Adjusting the Furnace and Converter Temperature of the Sulfur Recovery Units

Hamid Reza Mahdipoor, Hamid Ganji, Hamed Naderi, Hajar Yousefian, Hooman Javaherizadeh

Abstract—The modified Claus process is commonly used in oil refining and gas processing to recover sulfur and destroy contaminants formed in upstream processing. A Claus furnace feed containing a relatively low concentration of H2S may be incapable of producing a stable flame. Also, incomplete combustion of hydrocarbons in the feed can lead to deterioration of the catalyst in the reactors due to soot or carbon deposition. Therefore, special consideration is necessary to achieve the appropriate overall sulfur recovery. In this paper, some configurations available to treat lean acid gas streams are described and the most appropriate ones are studied to overcome low H2S concentration problems. As a result, overall sulfur recovery is investigated for feed preheating and hot gas configurations.

*Keywords*—Sulfur recovery unit, Low H2S content

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 Claus process is employed to convert hydrogen sulfide to elemental sulfur. This process was developed by Carl Friedrich in 1883 [2]. Several modifications were developed on the process to increase the overall conversion of sulphur and produce a tail gas which satisfies the environmental regulations. 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 because of low sulfur market price; nevertheless, they are necessary to match all stringent environmental regulations [4].

The modified Claus process consists of a high temperature

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front-end reaction furnace, followed by catalytic reaction stages. This process continues to be the most widely used process for the conversion of H2S 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 reactions occurring in the furnace are numerous. Several authors have attempted to delineate the important ones [5,6,7]. The overall reaction characterizing the process is as follows [4],

$$2H_2S + O_2 \Rightarrow S_2 + 2H_2O \qquad (1)$$
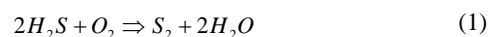
A key reaction that occurs in front-end reaction furnace is a two-step sequence, 1/3 of the acid gas is oxidized to SO2 using air,

$$H_2S + \tfrac{3}{2}O_2 \Rightarrow SO_2 + H_2O \qquad (2)$$
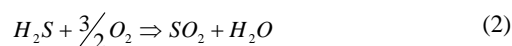
This combustion generates a large amount of heat. Further, the combustion products undergo Claus reaction between H2S and SO2,

$$2H_2S + SO_2 \Leftrightarrow \tfrac{3}{2}S_2 + 2H_2O \qquad (3)$$
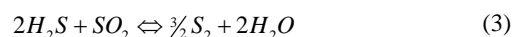
Reaction 3 is a reversible exothermic reaction. Thus, processing under adiabatic condition greatly increases temperature, which lowers equilibrium conversion to about 75%. Effluent gas from the reaction furnace passes through a waste heat boiler (WHB) to recover heat and produce high-pressure steam. 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 [7].

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 [1,8]. 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 inter-stage cooling and sulfur condensation [9].

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 [10]. Processing a lean acid gas requires some special consideration be given to the operation of the burner. A Claus furnace feed containing a relatively low concentration of H2S may be incapable of producing a stable flame. Also, incomplete

combustion of hydrocarbons in the feed can lead to deterioration of the catalyst in the reactors due to soot or carbon deposition [11].

Theoretical equilibrium conversion of H2S to elemental sulfur (see equation 1) could be enhanced by increasing the reaction furnace temperature [12]. Furthermore, the amount of CS2 which is a byproduct of reaction furnace will be decreased by increasing the furnace temperature [13]. Therefore, the reaction furnace is better to operate at high temperature. Although, it should not exceed 1400 °C in order not to exceed the maximum temperature limitations of the equipment materials and refractory [14,15].

There are several configurations available to treat lean streams, multi-bed Claus, acid gas preheating, fuel gas burner, acid gas bypass around the furnace, and oxygen enrichment of the combustion air. Having a stable flame in the burner needs using acid gas preheated to about 260 °C and fuel gas burned separately using a special burner. Alternatively, bypassing a portion of the feed around the furnace can solve the problem of insufficient combustibles in a lean acid gas. The bypassed gas is mixed with the burner effluent prior to the WHB. The amount of oxygen fed to the burner is the same as the amount that would be required to burn the entire stream, resulting in an increased flame temperature. One consequence of bypassing gas around the burner is that any hydrocarbons in the bypassed gas are not combusted, which may lead to problems in the downstream catalyst beds [10,11]. Another way for increasing the temperature of reaction furnace is using fuel gas. If fuel gas is added to the reaction furnace, the hydrocarbon has the effect of increasing the COS and CS2 initially, but as the temperature increases further with added fuel gas, the CS2 content drops off significantly [13]. Although, using fuel gas will increase the utility consumption of SRU, it can be applied together with feed preheaters.

Regarding above discussions, the first method, i.e. using air and acid gas preheaters seems to be the best alternative for increasing the reaction furnace temperature and is studied in this paper as a case study.

As mentioned before, the chemical reactions that can occur in the reaction furnace are numerous and many byproducts such as carbon disulfide (CS2) and carbon carbonyl sulfide (COS) are produced. These compounds can often contribute from 20 to 50% of the pollutants in the tail-gas [14,16-18]. Furthermore, presence of O2 traces in the CS2 - H2O mixture caused a decrease in the activity of alumina and titania catalysts due to sulfate formation [15]. Therefore, COS and CS2 should be hydrolyzed in the catalytic converter [19,20], as shown below:

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

$$CS_2 + 2H_2O \Rightarrow 2H_2S + CO_2 \qquad (5)$$
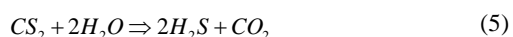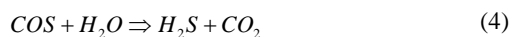
The temperature of the first catalytic reactor is maintained at about 350 °C to hydrolyze COS and CS2, while that of the subsequent reactors is just above the sulfur vapor dew point [21]. Transition metal oxides can be used to modify gamma-alumina to form a catalyst that is effective at temperatures higher than the dew point of sulfur [22-24].

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 [12].

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 [12].

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 SO3, 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 [12].

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 [12].

Regarding above discussions, the first method, i.e. the hot gas bypass method, seems to be the best alternative for reheating the process gas entering to first converter and is studied in this paper.

II. ADJUSTING REACTION FURNACE TEMPERATURE

As mentioned before, acid gas feed together with combustion air is normally fed to plant without any preheating. At this condition, the temperature of acid gas and air mixture is about 94 °C, and the overall sulfur recovery is equal to 96.5 percent. Furthermore, the reaction furnace temperature is 820 °C which is not appropriate for solving the unstable flame and hydrocarbon destruction problems. Therefore, in order to investigate the effect of feed preheating on the reaction furnace temperature, a typical unit of Claus sulfur recovery is considered. Then, the temperature of acid gas and combustion air are increased simultaneously. The schematic shape of such a modified two-stage SRU plant with feed preheating is shown in figure 1. Moreover, the conditions

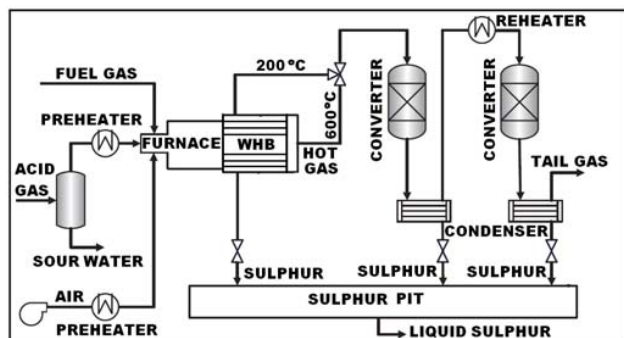of acid gas feed stream is presented in table 1.

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

There are some important constraints which limits feed preheating. As is shown in Figure 2, the temperature of preheating directly affects burner outlet temperature. Since there is a maximum allowable temperature for the reaction furnace in terms of material resistance and corrosion allowance, therefore, we can preheat just up to a limited degree. Furthermore, since we use often HPS (High Pressure Steam) as heating medium, heating over than about 250 ℃ is not achievable. Moreover, preheating more than 250 ℃ polymerize BTX components (benzene, toluene, and xylene) which may deposit into the heat exchanger tubes and increase the pressure drop.

Figure 2 shows that at the feed temperature of 250 ℃, the burner outlet temperature is about 905 ℃. At this point, the

TABLE I
THE CONDITIONS OF ACID GAS FEED STREAM

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

overall sulfur recovery is equal to 96.6 percent. As mentioned before, at this temperature. i.e. 900 ℃, unstable flame and hydrocarbon destruction are considerable problems yet. Therefore, the fuel gas should be applied together with feed preheaters to reach appropriate furnace temperature. Firstly, the temperature of gas feed is set at 250 ℃ using preheaters. Then, the flow rate of fuel gas is increased gradually. Figure 3 shows the changes in the reaction furnace temperature vs. fuel gas molar flow rate. As is shown in this figure, adding 35 Kmole/h fuel gas (natural gas), increase the temperature of reaction furnace up to 1050 ℃ which seems to be an appropriate temperature. The overall sulfur recovery of unit at this point is about 95.5 percent which is a bit smaller than performance of the unit before using fuel gas.
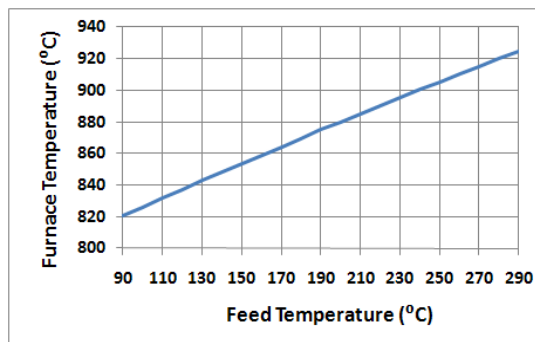

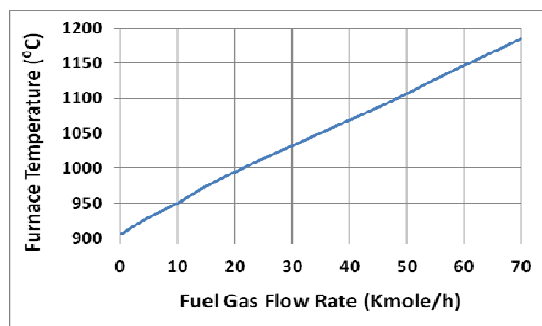Fig. 2 Burner outlet (furnace) temperature vs. feed temperature

Fig. 3 Burner outlet (furnace) temperature vs. fuel gas flow rate

III. ADJUSTING FIRST CONVERTER TEMPERATURE

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 4 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 ℃ 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.
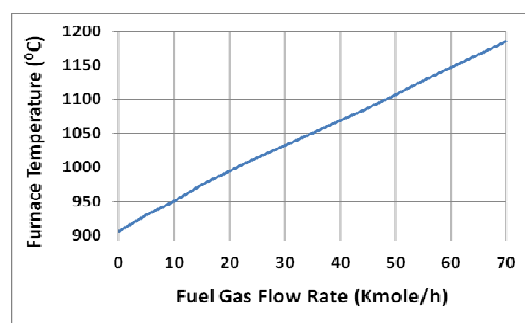

Fig. 4 The changes in temperature of first converter inlet stream vs. hot gas split ratio

IV. CONCLUSION

The modified Claus process is commonly used in oil refining and gas processing to recover sulfur and destroy contaminants formed in upstream processing. A Claus furnace

feed containing a relatively low concentration of H2S may be incapable of producing a stable flame. Also, incomplete combustion of hydrocarbons in the feed can lead to deterioration of the catalyst in the reactors due to soot or carbon deposition. Therefore, special consideration is necessary to achieve the appropriate overall sulfur recovery. In this paper, some configurations available to treat lean acid gas streams were described and the most appropriate ones was studied to overcome low H2S concentration problems. The achieved result show preheating acid gas feed and using hot gas to reheat first converter inlet stream is appropriate methods in sulfur recovery units.

ACKNOWLEDGMENT

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