Effect of O₂ Concentration on the Reaction Furnace Temperature and Sulfur Recovery Using a TSWEET® Process Simulator

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Abstract
In the present study, effect of a parameter for increasing the reaction furnace temperature and sulfur recovery of Claus sulfur recovery units (SRUs) is investigated by TSWEET process simulator based on Gibbs free minimization. The effect of oxygen enrichment on the reaction furnace temperature and sulfur recovery has been studied by proposed simulator. In the case of the effect of O₂ concentration, temperature of main burner increased monotonically. It is found that sulfur recovery (in the O₂ high concentrations) increases up to a maximum value and then decreases with increase of O₂ concentration, while this is not the case for O₂ low concentrations.

Keywords: Sulfur recovery; O₂ concentration; Reaction Furnace; Claus unit

Introduction
Sulfur recovery unit (SRU) is an important unit in natural gas processing units. It removes H₂S from acid gas feed before they can be released into the environment [1]. H₂S exists mainly as an undesirable by-product of gas processing units [2]. Different processes are applied to recover sulfur from H₂S. The most widely used process is Claus process [1,3]. It should be noted that several modifications were developed on the main Claus process in order to increase the overall sulfur recoveries.

The sulfur recovery requirements range from 97.5 to 99.8% for gas processing units and refining facilities processing 10 LT/d and greater of natural gas [4]. By increasing the number and type of beds in the case of rich acid gas feed, the sulfur recovery increases from 96.1% to 99.3%. In the case of lean acid gas feed, the sulfur recovery increases from 96.1% to 96.6%.

Recently, a number of studies have been studied the reaction furnace of Claus units. As the fraction of the AG splitter flow to main burner increased, initially the temperature of the main burner increased to a maximum temperature but it then decreased sharply as the flow was further increased. This was true for all three concentrations of oxygen [5]. However, if the concentration of H₂S, the H₂S/CO₂ ratio and the flow rate of air are increased, the temperature of the main burner increased [5].

In this paper, the simulation of Claus process was done, and also effect of O₂ concentration on the reaction furnace temperature and sulfur recovery is investigated. For these purposes, intake air and acid gas feed are classified into three different categories in terms of their composition. The first type contains 21 mol% of O₂ and 30 mol% of H₂S (usual feed and input air). The second type includes 50 mol% of O₂ and 50 mol% of H₂S. The last type contains 50 mol% of O₂ and 90 mol% of H₂S (O₂ enriched air–H₂S reach feed).

Methodology
Research methodology consists of a review on O₂ concentration (in the tail gas ratio of 2:0) effect on the reaction furnace temperature and sulfur recovery of Claus unit using a process simulator called TSWEET.

Figure 1 shows the flow diagram of the Claus unit. In this process, the acid gas (acid gas + fuel gas) enters SRU and is divided into two streams in the AG splitter. A part of the feed stream is sent to the main burner, and another part is sent to the acid gas heater (for hydrolyzing sulfur components to H₂S). 1/3 of H₂S in the acid gas is oxidized to SO₂ at the main burner using outlet air of air blower.

\[ H_2S + \frac{3}{2}O_2 \leftrightarrow SO_2 + H_2O \] (1)

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

\[ 2H_2S + SO_2 \leftrightarrow 3/2S_8 + 2H_2O \] (2)

Where n is in the range of 6-8. Reaction (2) is exothermic and reversible, thus, processing under adiabatic conditions increases temperature.

The effluent gas from the main burner (reaction furnace) passes through the first pass waste heat boiler (1st pass WHB) to recover heat and produce high pressure steam [1,6]. The second pass of the waste heat boiler is where the redistribution of S₂ to S₈ is the primary reaction. It should be noted that, side reactions involving hydrocarbons and CO₂ in the acid gas feed can result in the formation of carbonyl sulphide (COS) and carbon disulfide (CS₂) in the main burner [7]. The effluent streams from the 2nd pass WHB and acid gas heater is cooled in condenser 1 to condense and recover the liquid sulfur. The effluent gas of the condenser 1 is preheated in the reheater 1 and is sent to the catalytic converters where Claus reaction occurs at lower temperatures. This leads to higher equilibrium conversion because Claus reaction is exothermic.

Typically, COS and CS₂ are also hydrolyzed in the first catalytic converter according to the following exothermic reactions [2]:

\[ CO_2 + H_2O \rightarrow CO + H_2S \] (3)

\[ CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S \] (4)

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The first converter normally operates at temperature high enough to hydrolyze COS and CS₂. Usually, the catalysts, based on γ- Al₂O₃ or TiO₂, are used in the process [8]. Sulphate is formed on the γ- Al₂O₃ catalyst when a mixture of H₂S/SO₂ or H₂S and SO₂ separately, passes on the catalyst at industrial conditions [9]. Sulfur is recovered after each catalytic stage by cooling converter effluent gases in sulfur condensers. Finally, effluent gas from the process is incinerated to SO₂ and vented to the atmosphere.

The simulation was performed using the TSWEET (copyright® 2007, Bryan Research & Engineering, Inc.) version 2.0 (PROMAX). PROMAX is a powerful and jack of all trades stream based process simulation pack. It is used by engineers around the world to design and optimize gas processing, refining, and chemical processes.

TSWEET assumes that the Claus beds operate at equilibrium conversions equal to 95% and it also assumes 4 lb of sulfur/100 lb moles of gas are entrained in the sulfur condensers [10]. This simulator uses three unit operations (main burner, 1st pass WHB, 2nd pass WHB) to model the burner/waste heat boiler [10,11]. The burner unit operation simulates the combustion of acid gas, with COS and CS₂ formation being calculated by NSER 1993 correlation [12]. This correlation predicts the concentration of COS, CS₂, CO, H₂, and/or S₂ out of the burner. The correlation appears to be most accurate when NH₃ present.

The reaction furnace (modeled as the first pass of the waste heat boiler) is where large amounts of free sulfur, hydrogen and water recombine into H₂S and SO₂. The typical output temperature is about 315°C. The 2nd pass WHB is where the redistribution of S₂ to S₈ is the primary reaction, which the typically outlet temperature is about 315°C.

**Results and Discussion**

The first role of the reaction furnace in the Claus unit is to partially oxidize H₂S in the acid gas feed to SO₂ and it will also produce a significant amount of the total produced sulfur. A second role of the reaction furnace is to ensure of the destruction of other contaminants of the acid gas feed stream. This will ensure that these compounds do not break through the downstream process unit, where they can have a significant detrimental effect on the Claus catalyst activity. Therefore, it is critical to understand the effect of furnace operating parameter on the reaction furnace temperature and overall sulfur recovery.

There are different techniques to change the furnace temperature and sulfur recovery, including, O₂ concentration. The effect of this parameter on the reaction furnace temperature and sulfur recovery of the Claus unit is investigated by TSWEET simulator.

**Oxygen enrichment**

Many units are using oxygen enriched air in their SRUs for many reasons [9,13-15]. In most cases, oxygen enrichment is used to raise the throughput capacity of the plant. However, in some particular cases, oxygen enrichment has been used to improve the reaction furnace temperature. In some cases this has allowed for the processing of highly lean acid gas feed and in others it has utilized for better overall furnace and burner operation. The oxygen enrichment should be used with care. The accuracy control of the mixing of combustion gases is an essential factor in avoiding oxygen breakthrough into the catalytic converters. The poor concord in the combusting gases led to unreacted oxygen being accessible in the gas to further oxidize SO₂ or SO₃, either before the gas stream reached the catalyst bed, or on the catalyst bed itself. This SO₃ then reacts with the alumina catalyst and depraves it by forming aluminium sulphate. The SO₃ may also react with H₂O to produce sulphuric acid, which is corrosive for steel equipments [16].
In this study, using TSWEET simulator, effect of O2 concentration on the sulfur recovery and furnace temperature of unit was investigated.

It is concluded that increasing concentration of O2, temperature of main burner has increased monotonically (significant direct effect). As is found that sulfur recovery (in the O2 high concentrations) increases up to a maximum value and then decreases with increase of O2 concentration, while this is not the case for O2 low concentrations. Whereas, it is concluded that as oxygen concentration changes in the range 5-95%, sulfur recovery in 30% mol H2S was increased from 98.2 to 98.57%.

As seen in the figures 2a and b, by increasing oxygen concentration, in tail gas ratio of 2.0 (optimal ratio) [5], reaction furnace temperature increases. Increased H2S concentration in acid gas feed led to increase the reaction furnace temperature. In 30 mol% of H2S, temperature of the main burner increased from 598°C to 2000°C. In concentrations of 50 and 90 mol% of H2S, reaction furnace temperature was changed from 598°C to 2498°C and 624°C to 3143°C, respectively. Comparing these data with real ones indicates that when ratio of tail gas is 2.0, main burner temperature increases more. However, it is a general diagram because main burner temperature should be in the range of 700°C to 2000°C. The advantage of this study in comparison with other ones is that main burner temperature increases up to a maximum value and then decreases with increase of oxygen concentration.

To specify allowable range of oxygen concentration (in proportion to allowable range of reaction furnace temperature).

In this section the effect of oxygen concentration on sulfur recovery rate while changing the temperature of reaction furnace mentioned in the previous section has also been studied. Optimal temperature of reaction furnace is a temperature in which more sulfur recovery is obtained. So, in this study the changes in the rate of sulfur recovery were studied with respect to oxygen concentration in the intake air into the Claus unit. As seen in figures 2c and 2d, in 30 mol% of H2S concentration, sulfur recovery was increased relatively however in 50 and 90% concentrations first it was increased to a maximum, and then decreased with a sharp slope. It is concluded that in 30 mol% of H2S concentration, higher reaction furnace temperatures are required. However, in 50 and 90 mol%, optimum temperature was obtained in a specific concentration.

Also, as seen in figures 2c and 2d, as oxygen concentration changes in the range of 95-5%, sulfur recovery in 30 mol of H2S concentration was increased from 98.2 to 98.57%. However, in 50 and 90 mol% of H2S sulfur recovery had maximums in concentrations of 10 and 15 mol%, respectively. Optimal temperatures of reaction furnace corresponding to the values of sulfur recovery were 1271°C and 1050°C, respectively.

It is also concluded that increasing the concentration of H2S in acid gas feed leads to decrease in reaction furnace temperature.

### Conclusion

In this study, using TSWEET simulator, effect of O2 concentration on the sulfur recovery and furnace temperature of unit was investigated.

It is concluded that increasing concentration of O2, temperature of main burner has increased monotonically (significant direct effect). As is found that sulfur recovery (in the O2 high concentrations) increases up to a maximum value and then decreases with increase of O2 concentration, while this is not the case for O2 low concentrations. Whereas, it is concluded that as oxygen concentration changes in the range 5-95%, sulfur recovery in 30% mol H2S was increased from 98.2 to 98.57%.

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