1954**, *76* (19), pp 4806–4810.

5. SHAKIRULLAH, MOHAMMAD; AHMAD, IMTIAZ; AHMAD, WAQAS y ISHAQ, MOHAMMAD. DESULPHURIZATION STUDY OF PETROLEUM PRODUCTS THROUGH EXTRACTION WITH AQUEOUS IONIC LIQUIDS. *J. Chil. Chem. Soc.* [online]. 2010, vol.55, n.2, pp. 179-183. ISSN 0717-9707

6. Assessment of Thiol Compounds from Garlic by Automated Headspace Derivatized In- Needle-NTD-GC-MS and Derivatized In-Fiber-SPME-GC-MS, Jamie Marcus Warren, Don-Roger Parkinson, and Janusz Pawliszyn, *Journal of Agricultural and Food Chemistry***2013***61* (3), 492-500
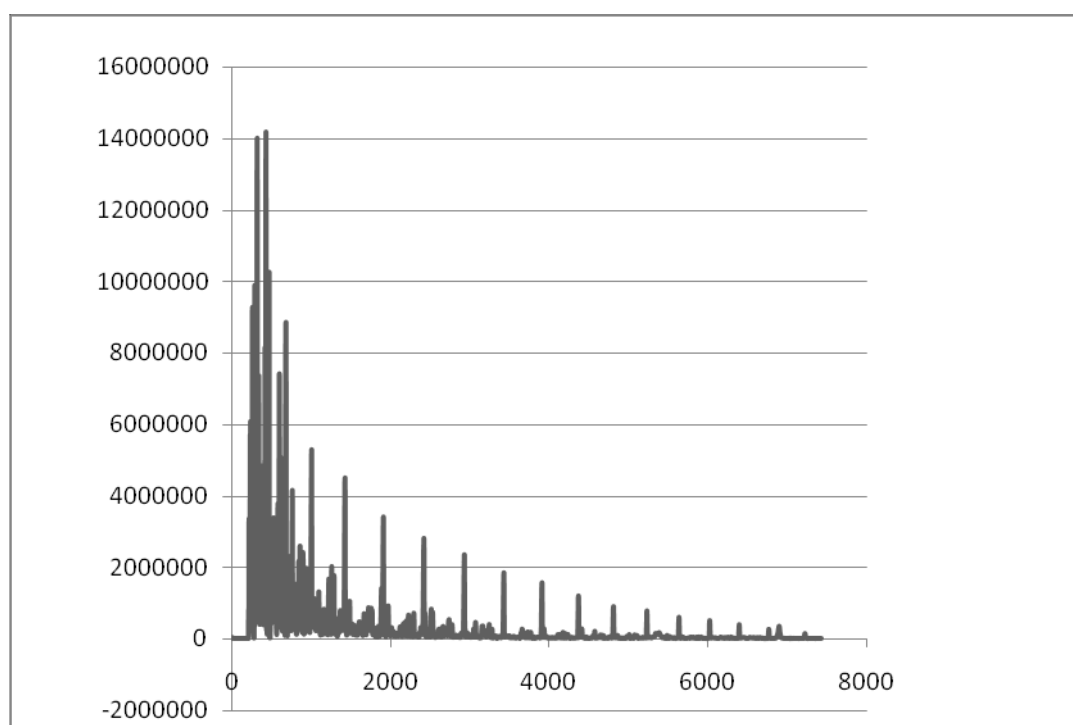
Figure 1: Chromatogram of Condensate
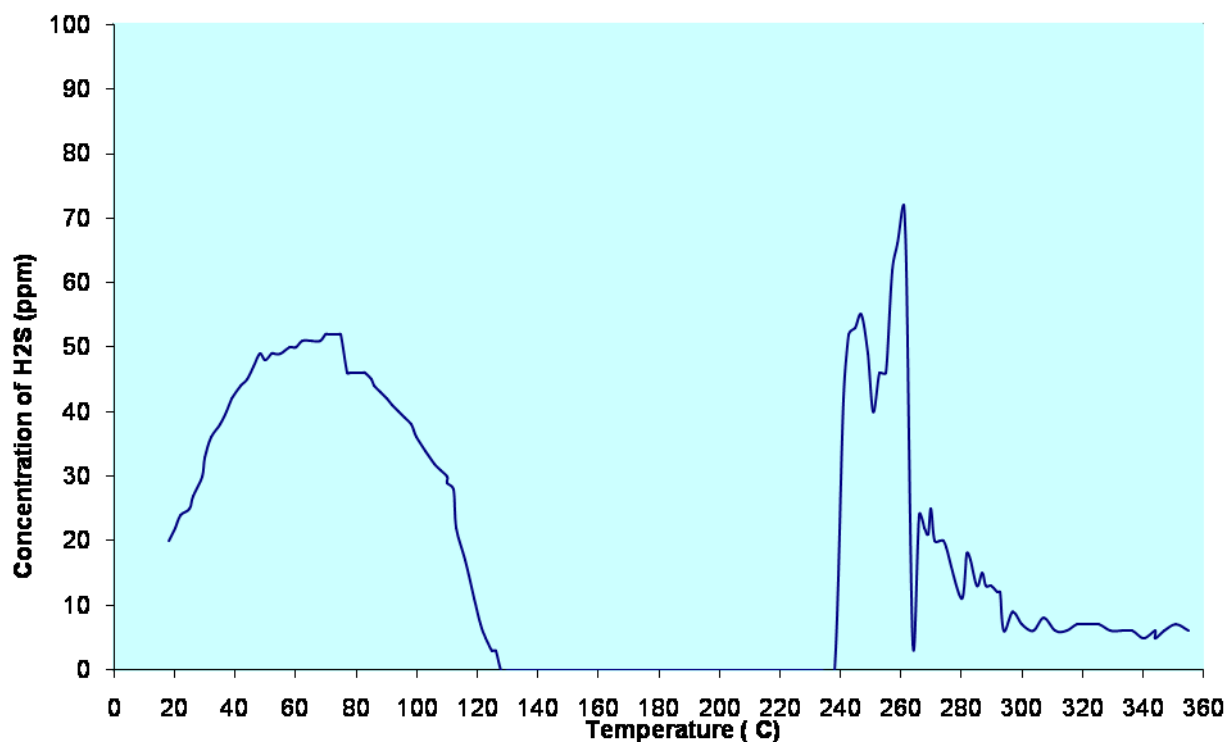
Thermal Decomposition of condensate

Figure 2: Graph showing the evolution of H$_2$S as a function of temperature.

Retention factor	Compound identified
1.725	2-butanethiol
1.763	1-propanethiol
1.870	1-butanethiol
2.063	2-pentanethiol
2.343	1-pentanethiol
2.54	Cyclopentanethiol
2.627	2-hexanethiol
3.287	cyclohexanethiol

Table 1: Thiol compounds identified using Headspace GC-MS