The Optimization of Sulfur Recovery Unit Using TAWEEET Simulator

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Abstract
In this sulfur recovery unit (SRU), hydrogen sulfide (H₂S) is converted to elemental sulfur using modified sulfur recovery unit. In the present study, first the simulation of Claus process has been considered using a process simulator called TSWEET then the effect of H₂S concentration, H₂S/CO₂ ratio and acid gas flow of AG splitter in three different concentrations of oxygen (in input air into the unit) on the main burner temperature and sulfur recovery have been studied and compared. It is shown that temperature of the main burner increases up to maximum temperature increasing fraction of AG splitter flow to main burner then it is reduced by a sharp slope; this is true for all three concentrations of oxygen. However, if two other parameters (concentration of H₂S and H₂S/CO₂ ratio) increase, temperature of main burner increases monotonically; this increase has different slopes depending on oxygen concentration in input air. Also in this paper it is shown that recovery rate of sulfur increases up to a maximum value then decreases as H₂S concentration and H₂S/CO₂ ratio (in all three concentrations of oxygen) increase. If 70-85% acid gas feed are entered the main burner, more optimal sulfur recovery rate than other flows would be achieved.

Keywords: Acid gas, Concentration of H₂S, H₂S/CO₂ ratio, Sulphur recovery, AG splitter flow, Claus unit.

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1. Introduction:

Sulphur recovery is an important refinery processing unit (SRU). It removes H₂S from acid gas streams before they can be released into the atmosphere (Bishtawi & Haimour, 2004). Furthermore, in industrial world H₂S exists mainly as an undesirable by-product of gas processing (Zarenezhad, 2009). Different processes are used for recovering sulphur from H₂S. The most widely used process is Claus process (Bishtawi & Haimour, 2004; Polasek & Bullin, 1993).

Recently, a number of studies have been performed on main burner and sulfur recovery in this process which are mentioned below. Wen et.al (1987) studied empirical prediction of CO, COS, CS₂ and H₂ through minimum equilibrium calculations of free energy. There is a study by Dowling in 1990 from Calgary University of Canada, on decomposition reaction of H₂S into hydrogen and sulfur which is one of reactions occurring in main burner and its kinetic was determined indicating that this reaction is performed very quickly and that in low temperatures the forward reaction and in high temperatures reverse reaction occur. Kinetic obtained for forward reaction is first order analysis reaction of H₂S (in general second order) and for reverse reaction (production of hydrogen sulfide) is first order too.

Reaction kinetic of formation of carbonyl sulfide has been determined through combination of carbon monoxide and hydrogen sulfide. Zarenezhad and Hosseinpour (2008) compared real data and data obtained from Gibbs minimization free energy and concluded that data obtained from this model is consistent with real data.

Claus process was developed by Carl Friedrich in 1883 (Fisher, 1974) in which an overall sulfur recovery of 94-97 % was achieved. Several modifications were developed on the main process in order to increase the overall sulfur recovery which is mentioned here. The sulfur recovery requirements range from 97.5% to 99.8% or higher for gas processing and refining facilities processing 10 LT/d and greater (Blevins, 1993). The higher recovery of 99.8+% is required for most facilities with 20 LT/d and higher (Polasek & Bullin, 1993; Covington & McIntyre, 2002). Changing the number and type of beds in the rich acid gas feed, the sulphur recovery rate increases from 96.1% to 99.3% while, in the case of lean acid gas feed, using modifications such as acid gas bypass and acid gas bypass with oxygen enrichment, causes to enhancement of the sulphur recovery from 96.1% to 96.6% (Mcintyre & Lyddon, 1997; Lins, & Guimaraes, 2007).

In the present paper, at first Claus process, then concentration effect of H₂S, H₂S/CO₂ ratio and acid gas flow of AG splitter were studied. For the purposes of this article, intake air is classified into three different categories in terms of composition and types of acid gas bypass with hot gas bypass Claus processes. The first type of intake air is diluted air, or intake air containing 21 mole % O₂. The second Type is medium air, or intake air containing 50 mole % O₂. The last type is enriched air, or intake air containing 85 mole % O₂.

2. Methodology

Research methodology consists of review and comparison of the effect of H₂S concentration, H₂S/CO₂ ratio and fraction of acid gas flow to main burner in three different concentrations of oxygen on the reaction furnace temperature and sulfur recovery using a process simulator called TSWEET.

Fig. 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 stream comes to main burner, and another part comes to acid gas heater (for hydrolyzing sulphur components to H₂S). 1/3 H₂S in the acid
gas is oxidized to $\text{SO}_2$ at the main burner using outlet air of air blower:

$$\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \leftrightarrow \text{SO}_2 + \text{H}_2\text{O} \quad (1)$$

This combustion generates a large amount of heat. Further, the combustion products undergo Claus reaction between $\text{H}_2\text{S}$ and $\text{SO}_2$.

$$2\text{H}_2\text{S} + \text{SO}_2 \leftrightarrow \frac{3}{n}\text{S}_n + 2\text{H}_2\text{O} \quad (2)$$

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 passes through the first pass waste heat boiler ($1^{st}$ pass WHB) to recover heat and produce high pressure steam (Bishtawi & Haimour, 2004; Boussetta, Lanoiselle, Bedel-Cloutour, & Vorobier, 2009). The second pass of the waste heat boiler is where the redistribution of $\text{S}_2$ to $\text{S}_8$ is the primary reaction. Furthermore, side reactions involving hydrocarbons and $\text{CO}_2$ in the acid gas feed can result in the formation of carbonyl sulphide (COS).

Figure 1: Flow diagram of simulated Claus process.
carbon disulfide (CS2) in the output of the main burner (Zarenezhad & Hosseinpour, 2008). The effluent streams from the 2
pass WHB and acid gas heater is cooled in condenser 1 to condense and recover sulphur. The effluent gas of the condenser 1 is preheated in the reheater 1 and is sent to three catalytic converters where Claus reaction occurs at lower temperature. 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 (Zarenezhad, 2009):

\[
\begin{align*}
\text{COS} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2\text{S} \quad (3) \\
\text{CS}_2 + 2\text{H}_2\text{O} & \rightarrow \text{CO}_2 + 2\text{H}_2\text{S} \quad (4)
\end{align*}
\]

The first converter typically operates at temperature high enough to hydrolyze COS and CS2.

Usually, the catalysts, based on γ-Al2O3 or TiO2, are applied in the process (Zagoruiko & Matro, 2002). Sulphate is formed on the γ-Al2O3 catalyst when a mixture of H2S/SO2 or H2S and SO2, separately, are passed on the catalyst at industrial conditions (Clarke, et al. 2001).

Sulphur is recovered after each catalytic stage by cooling converter effluent gas in a sulphur condenser. Effluent gas from the process is incinerated to SO2 and vented to 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 facilities. PROMAX is built on technology proven over the past 30 years. Its predecessors, TSWEET and PROSIM, are comprehensively recognized by the industry for their authenticity and efficiency. TSWEET and PROSIM®, the predecessors of PROMAX, are renowned in gas processing, refining and chemical industries for their accuracy, efficiency and ease-of-use. TSWEET has often been used as the industry standard for amine sweetening, sulfur recovery and tail gas cleanup modeling while PROSIM has been used for its multi-faceted common purpose simulation capabilities.

TSWEET will assume that the Claus beds operate at 95 percent of equilibrium conversion and 4 (lb) sulfur/100 Moles of gas are entrained in the sulfur condensers (Mattsson & Lyddon, 1997). TSWEET used three unit operations (main burner, 1st pass WHB, 2nd pass WHB) to model the burner/waste heat boiler (Mattsson & Lyddon, 1997; Lins & Guimaraes, 2007). The burner unit operation simulates the combustion of acid gas, with COS and CS2 formation being calculated by NSER 1993 correlation; 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 no sour gas (NH3) is 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 1200°F (600°C) since all significant reactions other than sulfur redistribution have ceased in 1200°F. The 2nd pass WHB is where the redistribution of S2 to S8 is the primary reaction, which the typically outlet temperature is about 600°F.

3. Results and discussion

The first role of the Claus unit reaction furnace is to partially oxidize H2S in the acid gas feed to SO2 and it will also produce a significant segment of the total sulphur product. A second role of the reaction furnace is to ensure destruction of many contaminants in 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 parameters on the reaction furnace temperature and overall sulphur recovery in the concentrations of oxygen.

There are different techniques to change the furnace temperature and sulphur recovery, including, concentration of H₂S in the acid gas feed, H₂S/SO₂ ratio and fraction of AG splitter flow to main burner. The usefulness of all of these methods in changing the furnace temperature and sulphur recovery are investigated by a process simulator at three different concentrations of oxygen (diluted, medium and enriched) in the input air to the simulated Claus unit. Of course, all results of this paper were obtained in constant conditions of flow rate of acid gas (108 lbmole/ hr).

### 3.1 Acid gas enrichment

In this section, using TSWEET, concentration effect of H₂S and H₂S/CO₂ ratio in acid gas feed in different concentrations of oxygen (in input air) on temperature of main burner and sulfur recovery were studied.

With the advent of selective amine systems, it is possible to enhance the quality of an acid gas stream in an amine treating unit (Maddox, 1998).

Acid gas enrichment has two important advantages:

1. Providing a high quality acid gas for processing in a Claus SRU.
2. Reducing the acid gas flow rate and size of SRU.

Enrichment of acid gas should be utilized with care, considering the Claus process features. If a lack of air occurred, less than 1/3 of H₂S would react and the H₂S would then be in excess. While in contact with a H₂S environment there are different forms of carbon and stainless still corrosions namely, sulfide stress cracking, hydrogen stress, cracking, hydrogen blistering, localized corrosion (Roberge, 1999; Chen, Liou, & Shih, 2005; Ramos, Mainier, & Pimenta, 1982) and cracking in the welded region. H₂S increases the speed of the hydrogen absorption in steel (Vagapov, Frolova, & Kuznetsov, 2002). Hydrogen sulfide reacts with iron in the presence of water and the produced hydrogen moves to the high stress concentration regions in the metal. When there is hydrogen in steel, it facilitates the motion of the linear effects in the crystalline structure of metal.

So we fixed the ratio of tail gas in 2.0 in order to not changing the ratio H₂S/SO₂ and being constant in 2.0 in all input concentrations of H₂S. The ratio is controlled by manipulating the flow rate of inlet air from the blower to the main burner (Mcintyre & Lyddon, 1997).

The effect of increasing the H₂S content of the acid gas on the main burner is predicted by the process simulator in Fig. 2a and b. It is obvious that increasing the H₂S content of the acid gas will significantly increase the main burner temperature.

As seen in the Fig. 2a and b, when concentration of H₂S in acid gas feed is 5 mole%, temperature of main burner in all three concentrations of oxygen in input air is the same and equal to 1000 °F and as H₂S concentration increases the difference between lines are increased.

As concentration of oxygen increases in constant concentration of H₂S, the distance between three diagrams becomes low or temperature difference of main burner becomes less. For example when concentration of H₂S in the acid gas feed is 50% mole, temperature of main burner is 2900°F (21% mole oxygen), 4020°F (50% mole oxygen) and 4450°F (85 % mole oxygen) respectively, in which temperature difference in the first and second cases is about 1120°F and in the second and third cases is 430°F.
When concentration of oxygen in input air into simulated Claus unit is 21% mole, by changing concentration of H$_2$S in the range 5-95%, temperature of main burner increases from 1000°F to 3387°F, indicating an increase of 2390°F. However, in the cases in which oxygen concentrations in input air are 50% and 85% temperature of the main burner (by rising concentration of H$_2$S) has increased from 1000°F to 5041°F and 1000°F to 5700°F in which the increase extent of the main burner is 4041°F and 4700°F respectively. So, as oxygen concentration increases, temperature of the main burner (by changing H$_2$S) increases more.

As studied in Fig. 2a and b, the temperature of main burner inconsistently increases as H$_2$S concentration existing in acid gas feed increases while recovery rate of sulfur increases up to a maximum value then decreases by different slopes (as seen in Fig. 2c and d). Here column graphs (Fig. 2d) are used to shed light on variability of recovery rate of sulfur relative to H$_2$S concentration. As seen in the graph, maximum recovery percent of sulfur is 98.58% (21% mole oxygen), 98.64% (50% mole oxygen), and 98.66% (85% molar oxygen); this maximum rates have been obtained in H$_2$S concentrations in the range 25-30% mole (in all three concentrations of oxygen). Also as seen in Fig. 2d, in concentrations lower than 35% mole, recovery rate of sulfur in the case of 58% mole oxygen has been doubled with respect to the other two. However, in concentrations higher than 35% mole for H$_2$S contained in acid gas feed, recovery rate of sulfur in 21% mole oxygen is more than the other two. Of course, other results can be derived from this figures which are obvious.

As seen in Fig. 3a and b, as H$_2$S/CO$_2$ ratio increases in acid gas feed, temperature of main burner in all three concentrations of oxygen in air increases proportionally and also temperature of main burner in H$_2$S/CO$_2$ ratio of 0.05 is the same for all three concentrations of oxygen and equal to 1000°F. When oxygen concentration is 21 mole%, temperature of main burner increases rapidly until H$_2$S/CO$_2$ ratio reaches 0.8; this increase is 1800°F; but in ratios higher than 0.8, temperatures of main burner has changed slightly which is an increase of 583°F. However, for oxygen concentration of 50%, temperature of main burner has increased rapidly until the ratio of 1.0 which is 329°F. But in H$_2$S/CO$_2$ ratios above 1.0, temperature of main burner has increased from 4290°F to 5041°F. In the case oxygen concentration in input air into Claus unit is 85%, temperature of main burner has increased rapidly as ratio H$_2$S/CO$_2$ increases to ratio of 1.223 but in ratios above this, an increase of 1000°F was obtained for the temperature of main burner. Also seen in Fig. 3a and b, as oxygen concentration in input air to Claus unit increases in a constant H$_2$S/CO$_2$ ratio in acid gas feed, the distance of each diagram respect to pervious one was shortened or in other words, temperature difference of main burner has become less as oxygen concentration increased. For example, temperature of main burner in H$_2$S/CO$_2$ ratio of 4.0, in the first case (21mole% oxygen) is 3270°F, in the second case (50 mole% oxygen) 4760°F and in the third state (85 mole% oxygen) is about 5380°F.

The output value of H$_2$S and CO$_2$ from stripper tower of gas sweetening unit is different depending on amine type used in this unit so that the effect of the ratio H$_2$S/CO$_2$ on the recovery rate of sulfur was examined to optimize H$_2$S/CO$_2$ ratio and recovery rate of sulfur according to this ratio (Fig. 3c and d). As seen in this figures, recovery rate of sulfur first increases up to a maximum value then decreases by different slopes (in proportion with different concentrations of oxygen). Maximum value of sulfur recovery in each concentration of oxygen is 98.58% (21 mole oxygen), 98.64% (50% oxygen) and 98.66% (85% mole oxygen), respectively. These values have
been obtained in ratios of 0.45, 0.33 and 0.33 respectively which is the same in two concentrations of 50% and 85% mole oxygen.

The results discussed as to the effect of H₂S concentrations (Fig.2a and b) and H₂S/CO₂ ratio (Fig. 3a and b) on the reaction furnace temperature were comprehensive. But there are limitations in using Fig. 2a and b since the temperature of reaction furnaces used in the Claus sulphur recovery units are at least ~1700 °F (for flame stability) and maximum ~2700-3000 °F (Zarenehzad and Hosseinpour, 2008). So according to the Figures, concentration variations of H₂S should be almost in the range 15-55 mole% (21 mole% oxygen), 11-25 mole% (50 mole% oxygen) and 10-22 mole% (85 mole% oxygen). As oxygen concentration increases in the input air, range of H₂S concentration is reduced.
Figure 2: Effect of H$_2$S concentration on the reaction furnace temperature (a,b), and overall sulphur recovery (c,d).

![Graph showing the effect of H$_2$S concentration on the reaction furnace temperature](image_a)

![Graph showing overall sulphur recovery](image_c)

Figure 3: Effect of H$_2$S/CO$_2$ ratio obtained from main stripper of amine sweetening unit on the reaction furnace temperature (a,b), and sulfur recovery (c,d).

![Graph showing the effect of H$_2$S/CO$_2$ ratio on the reaction furnace temperature](image_b)

![Graph showing overall sulphur recovery](image_d)
3.2 Acid gas flow of AG splitter

Modified Claus process has different arrangements. Different kinds of chain arrangements include reaction furnace, condenser, WHB and converter. The difference among different arrangements is in the way they transport feed flow of process. The arrangement used in the present paper is bypass. The reason is that it is used in most of available processes in Iran (Because of low concentration of hydrogen sulfide (H2S) in acid gas feed). In this arrangement, part of acid gas is passed across main burner and WHB and the residue of acid gas (as bypass) is mixed with output gases from converter (WHB).

In the previous sections, 1/3 acid gas entered the main burner and the other 2/3 entered condenser accompanied with output gas of converter (WHB) in order to reuse sulfur in the flow (formed in main burner). However, in this section by changing fraction of AG splitter flow to main burner, the effect of main burner temperature and sulfur recovery (in the case 31 mole% H2S in acid gas feed) has been studied.

As seen in Fig. 4a and b, by increasing fraction of acid gas flow to main burner, temperature of main burner (in all three concentrations of oxygen) increases up to maximum then decreases by sharp slope.

In the case all acid gas flow enter bypass flow following splitter, temperature of main burner is constant for all three concentrations of oxygen and is equal to 220°F. Since oxidization reaction of H2S in the main burner isn't performed, temperature of main burner should be equal to output temperature of air blower (220°F). Also seen in Fig. 4a and b, when oxygen concentration in input air is 21%, temperature of main burner has increased rapidly to 2296°F (maximum) which has been obtained in 35 mole% of acid gas to main burner. In concentrations above 35 mole%, temperature of main burner has decreased with a sharp slope changing from 2296°F to 1363°F. When oxygen concentration in input air is 50 mole%, maximum temperature of main burner in 30 mole% of acid gas to main burner has been obtained to be 3223°F. However, in concentrations above 30%, temperature of main burner has been decreased from 3223°F to 1562°F. Again, in oxygen concentration of 85 mole%, temperature of main burner has increased up to 3607°F (at 30% of acid gas flow entered into the main burner) then decreased to 1565.58°F. It is also concluded from the Figures that by increasing acid gas flow to main burner in concentrations lower than maximum (by increasing oxygen concentration), larger distance between diagrams might be observed and in higher concentrations (temperature difference of main burner) the distance has become shorter.

So far the effect of fraction of AG splitter flow to main burner (Fig.4a and b) on the reaction furnace temperature (in the range of 0-100%) was investigated and the results were analyzed. But there are limitations in using Fig. 4a and b which was mentioned in the previous section. So the fraction of AG splitter flow to main burner must be in range 17-100% (21 mole% oxygen), 7-22% and 37-80% (50 mole% oxygen), 5-15% and 40-85% (85 mole% oxygen).

As said previously, increases in fraction of AG splitter flow to main burner might lead to increase in temperature of main burner up to maximum temperature then it decreases by different slopes (depending on oxygen concentration). However, recovery rate of sulfur has decreased to a minimum value then increased by a deep slope which is different for each concentration of oxygen (as seen in Fig.4c and b). However, this increase continues by a deep slope to a fraction of AG splitter flow to main burner then increases by a very slow slope (slight increase in recovery rate of sulfur). This increase is more than the other two concentrations in the case 85 mole% (21 and 50 mole% oxygen). Recovery rate of sulfur in
fraction of AG splitter flow lower than 30% (70% splitter flow enter bypass) in concentration of 21% mole oxygen is higher than the other two. However, in concentrations 30% and more of AG splitter flow fraction, recovery rate of sulfur in concentration 85% mole oxygen is higher than the other two.

Overall, recovery rate for each concentration of oxygen has increased from 98.66% to 98.62% (21% mole oxygen), from 97.60% to 98.70 % (50% mole oxygen) and from 97.56% to 98.72% (85% oxygen), respectively. Also it is seen in the Fig. 4c and d, if total flow (without bypass) enter main burner, recovery rate of sulfur is less than the case in which flow is 70-85% (in the low concentrations of H$_2$S).

![Figure 4: Effect of fraction of AG splitter flow to main burner (% acid gas flow) on the reaction furnace temperature (a,b), and sulfur recovery (c,d).](image-url)
4. Conclusion

Many Claus sulphur recovery units suffer from poor flow stability and hydrocarbon destruction in the reaction furnace due to a low flam temperature in reaction furnace. In order to reduce this problem, various techniques were investigated by a process simulator, TSWEET, to optimize the furnace temperature, including, changing the concentration of H$_2$S, H$_2$S/CO$_2$ ratio and fraction of AG splitter flow to main burner. Also this process simulator is used for prediction of overall sulphur recovery and the predicted results are compared in three oxygen concentrations. In this study it is concluded that the main burner temperature increases up to a maximum value and then decreases by a sharp slope (Increasing fraction of AG splitter flow to main burner). However, increasing concentration of H$_2$S and H$_2$S/CO$_2$ ratio, temperature of main burner has increased monotonically (significant direct effect). As oxygen concentration in the input air has increased, permissive range of H$_2$S concentration has decreased. In addition it is concluded that sulfur recovery has increased to a maximum value and then has decreased, increasing H$_2$S concentration and H$_2$S/CO$_2$ ratio. If 70-85% acid gas feed entered main burner, more optimal sulfur recovery than other flows would be achieved (tail gas ratio of 2.0).

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