

INTERNATIONAL GAS UNION RESEARCH CONFERENCE 2011

**OPTIMIZING OF MODIFIED CLAUSE SULPHUR PLANT WITH
OBJECTIVE OF MAXIMUM BTX DESTRUCTION AND HIGHER
REACTORS PERFORMANCE**

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ABSTRACT

In this paper experimental and theoretical investigation related to possible solutions for environmental problems faced in sulphur plant of South Pars Gas Complex with BTX (Benzene, toluene, Ethyl Benzene and xylene) has been conducted. The Amine process absorbs heavy hydrocarbons and aromatics from gas stream in addition to the acid components. Whether the acid gas is to be vented or fed to a sulfur plant, it is highly desirable to remove these compounds from the acid gas. The amount of BTX components emitted from most gas processing facilities has become a significant environmental concern. The analysis showed that amine circulation rates and temperature have been a significant effect on limiting overall BTX emissions. Also, in our experimental and simulating data, we focused on acid gas enrichment, fuel gas spiking in reaction furnace and reactor temperature adjustment and indicated that reaction furnace temperature is the most effective parameter for BTX removal. Optimization in fuel gas flow rate and acid gas concentration was done and a new catalyst arrangement and some other operational measurements were suggested in this research. Recovery Efficiency increased from 85.49% to 95.47% and from commercial point of view, catalyst life time and sulphur efficiency (about 10%) increased considerably with no capital equipment cost. From environmental point with modifications, BTX were decreased from 630 to 30 ppm considerably.

TABLE OF CONTENTS

1. Abstract
2. Introduction
3. Experimental equipment and procedure
4. Result and discussions
 - Acid gas enrichment
 - Reaction furnace temperature (Fuel gas spiking)
 - Adjusting reactor temperature
5. Conclusions
6. Acknowledgements
7. References

Paper

1. INTRODUCTION

The acid gas produced by MDEA sweetening units is routed to the Claus unit that was designed with objective of 95% sulphur recovery. The trains are identical parallel three stages Claus sulphur recovery unit. The trains also have capability of bypassing acid gas around the reaction furnace (split flow configuration) in order to maintain higher furnace temperature. The first convertor stage use acid gas auxiliary burner and the second and the third stage use steam reheated. South Pars gas complex (SPGC) and many of Claus sulphur recovery plants with poor acid gas quality suffer poor hydrocarbon (H.C) destruction in the reaction furnace. It is highly desirable to remove these compounds from the acid gas.

The amount of BTX components emitted from most gas processing facilities has become a significant environmental concern. BTX especially benzene is known carcinogen. American Petroleum Institute (API) stated that "it is generally considered that the only absolutely safe concentration for benzene is zero". Aromatic hydrocarbons compounds especially xylene have been identified as the worst offenders in causing severe deactivation of catalyst [1]. High BTX level will also cause a higher air demand, darkened sulphur, plugging of sulphur rundown filter, decreasing SRU capacity and the increasing COS and CS₂ production in the furnace.

Our gas plants process acid gases that range in composition from 29 percent to 36 percent H₂S with several hundred ppmv of BTX. And the result of BTX presence is shorter catalyst life time.

It is obvious that reaction furnace temperature as a most effective parameter for BTX removal. However, the plants with poor acid gas quality suffer form relatively low furnace temperature and BTX destruction.

The modified Claus process is capable of handling acid gas even as low 17 percent H₂S if sufficient preheat of the air and acid gas are provided [2]. By passing acid gas around the reaction furnace will help maintain a higher flame temperature and a stable flame. However it will also lead to bypassing the acid gas contaminants (BTX) in the reaction furnace [3, 4] where there is opportunity to be destroyed if the furnace temperature is high enough. This will result in BTX entering the Claus converter where they will likely cause catalyst deactivations over time. Since the bypassed acid gas does not go through the reaction furnace flame zone, the aromatic components in the bypass are not burned and flow directly to the first converter and undergo a cracking reaction within the catalyst beads. The reaction products of cracking are coke deposits that block active catalyst sites. This reduces the activity for the desired Claus and COS, CS₂ hydrolysis reactions [5].

Many plant operators have been dealing with this issue and have long recognised the need to either remove the aromatic compounds from the acid gas stream or maintain higher furnace temperature. Various methods have been under consideration to increase the reaction furnace: fuel gas spiking, indirect air and acid gas preheating, oxygen enrichment, acid gas enrichment and direct air preheating. In our experimental and simulation data, we focused on three options: acid gas enrichment, fuel gas spiking in reaction furnace and reactor temperature adjustment [6].

This paper presents field studies with SRU modelling (Sulsim#7 simulation) in order to solve this problem.

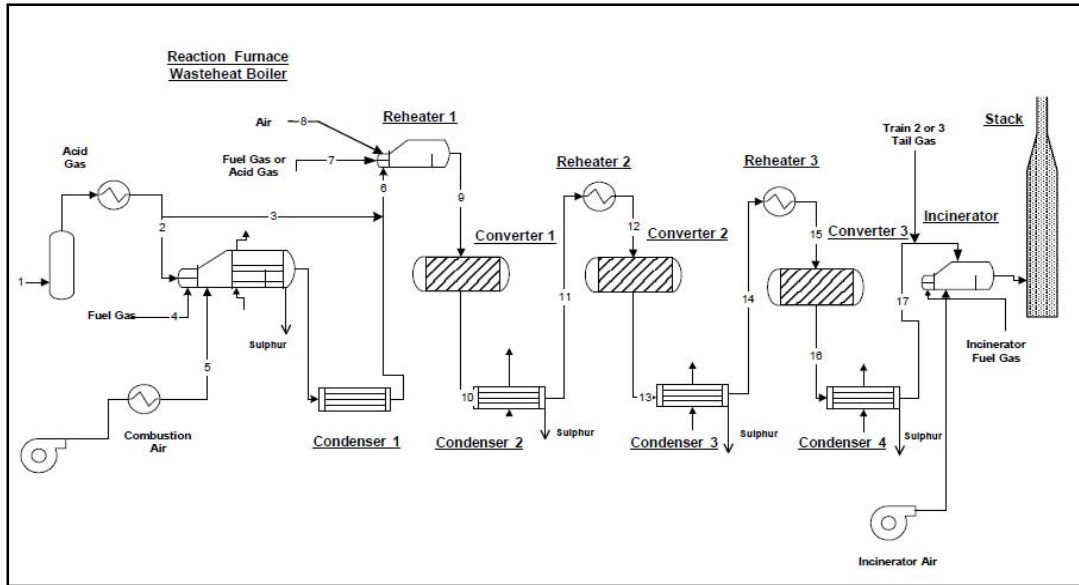


Figure 1. Schematic SPGC Claus sulphur plant

2. EXPERIMENTAL EQUIPMENT AND PROCEDURE

Analytical works were performed by SPGC laboratory personnel using a gas chromatograph together with ancillary equipment on water and sulphur free basis. The water concentrations of the acid gas stream were calculated on the assumption that this stream was saturated on that knockout drum condition.

Sulphur plant performance test were conducted according sampling and test procedure that provide sufficient data for heat and material balance for each stream. Sulphur plant sampling requires the special precautions to be taken in order to ensuring representative sample. The primary concern is ensuring that the sampling equipment is inert to have representative process gases, then sampling were done from the center of process line. The various operational parameters were logged during the test and all metering data was obtained from existing plant instrumentations.

The sampling techniques are those developed by western research and development for particular application to sulphur plant gas stream. The results of thermodynamic equilibrium calculations referred to a computer simulation model of a clause plant which was developed by western research.

3. RESULTS AND DISCUSOINS

- Acid gas enrichment

The analysis showed that amine circulation rates and feed tray to the absorber have been a significant effect on limiting overall BTX emissions. Amine flow rate was decreased from 155 to 135 kg/hr and amine feed tray was changed from 27 to 25 tray with 515 ton/h feed gas. So quality of acid gas stream by rejecting CO₂ in the amine sweetening unit was improved and consequently H₂S content of the acid gas increased from 34.3% to 36.7%. In conclusion, the furnace temperature was increased about 21 °C while a theoretical result was calculated about 24 °C.

On the other side, since a relatively small portion of the HC and BTX are absorbed by the amine solution, the amount of HC and BTX picked up increases directly with circulation rate[7, 8, and 9]. Thus, the circulation rate should be maintained as low as possible but not exceed the maximum acid gas loading that would lead to excessive corrosion and off spec products. Unfortunately, there were not actual data for BTX with amine flow rate changes.

- **reaction furnace temperature (Fuel gas spiking)**

In order to guarantee complete destruction of BTX ,fuel gas (FG) stream -was added to the acid gas feed in reaction furnace- was increased from 120 to 250 kg/hr in order to increasing the BTU value of the furnace feed gas[3].

Reaction furnace temperature was increased to 1050 °C from an initial temperature of 904 °C and consequently BTX decreased from 630 to 30 ppm. Optimum of FG flow rate was 250 kg/hr (see figure 2). It was seen adjusting reaction furnace temperature higher than 970 °C caused to 80% BTX destruction.

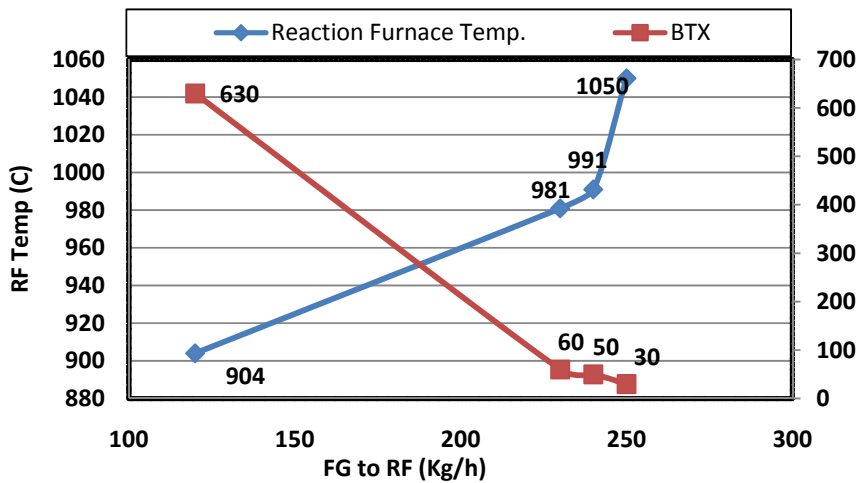
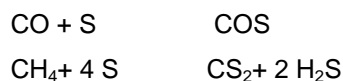


Figure2: Effect of fuel gas to reaction furnace versus its temperature and BTX removal.

Since rate of COS and CS₂ formation may become higher in reaction furnace due to high concentration of CO₂ and high level of hydrocarbons mostly from fuel gas co-firing, this method was done while COS and CS₂ analysis were monitored closely.

Side reactions in reaction furnace:



As per available research result xylene had more effect on catalyst deactivation rather than toluene and benzene [1, 5, and 9]. The results for xylene destruction shows complete destruction happen at 975 °C. With increasing reaction furnace temperature amount of xylene reach to zero percent in outlet of reaction furnace (see figure 3).

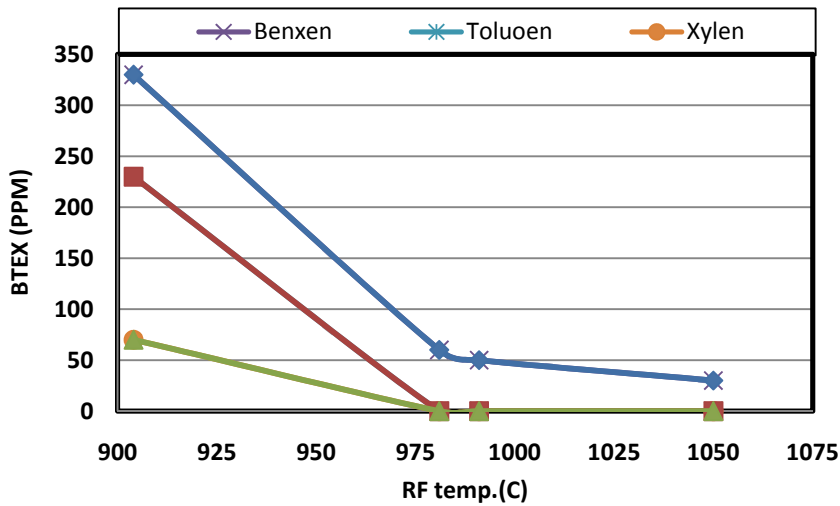


Figure 3: Effect of temperature versus aromatic hydrocarbon destruction

In second step in order to reach target reaction furnace temperature more than 1050 °C for complete BTX destruction, it was decided to open by pass acid gas flow rate in order to increase reaction furnace temperature .By passing acid gas around the reaction furnace will help to maintain a higher reaction furnace temperature and a stable flame however, it will also lead to bypassing the contaminant (BTX) in the acid gas around the reaction furnace where they have the opportunity to be destroyed if the furnace temperature is high enough. The benefit of bypassing acid gas, as opposed to co-firing with fuel gas is that the CS₂ formation rate in reaction furnace will be lower.

With above changes reaction furnace temperature increased up to 1035-1050 °C. Acid gas flow rate to reaction furnace was 20000 kg/h and acid gas bypass was 2000 kg/h. by pass valve was opened between (5-10%) and fuel gas consumption decreased to 200 from 250 kg/h.

As per table 1, BTX destruction in the reaction furnace will be increased with reducing acid gas flow rate & consequently increasing reaction furnace temperature.

| Reaction furnace temperature(°C) | BTX (ppm) |
|----------------------------------|-----------|
| 904 | 630 |
| 981 | 60 |
| 991 | 50 |
| 1050 | 30 |

Table 1: Effect of reaction furnace temperature on BTX removal.

It seems with opening by pass valve of reaction furnace there was approximately same result on BTX destruction comparison to first option without bypassing the reaction furnace. It shows that by opening by pass, if reaction furnace temperature can be raised up to 1050 °C, there would be more BTX destruction on the reaction furnace and consequently after mixing with by pass flow still the result of BTX would be acceptable.

As might be expected (figure 4), the propane destruction is complete even at the relatively low furnace temperature. All of the other saturated, straight chained hydrocarbon species in this range (C1, C8) demonstrated similar behaviour. The results for xylene and toluene were indicated complete destruction at 975 °C. Clearly, the benzene component was efficiently destroyed at relatively high temperature as compared to xylene and toluene. The effect of reaction furnace temperature was clearly demonstrated that at temperature higher than 1050 °C no BTX were seen.

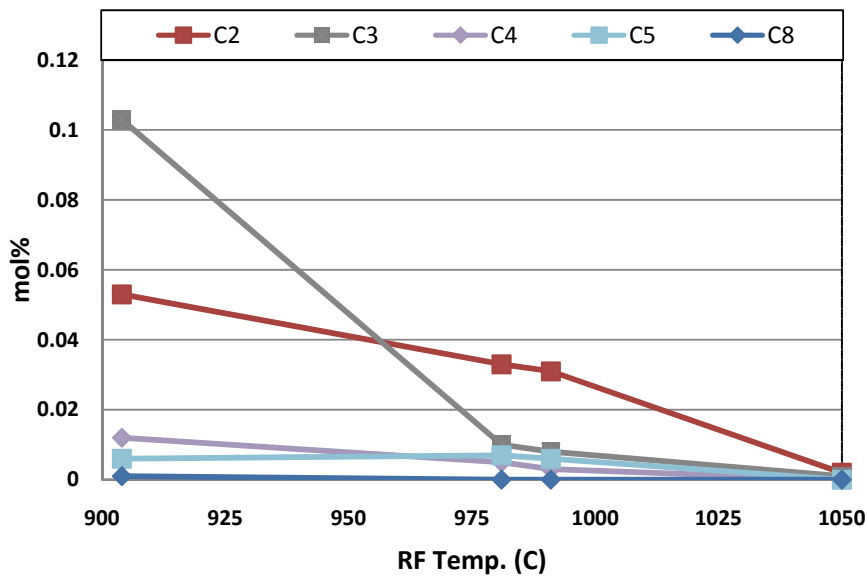


Figure 4: Effect of temperature versus destruction of straight chained hydrocarbons

- Adjusting reactor temperature**

Furthermore, the subsequent COS and CS₂ conversion in the first reactor is critical to maintaining acceptable overall recovery efficiency [6]. The effect of inlet temperature to the first reactor on COS and CS₂ hydrolysis was investigated. Theoretically COS and CS₂ hydrolysis was done completely above 320 °C. So, Inlet temperature of the first reactor was increased from 235 to 245 °C. Thus, first bed reactor temperature reached to 317 °C from initial temperature 290 °C. The extra required fuel gas is 25 kg/hr. Using COS and CS₂ analysis results concluded optimum inlet first reactor temperature is 245 °C. COS and CS₂ hydrolysis were increased from 79.1 up to 82.7% and 62.8 to 71.2%, respectively (figure 5).

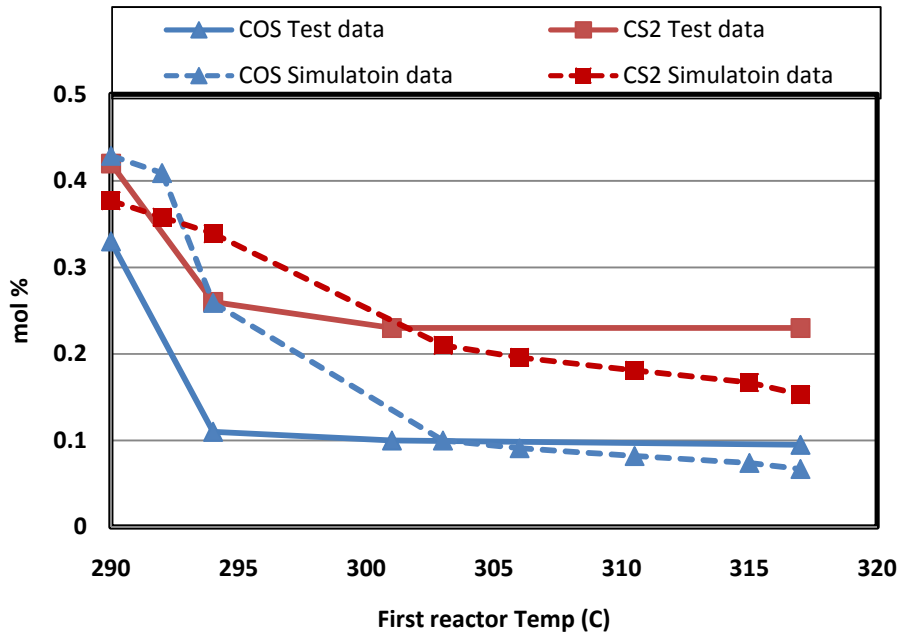


Figure 5: Effect of first reactor temperature versus COS and CS₂ hydrolysis (test data and simulated data with Sulsim #7).

| Hydrolysis | COS% | CS ₂ % |
|--------------------------|-------|-------------------|
| Before test | 5.71 | 35.38 |
| New catalyst arrangement | 80.18 | 62.86 |
| Increase fuel gas | 81.82 | 67.14 |
| Increase fuel gas | 82.73 | 71.25 |

Table 2: Hydrolysis of COS and CS₂.

In fact, actual COS and CS₂ hydrolysis percent can be higher due to there was higher flow rate through the sulphur unit during sampling (10% over design) (table 2). Both actual plant test data and simulated values are in good agreement.

In the course of this investigation catalyst arrangement was conducted on the first reactor with modification. In the design of catalyst arrangement, alumina catalysts are in the first reactor. Alumina was replaced with Titanium base catalyst. COS and CS₂ hydrolysis were done better with titanium catalyst. For new catalyst arrangement there were reduction measured COS and CS₂. Increasing in combined COS and CS₂ hydrolysis after new arrangement was approximately 66%.

4. CONCLUSOIN

South pars gas plant (Iran) faced with problems of lean acid gas with high aromatic content. In our experimental and simulating data, we focused on three options: acid gas enrichment and fuel gas spiking in reaction furnace and reactor temperature adjustment. It is clear that reaction furnace temperature as a most effective parameter for BTX removal.

After on site test run, measured recovery Efficiency increased from 85.49% to 95.47%. From commercial point of view, catalyst life time and sulphur efficiency (about 10%) increased considerably with no capital equipment cost while fuel gas consumption increases just 155 kg/hr.

From environmental point with modifications, BTX were decreased from 630 to 30 ppm considerably.

Finally, the preceding findings suggest these modification measurements to a large proportion of the Claus plants in the world that there are these common problems to improved sulphur recovery plant.

5. Acknowledgements

The authors wish to thank the Mr. Jahanbazi and colleagues at SPGC Phases 2& 3 laboratory. And thanks a lot from sulphur expert company for their support in various stages of this project.

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