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Investigating Different Options for Reheating the First Converter Inlet Stream of Sulfur Recovery Units (SRUs)

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***Abstract*—**The modified Claus process is the major technology for the recovery of elemental sulfur from hydrogen sulfide. The chemical reactions that can occur in the reaction furnace are numerous and many byproducts such as carbon disulfide and carbon carbonyl sulfide are produced. These compounds can often contribute from 20 to 50% of the pollutants and therefore, should be hydrolyzed in the catalytic converter. The inlet temperature of the first catalytic reactor should be maintained over than 250 °C, to hydrolyze COS and CS2. In this paper, the various configurations for the first converter reheating of sulfur recovery unit are investigated. As a result, the performance of each method is presented for a typical clause unit. The results show that the hot gas method seems to be better than the other methods.

***Keywords*—**Sulfur recovery unit, reaction converter.

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I. Introduction

MOST of the catalysts used for the treatment of hydrocarbons in the petrochemical industries are highly susceptible to poisoning by sulphur compounds. It is thus essential to separate hydrogen sulfide from feed stocks such as sour natural gases or crude oil [1]. The modified Claus process is the major technology for the recovery of elemental sulfur from H S and SO2 [2]. All requirements to be met by Claus plants are dictated by the operating conditions of modern, flexible refineries and natural gas plants and increasingly stringent emission control regulations [3]. Therefore, Sulfur recovery units (SRUs) do not directly increase the net present value of the refinery and they are necessary to match all stringent environmental regulations [4].

The modified Claus process consists of a high temperature front-end reaction furnace, followed by catalytic reaction stages. This process continues to be the most widely used process for the conversion of H_2S to sulfur. Generally, Byproduct gases originating from physical and chemical gas and oil treatment units in refineries, natural gas processing and gasification plants are also routed to Claus unit [3]. The overall reaction characterizing the process is as follows [4],

$$2H_2S + O_2 \Rightarrow S_2 + 2H_2O \quad (1)$$

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A key reaction that occurs in front-end reaction furnace is a two step sequence, 1/3 of the acid gas is oxidized to SO2 using air,

$$H_2S + \tfrac{3}{2}O_2 \Rightarrow SO_2 + H_2O \quad (2)$$

This combustion generates a large amount of heat. Further, the combustion products undergo Claus reaction between H2S and SO2,

$$2H_2S + SO_2 \Leftrightarrow \tfrac{3}{2}S_2 + 2H_2O \quad (3)$$

Reaction 3 is a reversible exothermic reaction. Thus, processing under adiabatic condition greatly increases temperature, which lowers equilibrium conversion to about 75%. Effluent gas from the reaction furnace passes through a waste heat boiler (WHB) to recover heat and produce high-pressure steam. Likewise, a large amount of elemental sulphur (S2) are produced during of thermal decomposition H2S. In fact, Elemental sulfur produced in the furnace is about 50-60% of the total sulfur production of the plant [5].

In the second step or catalytic reaction stages, the remained unreacted H2S are reacted with SO2, over an alumina catalyst to form elemental sulfur in fixed bed reactors. The reaction is the same as eq. 3 [1,6]. Since this reaction is exothermic, decreasing the temperature leads the equilibrium reaction toward right hand, i.e. more sulfur yields. On the other hand, low temperatures decrease the reaction rate. Therefore, an appropriate catalyst must be used to increase the reaction rate. However, high sulfur yields still necessitate a multistage process with interstage cooling and sulfur condensation [7]. Although the modified Claus process has remained relatively unaltered since its introduction, further modifications to the basic process have been introduced in order to increase the plant capacity or efficiency [8].

As mentioned before, the chemical reactions that can occur in the reaction furnace are numerous and many byproducts such as carbon disulfide (CS_2) and carbon carbonyl sulfide (COS) are produced. These compounds can often contribute from 20 to 50% of the pollutants in the tail-gas [9-12]. Furthermore, presence of O_2 traces in the CS_2 - H_2O mixture caused a decrease in the activity of alumina and titania catalysts due to sulfate formation [13]. Therefore, COS and CS_2 should be hydrolyzed in the catalytic converter [14,15], as shown below:

$$COS + H_2O \Rightarrow H_2S + CO_2 \quad (4)$$

$$CS_2 + 2H_2O \Rightarrow 2H_2S + CO_2 \quad (5)$$

The temperature of the first catalytic reactor is maintained at about 350 °C to hydrolyze COS and CS_2, while that of the subsequent reactors is just above the sulfur vapor dew point

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[21]. Transition metal oxides can be used to modify gamma-alumina to form a catalyst that is effective at temperatures higher than the dew point of sulfur [16-18].

As mentioned before, effluent gas from the reaction furnace passes through a WHB which makes it cold to condense produced sulfur. Several ways are available for reheating the process gas entering to first converter, including the hot gas bypass method, the direct fired method, and the indirect reheat methods [19].

The hot gas bypass method takes a slip-stream of hot process gases from the waste heat recovery unit, usually at 480 - 650 °C, and mixes this stream with the sulfur condenser outlet gases upstream of the catalytic converter. Hot gas bypass reheating is normally the lowest cost alternative, is relatively simple to control, and results in low pressure drop. Its disadvantage is lower overall sulfur recovery, particularly at reduced throughput [19].

The direct fired method of reheating uses inline burners to burn either fuel gas or acid gas, and mix the combustion products with the WHB outlet gases. Potential disadvantages of inline burners are the possible formation of SO_3, if acid gas is burned (sulfates deactivate the catalyst) and of soot, if fuel gas is burned. Soot can plug and also deactivate the catalyst. Moreover, Oxygen in as low a concentration as 30 ppmv can rapidly sulfate the catalyst [19].

The indirect reheat methods use direct fired heaters or heat exchangers to heat the sulfur condenser outlet gases; high pressure steam, hot oil, and hot process gases have been used. Electrical reheating has also been used. Indirect reheating, which involves a heat exchanger ahead of each catalytic converter, is the most expensive alternative and results in the highest pressure drop. In addition, converter inlet temperatures are limited by the temperature of the heating medium. For example, the use of 4140 KPa steam at 254°C as the heat source would limit the converter inlet temperature to a maximum of about 243°C. Thus, catalyst rejuvenation is usually not possible and COS and CS2 hydrolysis may be more difficult [19].

II. Adjusting First Converter Temperature

A typical unit of Clause sulfur recovery is considered. The schematic shape of such a modified two-stage SRU plant is shown in figure 1. In order to investigate different options for the first converter reheating, a typical unit of Claus sulfur recovery is considered. The conditions of acid gas feed stream is presented in Table I.

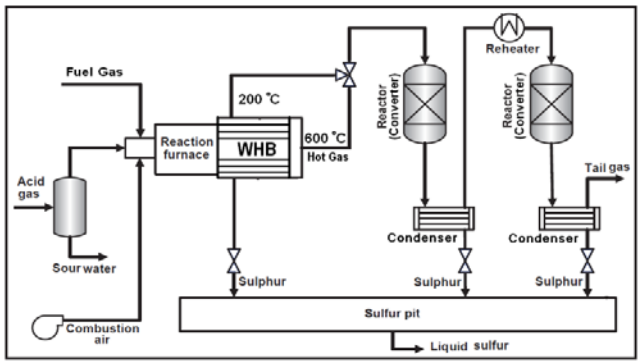


Fig. 1 A schematic shape of a modified two-stage Claus process with acid gas and air preheating and hot gas configurations

TABLE 1
The conditions of acid gas feed stream

Property	Value
Temperature	60 °C
Pressure	1.8 bara
Molar Flow	750 Kmole/h
Composition (molar)	
H2S	33
CO2	57
H2O	10

At the first step, we study indirect method for reheating the inlet stream of first converter. Since we use often HPS (High Pressure Steam) as heating medium, heating more than 250 C is difficult. In this study, super heated steam at 260 C and 41.5 bar is used. Figure 2 represents the changes of HPS mass flow rate vs. the temperature of first converter inlet stream. As is shown in this figure, it seems that temperature of first converter inlet stream will increase linearly with increasing the steam mass flow rate. But since the temperature of super heated steam is 260 °C, reheating more than 250 °C lead to approach temperature and internal pinch point problems in heat exchanger design and design in this condition is not possible. As mentioned before, increasing this temperature will improve COS and CS2 Hydrolyze in the first converter and using direct method may not be a good alternative in serious cases with high COS and CS2 contents. Furthermore, using HPS will increase working capital and maintenance costs and enhance overall pressure drop of SRU which is a critical parameter in operability of unit.

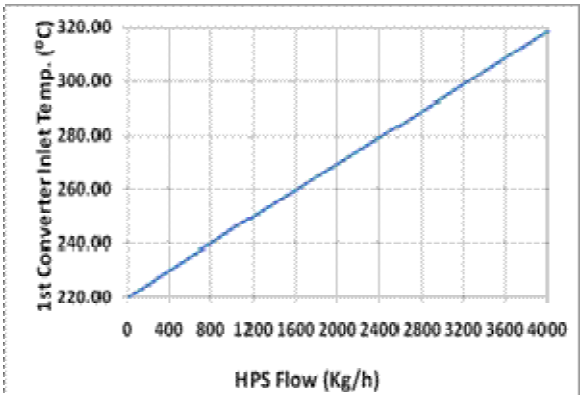


Fig. 2 The changes of HPS mass flow vs.the temperature of first converter inlet stream

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At second step, using hot gas will be studied. As mentioned at introduction, among available alternatives, the best configuration for reheating of firs reactor inlet stream seems to be using hot gas (see figure 1, after WHB). Figure 3 represents the changes in the temperature of first converter inlet stream with changes in the hot gas split ratio. As is shown in this figure, the temperature of 250 C which is an appropriate temperature for first converter inlet stream is achievable at hot gas split ratio equal to about 6.5 percent. Although using hot gas omits the cost of using high pressure steam, it can decrease overall sulfur recovery of unit. However, it can be compensated when tail gas treatment unit is applied after Claus sulfur recovery unit. More increase in the temperature of first converter inlet stream is possible by increasing the hot gas bypass ratio.

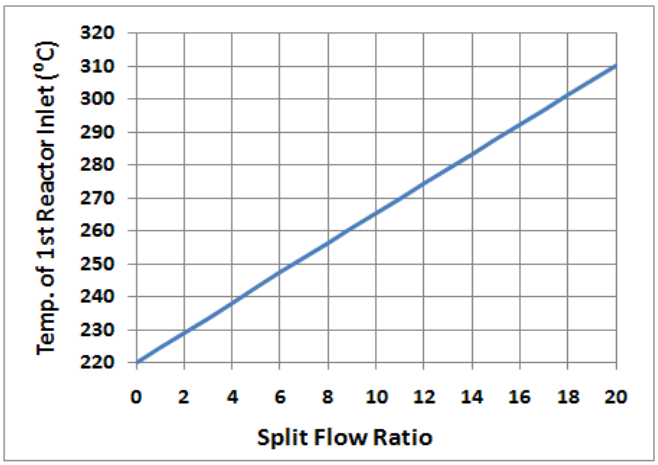


Fig. 3 The changes in temperature of first converter inlet stream vs. hot gas split ratio Figures

Finally, the use of inline burners will be investigated for reheating the process gas flowing to first converter. The inline burner burns a portion of acid gas feed to SRU or the fuel gas to produce a hot gas. Mixing this hot gas with outlet stream of WHB will increase the temperature of first converter inlet stream. This method omit the pressure drop of the heat exchanger in the first method and operability problems of second one, but decrease of overall sulfur recovery is present yet, because it insert the large amounts of inert gas to the process gas. Moreover, the cost of fuel gas will increase working capital investment. For this case study, using a fuel gas inline burner is supposed. Figure 4 show the increase in the temperature of first converter inlet stream with the increase of fuel gas (hear we use natural gas) flow rate. As is shown in figure, 55 Kg/h is required to reach the temperature of first converter inlet stream above 250 °C.

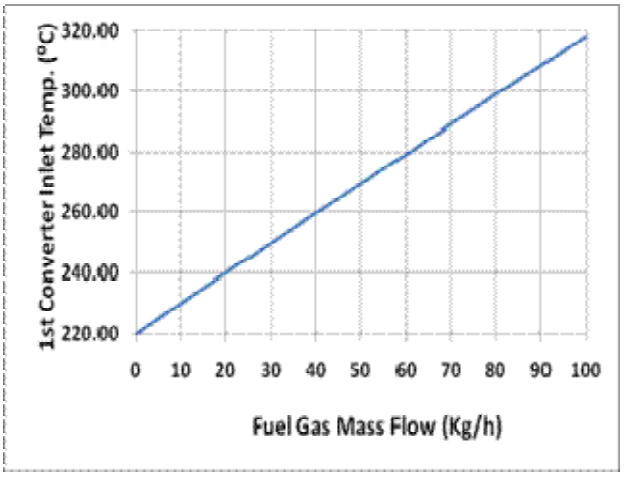


Fig. 4 The changes in temperature of first converter inlet stream vs. mass flow rate of fuel gas inserting into the inline burner

III. Conclusions

The modified Claus process is the major technology for the recovery of elemental sulfur from hydrogen sulfide. The chemical reactions that can occur in the reaction furnace are numerous and many byproducts such as carbon disulfide and carbon carbonyl sulfide are produced. These compounds can often contribute from 20 to 50% of the pollutants and therefore, should be hydrolyzed in the catalytic converter. The inlet temperature of the first catalytic converter should be maintained over than 250 °C, to hydrolyze COS and CS2. In this paper, the various configurations for the first converter reheating of sulfur recovery unit were investigated. The achieved results show that the performance of each method and it was shown that using hot gas seems to be better than the other methods, especially when COS and CS2 are major problem in SRU.

Acknowledgment

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