The 47th Annual

Laurance Reid Gas Conditioning Conference

Agenda

March 2-5, 1997

Presented by

The University of Oklahoma
College of Continuing Education
Engineering and Geosciences Programs

Norman, Oklahoma

Project Experience

Installation of BOC SURE burner at the BP Lima refinery

Neal Zislin, Process Engineering Team Leader
BP Oil, Lima Refinery

Ron Schendel, Process Consultant
BOC Gases

Lisa Paszkowski, Senior Development Engineer
BOC Gases

Introduction

In April of 1996, BP Oil installed a BOC SURE burner on the reaction furnace of its sulfur recovery unit at its refinery in Lima, Ohio. The intent was to improve operational reliability by replacing the existing burner with one of equal capacity, but having the capability to expand capacity through the use of oxygen in the future. The plant had been experiencing chronic fouling in the waste heat boiler (WHB), and high pressure drop across the burner on the acid gas side. The new BOC burner would allow use of oxygen and operation at higher throughputs. Though the burner has oxygen enrichment capability, BP has not pursued it due to reasons not related to the sulfur plant. However, modified operation with the new burner has resulted in elimination of the chronic fouling problem, and a projected increase in capacity of approximately 10% (air operation) as a result of lower pressure drop with the new burner. This paper describes the plant history, project execution , installation and operation of the BOC burner since its installation.

Overview of BOC SURE technology

BOC Gases is a leading, worldwide supplier of industrial gases including oxygen, nitrogen, and hydrogen which are used in refineries for various purposes. One application for oxygen is the expansion of sulfur recovery capacity. BOC has developed technologies and equipment in this area to support its position as a supplier of oxygen.

Oxygen can be mixed safely with air up to a concentration of 28%. Therefore, with operations at up to 28% oxygen, the existing burner in a Claus sulfur plant may often be retained. BOC provides diffuser pipes for introduction and mixing of oxygen into the air stream (see Figure 1 - Photo of Diffuser Pipe on page 10. The Diffuser Pipe shown in this photo is actually for a FCC oxygen enrichment project, and is much larger than what would be used in a sulfur plant. The larger unit is shown here for added clarity.). BOC also provides oxygen control skids for this purpose.

At levels above 28%, oxygen should be introduced into the reaction furnace separately from the air supply. BOC supplies a burner specifically designed for this purpose. The burner is a tip mix burner with separate ports for acid gas, oxygen, and air supply. There are currently 8 BOC SURE burners in operation at 7 different refineries. One of these refineries is the BP Oil refinery located in Lima, Ohio. This paper describes the installation, and operation of the BOC SURE burner at that refinery.

The BOC tip mix burner, is designed to provide hot zones which enhance endothermic dissociation reactions. Therefore, this burner will allow oxygen concentrations as high as any available today, and decidedly higher than premix type burners. The exact level of enrichment, and associated capacity increase will vary with the feed. However, for a typical refinery with high H_2S concentration and significant sour water stripper gas, 45% oxygen and 75% increase in capacity is realistic.

At higher concentrations the reaction furnace temperature would exceed refractory limits. Also, the capability of the existing waste heat boiler may limit oxygen usage, even before temperature limits are encountered. Therefore, BOC also offers the Double Combustion process which allows operation up to 100% oxygen while maintaining safe conservative temperatures. Again, for a typical refinery acid gas feed (including sour water stripper gas) this equates to a new capacity 2 ½ times the original capacity. There are two refineries operating today with the full Double Combustion process.

The Double Combustion process uses the same BOC burner on a new reaction furnace and waste heat boiler installed upstream of an existing plant (see Figure 2 - Process Sketch Double Combustion Process on page 11). Process gas from the new waste heat boiler is now the feed to the front end of the existing sulfur plant. It is at a temperature significantly higher than its autoignition temperature. Therefore, a burner is no longer required on the existing reaction furnace, and it is removed. The portion of oxygen, which is supplied to the existing reaction furnace, is introduced through a simple lance. The oxygen is immediately and completely consumed.

Sulfur Recovery Unit at BP Lima refinery - Background

The Claus sulfur plant at the BP refinery in Lima, Ohio was first installed in 1974. It is a Ford Bacon & Davis design. It has 3 catalytic stages, and no tail gas treating unit. Reheat upstream of the catalytic converters is by heat exchange against steam. For ammonia destruction, temperature in the front section of the reaction furnace is maintained by splitting a portion of the flow of amine acid gas to the rear section. All sour water stripper gas containing ammonia is fed to the front section. Consistent with typical Ford Bacon & Davis designs, oxidative conditions are maintained in the front section (see Figure 3 - Oxidative Mode v. Reductive Mode on page 12). This means that enough amine acid gas is diverted to the rear section, so that an excess of oxygen, beyond stoichiometric requirements for complete oxidation of hydrogen sulfide to sulfur dioxide, exists in the front section. The excess oxygen is consumed in the rear section by the amine acid gas diverted to this section.

As configured, the historical sustainable operational capacity was limited to 49 long ton per day. There were two basic constraints that prevented exceeding this limit. The first was pressure drop in the burner itself on the acid gas side. The second limit was ability of the waste heat boiler to remove heat beyond that throughput. The waste heat boiler limit was probably due to fouling.

After turn-arounds, where the burner was replaced, and the waste heat boiler tubes were cleaned, a temperature rise of 100 ^{o}F or more would be experienced within only one week of operation. During turnarounds, hard deposits would have to be removed from the waste heat boiler tubes. These deposits are believed to be refractory material which was vaporized in the transition pipe between the rear zone of the reaction furnace, and the entrance to the waste heat boiler. Refractory damage would be noted in this area during turn around inspection. It is believed that because of the oxidative conditions in the front zone of the reaction furnace, free oxygen would still exist in the transition pipe, reacting with acid gas which was split and fed to the rear section of the reaction furnace, causing local zones of high temperature in the transition pipe near the refractory lined wall.

Plans for Expansion

In addition to finding a solution to the operational problems described above, BP entertained the possibility of expanding capacity to a nominal 80 long ton per day. This expansion objective was based on a desire to process heavier, and more sour crude. Sulfur feed comes from the isocracker, cat cracker (FCC), naphtha hydrotreater, coker, and sour water stripper units. A more sour crude would result in increased hydrogen sulfide from these units.

Oxygen enrichment was seen as a viable option to reach the expansion objective. BOC Gases supplies the BP Lima refinery with nitrogen and has a cryogenic nitrogen generation unit on site. The waste gas from this unit is approximately 40% oxygen. This waste stream was seen as a low cost source of oxygen for the sulfur recovery unit. In addition, BOC has 4 merchant air separation plants in the immediate vicinity. While the nitrogen generation unit is extremely reliable, these merchant plants could easily supply liquid oxygen, during any unforeseen outage of the nitrogen generation unit to ensure an uninterruptible stream of oxygen to the sulfur recovery unit.

Calculations indicated that both the oxygen concentration and quantity of waste gas would be sufficient to meet the expansion objectives. However, free energy calculations indicated that marginally excessive furnace temperature might be encountered with a burner changeout alone. With a burner that promotes endothermic dissociation reactions, it might be possible to achieve the expansion goal with a burner changeout alone. The BOC SURE burner is a tip mix type burner which by design promotes hot zones within the flame, and these hot zones enhance the dissociation reactions. The primary example of these dissociation reactions is hydrogen sulfide producing hydrogen plus sulfur. This reaction is endothermic, and does not require oxygen. On the other hand, the more dominant Claus reaction requires oxygen and produces water and sulfur. The reaction of oxygen with hydrogen sulfide is highly exothermic.

The existing Ford Bacon & Davis burner, although of a different design to accommodate oxidative conditions in the front zone of the reaction furnace, is a tip mix type burner. Temperatures experienced in the reaction furnace were lower than one would expect based on free energy calculations, and significant hydrogen was detected in the process gases downstream of the reaction furnace/waste heat boiler. Therefore, there was good reason to believe that, with a properly designed tip mix burner, capacity increase approaching expansion objectives could be met.

The other concern was capacity of the existing waste heat boiler. It was felt that if the fouling problem could be solved, then the existing waste heat boiler would probably have enough capacity even at the increased throughput. Eliminating oxidative conditions in the front section of the reaction furnace, combined with a burner that provides excellent mixing, could well overcome the refractory damage, and WHB fouling problems.

When operating with oxygen there is no need for a split flow to maintain adequate temperatures in the reaction furnace for ammonia destruction. Therefore, oxidative conditions would not exist in the reaction furnace. However, during air only operation, a split would be required. The basic engineering package offered by Parsons included a modification of the split flow scheme to maintain reductive conditions in the front zone of the furnace (see Figure 3 - Oxidative Mode v. Reductive Mode on page 12). This means that enough amine acid gas would be split to the rear section of the reaction furnace to reach the desired temperature, but not so much as to leave an excess of oxygen. Instead, hydrogen sulfide would be in excess, even in the front section of the reaction furnace.

If capacity would be required in excess of what is possible with the BOC tip mix burner alone, then Double Combustion using the same BOC burner could be added later. This would involve addition of a new reaction furnace and waste heat boiler upstream of the existing reaction furnace. The same BOC burner would be moved from the existing furnace to the new reaction furnace.

A refinery turn around was approaching which would require replacement of the burner. Historically, BP had replaced the burner in kind. However, burner replacement or major rework had been required every 2 years. This seemed like an opportune time to consider alternatives.

Besides the BOC burner option with a BOC Double Combustion contingency, two other options were considered. TPA's offering included a burner design which was very similar to the FBD design plus oxygen enrichment up to 28% oxygen via diffusion of oxygen (or the 40% oxygen rich stream) into the air stream. This option was rejected primarily because it would not meet capacity objectives. Also, air operation would be very similar to current operation, and it was hoped that a change would overcome the operational problems described above.

The Goar Allison offering, known as COPE, included a pre mix type burner manufactured by Duiker, a new larger waste heat boiler, and a recycle blower to recycle gases from the #1 sulfur condenser. The recycle gases would be required to limit temperature rise in the reaction furnace. This option was rejected because it was potentially more capital intensive, and added operational complexity.

The decision to proceed with the installation of a BOC burner was supported by detailed "Computational Fluid Dynamics" modeling, which confirmed the ability to operate with air at the current maximum capacity, with 40% oxygen to increase capacity, and also to maintain turn-down to the existing minimum throughput operation.

The project was initiated to replace the existing burner with a new BOC burner within the upcoming refinery turnaround schedule. Initial operation would be with air only, and reject gas from the nitrogen generation unit would be brought in after the reject gas compressor became operational, and approvals from environmental agencies were obtained.

Project Execution

There is only one sulfur recovery unit at the Lima refinery. Therefore, it was critical that modifications be completed during the turn-around. This put significant pressure on delivery schedules. In all, a total of only 14 weeks expired from the placement of the burner order to actual start up and operation of the unit.

Modifications which occurred during this time include:

- removal of the old burner
- installation of the air annulus onto the existing furnace
  (see **Error! Reference source not found.** on page **Error! Bookmark not defined.**)
- refractory repair
- installation of the new BOC Burner
  (see **Error! Reference source not found.** on page **Error! Bookmark not defined.**)
- new piping and instruments including the addition of penetration purges and fuel gas block & bleeds, and piping to accommodate feed streams to the new burner, and operation with either only air, 28% enriched air (interim operations), or a combination of air and 40% oxygen.
- new PLC alarm monitoring, and shutdown system

Note: split flow was required and retained for operation before oxygen would become available to ensure ammonia destruction. However split flow was changed from oxidative to reductive mode.

Error! Reference source not found. on page **Error! Bookmark not defined.** shows the reaction furnace after the BOC Burner installation and piping modifications.

The BOC technology (Burner installation) was supported by basic engineering from the R.M. Parsons company. Full services are also available from Parsons, including detailed engineering, and construction. However, for this project, BP elected to use local contractors for detailed engineering and construction. Parsons supplied the basic engineering package, including mark ups of existing P&IDs, plus close support for BP in the design of the revised control systems.

The detailed engineering for modification of the reaction furnace, which consisted primarily of the installation of an air annulus for the BOC burner gun, was performed by RMF Industrial Construction. Piping detailed engineering was performed by Middough Engineering.

A new pilot flame was specified as an accessory to the new burner installation. However, due to long delivery times, an existing ignitor available on site had to be employed for the project.

Project management was undertaken by BP.

Plant Performance

Both BOC/Parsons and BP normally prefer that the dry out of new refractory begin with slow controlled heating supplied by a pilot flame alone. In this instance, it turned out that the unit installed was an ignitor and not a separate pilot flame. Therefore, the ignitor was used to fire the BOC burner operating with natural gas and air under extreme turn down conditions. While this was not the preferred method, the dry out went very well and the BOC burner demonstrated great flexibility and extreme turn-down capability.

After the refractory had gone through its dry out, and acid gas had been introduced into the system, there was one sulfur plant shut down trip which occurred while the combustion air flow transmitter was being calibrated. The unit was restarted within 2 minutes, the restart was uneventful, and the plant has been running continuously since then.

At first, there appeared to be some problems with the acid gas analyzer which provides the feedback signal for trim air, and it was very difficult to keep the plant lined out with the desired 2:1 ratio of hydrogen sulfide to sulfur dioxide in the tail gas. However, the instrument repair people indicated that everything was calibrated and working properly. After a few days the control system lined out and began working normally. It was concluded that the sample line to the analyzer was temporarily plugged with solid sulfur, and the sulfur melted as soon as the plant warmed up to its steady state conditions.

Within the first week of operation it was obvious that the temperature at the exit of the waste heat boiler was not rising as had been the experience with the previous configuration. The temperature remained consistent, varying only as expected with throughput, and returning to the same temperature for any given flow. After some months of operation, there was a period of substantial, and rapid changes in acid gas flow rate. During this period there was some rise in the waste heat boiler temperature. However, after 7 months of operation there is still less temperature rise than previously experienced in 1 week of operation (refer to Figure 4 - Waste Heat Boiler Exit Temperature on page 16). It is believed that the temperature rise coincided with poor control of required air, and that the plant was temporarily, and unintentionally operating in the oxidative mode when the temperature rise occurred.

Also noted, is a definite decrease in acid gas pressure drop. Based on the pressure drop an increase of 10% in capacity during air only operation is expected. The refinery feed slate has not produced enough feed to the sulfur plant to demonstrate this on a long term basis. However, data from a single day of recent operation, achieving 51 long tons per day, does suggest that a throughput of 54 long tons per day (10% greater than historical maximum capability) may be achievable.

Brimstone Engineering was contracted to do the analysis for a performance test of the sulfur recovery unit after modification. Brimstone had also run a previous analysis of the plant streams under the old configuration immediately prior to an earlier turn-around. The analytical results of the stream exiting the #1 sulfur condenser for both sets of data are shown as Table 1 on page 17.

The low levels of CS_2 indicate complete hydrocarbon destruction, and by implication complete ammonia destruction and good mixing for both the old and new burners. The one analysis indicating 0.7 mol % CS_2 for operation with the old burner occurred during a plant upset in which very high levels of hydrocarbons were present in the feed. Analysis was also carried out for ammonia at various locations in the plant, and none was detected.

As discussed earlier, the previous Ford Bacon & Davis design burner is also a tip mix burner, even though it operates in an oxidative mode rather than reductive mode. The 3 % hydrogen level (dry basis) indicates a fair amount of dissociation reactions for this burner. This is a level quite a bit higher than typically found with either a pre mix type burner or tip mix burner not designed to promote intense mixing.

What is particularly interesting is the much higher hydrogen level for the new BOC burner. Analysis indicates a level of 5 ½ % hydrogen (dry basis). This is with air only operation. Yet even with air, the new BOC burner does such an effective job of mixing and promoting dissociation reactions that these high levels of hydrogen are realized.

Current Status of Refinery

Early on in the operation of the plant with the new BOC burner, BP had announced its intention to sell the Lima refinery as part of its refinery consolidation program. BP followed with an announcement in November, 1996, its intention to cease crude processing operations in approximately 2 years. Therefore, it now appears that the sulfur recovery unit will continue to operate on air only (no oxygen enrichment) until the unit is shut down.

The plant continues to run extremely well, particularly in contrast to previous operation, and the project is considered a complete success. The limited life for this refinery is an unfortunate, and unforeseen circumstance not related to the operation of the sulfur recovery unit.

Conclusions

Fouling which had been experienced earlier at the BP Lima refinery seems to be eliminated by the combination of operation in the reductive mode, and installation of the BOC SURE burner. In addition, the straight forward design of the BOC burner allows for quick delivery to meet tight schedules and windows of opportunity.

In recent years, much attention has been paid to the functions of the Claus reaction furnace burner. These burners should provide excellent mixing to ensure destruction of hydrocarbons, and ammonia. When used with oxygen enrichment, the intentional promotion of dissociation reactions can be used to increase oxygen concentration and the associated level of capacity increase possible. The BOC burner has demonstrated its ability to meet all these criteria. Based on high levels of hydrogen production, maximum possible enrichment should be attainable with this effective yet uncomplicated burner.

Also, although the unforeseen turn of events prevented use of oxygen at the Lima facility, the use of reject gas from a cryogenic nitrogen generation unit, as the source of oxygen for increased throughput, should prove to be an economically attractive option to other refiners.

List of Figures

List of Tables

Figure 1 - Photo of Diffuser Pipe

Figure 2 - Process Sketch Double Combustion Process

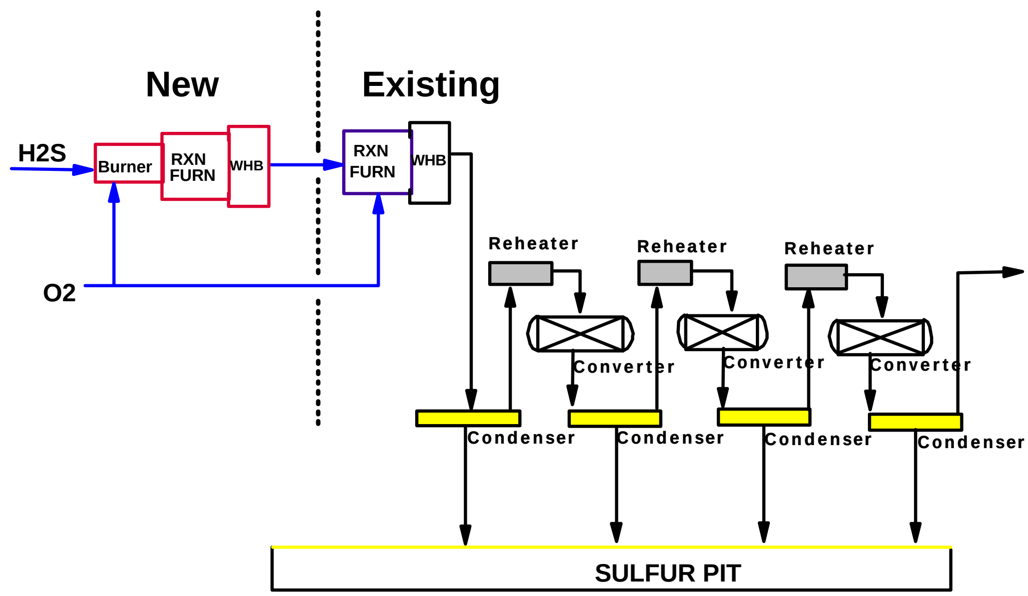

Figure 3 - Oxidative Mode v. Reductive Mode

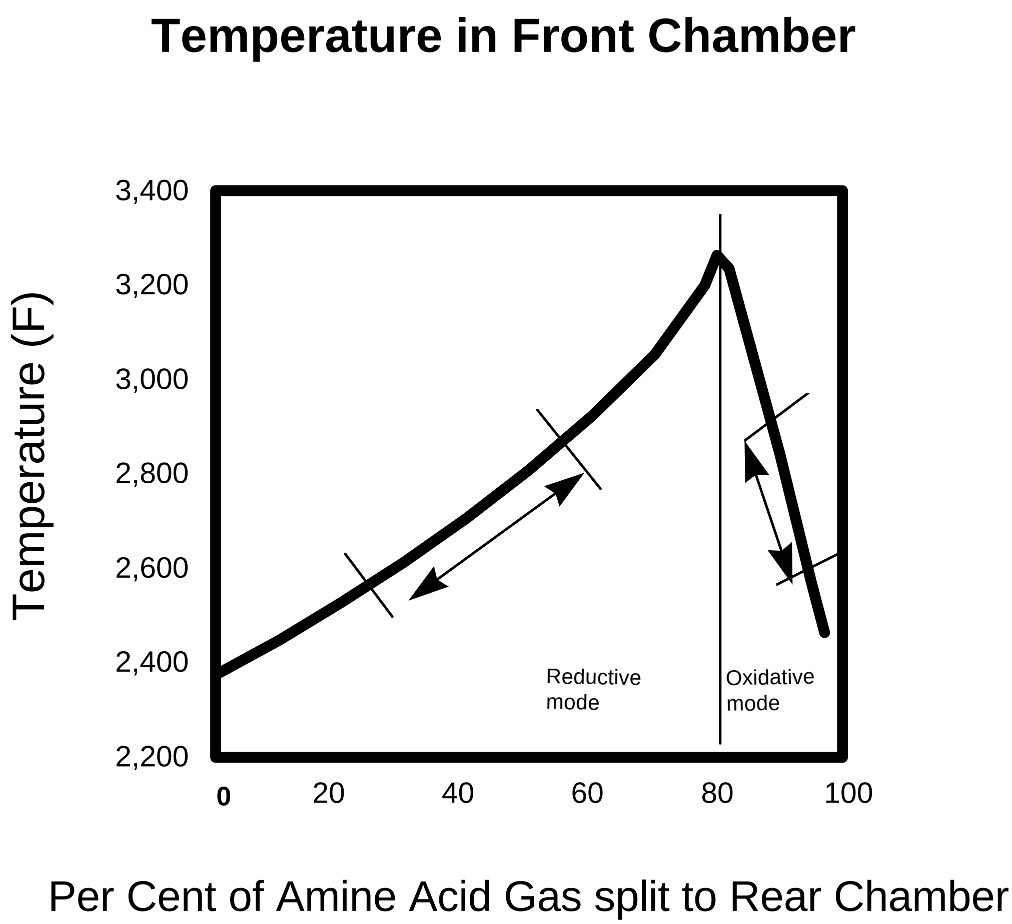

Figure 4 - Installation of Air Annulus

Air

Figure 5 - BOC Burner before installation

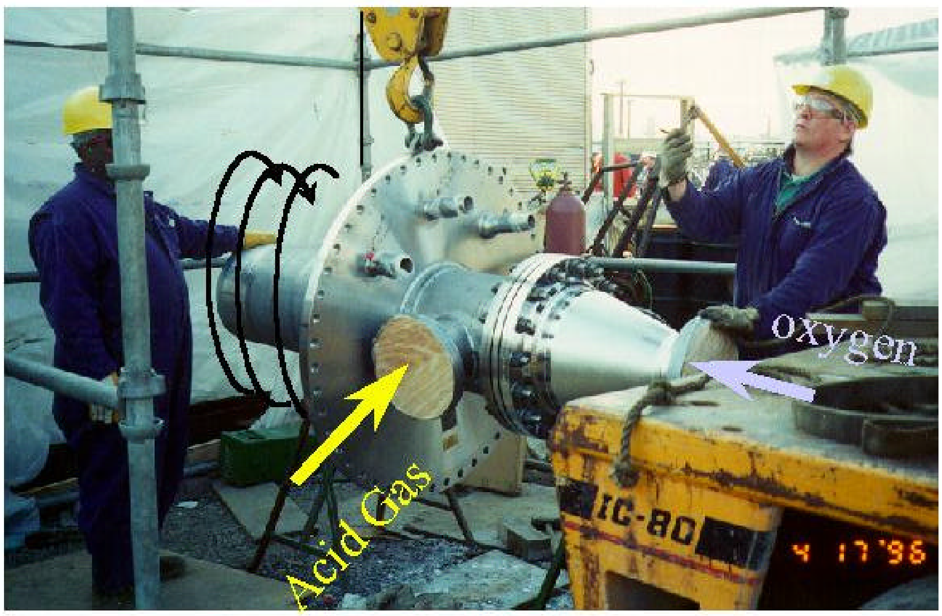

Figure 6 - Completed Installation

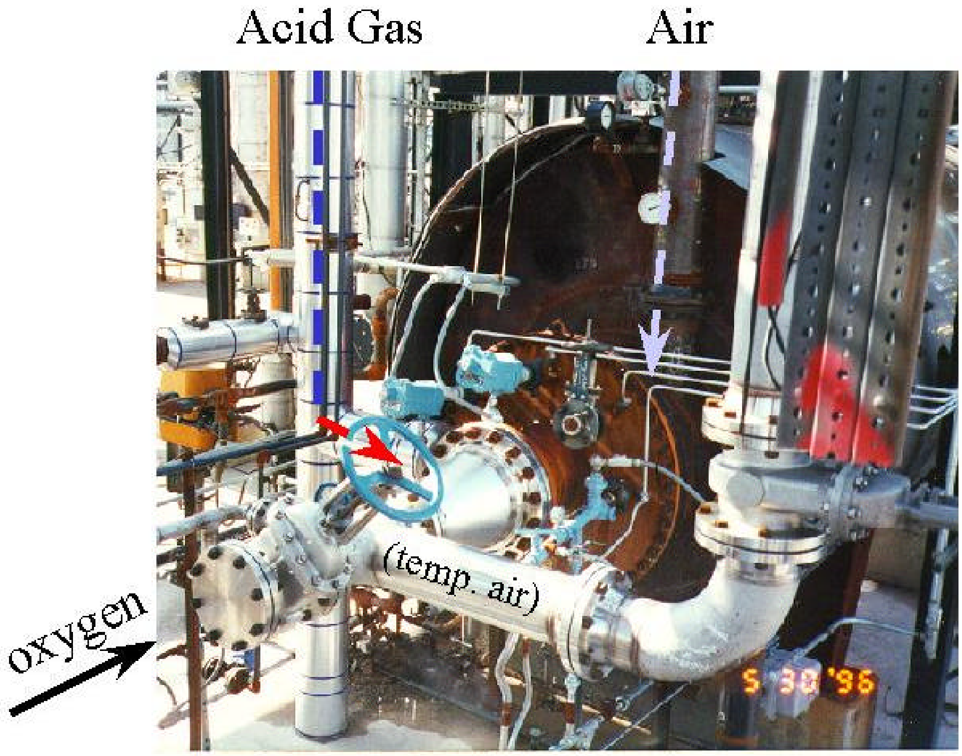

Figure 4 - Waste Heat Boiler Exit Temperature - Before & After

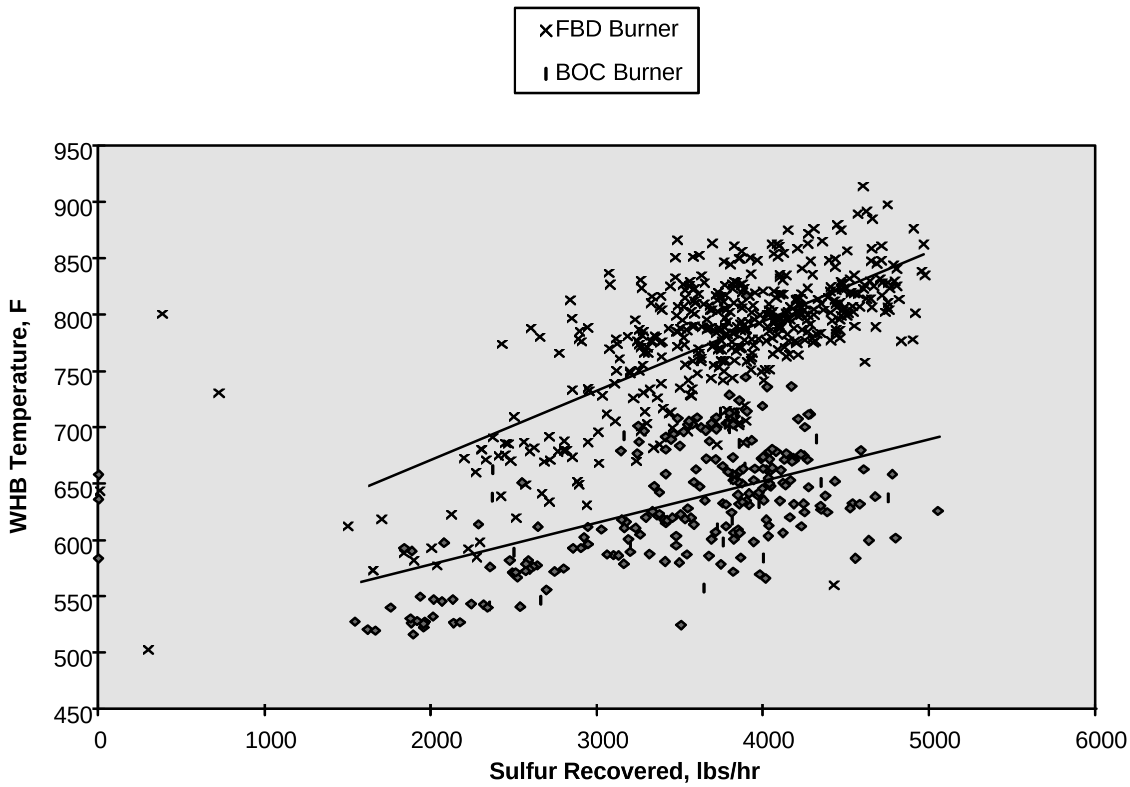

Table 1 - Performance Test Data

	Original Burner sample1 & 2		BOC Burner sample 1	2	3
Hydrogen	**3.362**	**3.320**	**5.466**	**5.706**	**5.739**
Argon	0.943	0.941	0.933	0.949	0.936
Oxygen	0.000	0.000	0.000	0.000	0.000
Nitrogen	78.887	78.651	78.003	79.315	78.279
Carbon monoxide	0.759	0.990	0.946	0.963	0.945
Carbon dioxide	3.654	3.931	3.570	3.379	3.734
Hydrogen Sulfide	7.939	7.656	6.765	6.837	6.584
Carbonyl Sulfide	0.164	0.202	0.197	0.183	0.187
Sulfur dioxide	4.074	3.789	3.833	2.505	3.361
Carbon disulfide	**0.218**	**0.719**	**0.287**	**0.162**	**0.230**