Acid gas fired reheater control

Operating close to the stoichiometric air-to-fuel ratio is advised when operating acid gas fired reheaters

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Modified Claus based sulphur recovery units (SRUs) require successive cooling and reheating of the process gas stream as it passes through several catalytic converter stages. Between each converter, the gas is cooled to condense and remove elemental sulphur, then reheated to allow production of additional elemental sulphur in the next stage. **Figure 1** shows a typical three-converter configuration.

There are several common methods to reheat the stream including indirect steam heat, electric heaters, hot oil, gas/gas, and direct-fired reheaters. This article focuses on direct-fired reheaters which use some of the SRU's acid gas feed as fuel. Acid gas fired reheaters (AGFR) are burners positioned between the sulphur condenser and the next converter bed. The hot combustion gases from the burner are mixed with the main process stream in order to heat it to the desired converter temperature.

Since these reheaters are burners, they require a strategy to control the flow rate of air and fuel (acid gas). One part of this control strategy is determined by the amount of heat release needed to achieve the desired temperature rise in the process stream: this temperature sets the total amount of H_2S combustion needed in the reheater.

After the temperature requirement is set, there is still a degree of freedom left in the control philosophy: should we feed the stoichiometrically required amount of acid gas such that it is all burned, should we feed an excess amount of acid gas so that the combustion products contain a 2:1 ratio of $H_2S:SO_2$, or does the best answer lie somewhere between these two approaches? Here we use a rate-based simulation to explore the process implications of this choice. Specifically, the question to be answered is what effect does the reheater's air-to-acid-gas ratio have on overall sulphur recovery and COS generation?

Process description

The chemistry pertaining to AGFRs is generally similar to chemistry in the SRU thermal reactor (TR), although the process objectives are not identical. One of the primary objectives for the TR is to create the stoichiometric amount of SO_2 that will allow the overall conversion of H_2S to elemental sulphur to proceed as far as possible through the Claus reaction (**Equation 1**). This objective causes the optimal $H_2S:SO_2$ ratio in the TR to be close to 2:1 to match Claus reaction stoichiometry. In contrast, the primary process objective in a fired reheater is simply to liberate enough heat of combustion with a stable flame to achieve the required temperature increase in the process stream.

$$2\,H_2S + SO_2 \leftrightarrow \frac{3}{2}\,S_2 + 2\,H_2O \qquad [1]$$

As per the TR flame control strategy, in order to maintain reliable AGFR operation, it is imperative to have a proper air control system that maintains flame stability to satisfy the required temperature control setpoint. The control scheme should be programmed to allow for independent feed flow measurement on all feed streams to the AGFR burner; this includes amine acid gas and, where applicable,

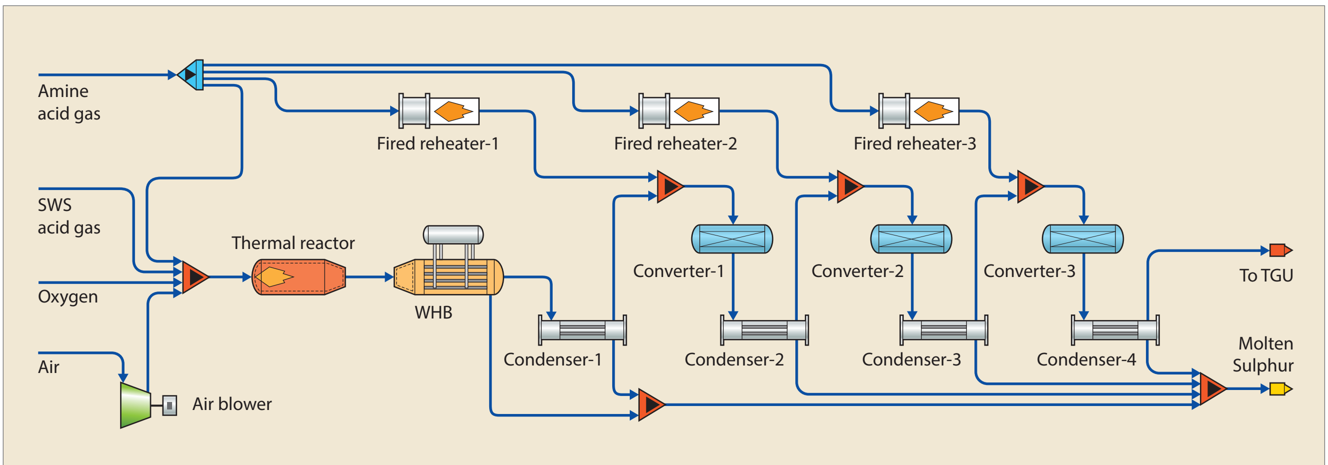

Figure 1 Flowsheet for case study

Flowsheet operating conditions for case study

Amine acid gas feed rate	450 lbmol/h	
Amine acid gas composition	Test Run 1 composition (wet basis)	Test Run 2 composition (wet basis)
	H_2S = 92%	H_2S = 83%
	CO_2 = 5%	CO_2 = 14%
	CH_4 = 0.5	CH_4 = 0.5
SWS gas feed rate	81 lbmol/h	
BTEX composition in SWS	1900 ppmv	
Oxygen enrichment	29%	
Outlet temperature of 1st sulphur converter	650°F	
Outlet temperature of 2nd sulphur converter	~ 485°F*	
Outlet temperature of 3rd sulphur converter	~ 420°F*	

*Temperatures of 2nd and 3rd converters set to maintain 25°F approach to sulphur dew point temperature

Table 1

all fuel gas streams with steam moderation cascaded to fuel gas flow. Each feed stream will have an air demand multiplier that can be adjusted based on composition in order to provide the total flow target dependent on the cascade temperature control setpoint. Air demand requirement for each stream is then fed to a summation block to allow for ratio air control. In gas plants, it is common to have lean amine acid gas with less than 50% H_2S. For lean amine acid gas and/or turndown operation (refinery applications included), it may be necessary to co-fire the burners with supplemental fuel gas to sustain a stable flame.

Another important difference from the TR is vessel size and residence time. TRs typically accommodate most of the acid gas fed to the SRU and provide enough residence time such that slower reactions (including the Claus reaction) can approach thermodynamic equilibrium. Since fired reheaters will typically take only a small percentage of the total acid gas flow, they are designed with much shorter residence times. As a consequence of shorter residence time, kinetically controlled reactions (such as the Claus reaction) will not typically be able to achieve equilibrium in a fired reheater before the hot gases are cooled by mixing with the main process stream.

In reality there are several kinetically controlled reactions taking place in AGFRs in addition to Claus: for example, thermal splitting of H_2S into H_2 and S_2. For the present study we will use Claus as a proxy for all of them. The extent of Claus conversion taking place in a reheater depends on the size and configuration of the equipment. If the residence time is long enough, the reaction will proceed to equilibrium. Conversely, if the residence time is very short, the Claus reaction may not occur to any appreciable extent.

Our study starts with a base case which is burning enough H_2S to achieve the temperature targets for the unit operation. The amount of acid gas fed to the burner (% stoichiometric air-to-fuel ratio) is varied along with the extent that the Claus reaction is allowed to proceed. The primary design and operating decisions discussed in this article address the question as to whether the air and acid gas should be fed in stoichiometric proportions, or should the acid gas be fed in excess? How much does the design of the particular reheater vessel influence this decision?

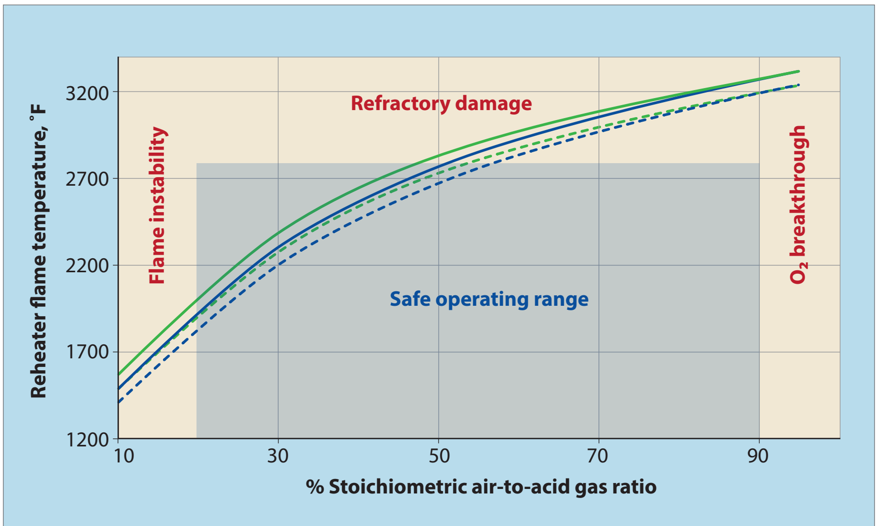

Figure 2 Reheater flame temperature changes with burn strategy. Green lines represent cases with no Claus reaction. Blue lines represent cases with Claus reaction proceeding to equilibrium. Solid lines represent Test Run 1 with higher H_2S concentration in amine acid gas. Dashed lines represent Test Run 2 with lower H_2S concentration. Shaded regions indicate approximate ranges where undesirable effects may occur

Case study

The case study is based on a typical refinery SRU (see **Figure 1**). The unit feed and operating conditions are shown in **Table 1**. Two amine acid gas compositions were used: Test Run 1 with 92% H_2S and Test Run 2 with 83% H_2S. The model includes only the conversion section of the SRU. It does not include the tail gas treating unit (TGTU).

To explore the process implications of reheater operation, we ran a rate based sulphur plant simulation in SulphurPro with varying burn strategies from 30% to 90% of stoichiometric air-to-fuel ratio. The heat release requirement for a reheater does not change very much with burn strategy. Therefore, the air supply to each reheater also does not change very much; instead, we change the amount of excess acid gas sent to the reheater beyond the amount required to consume all the oxygen.

It is difficult to know the extent of Claus conversion that will occur in a reheater because it is a strong function of the size and configuration of the equipment. From a modelling perspective, the uncertainty was bounded by running the models in two different reaction modes to represent the two limiting cases. One limiting case allows all reactions to come to equilibrium by Gibbs energy minimisation which simulates a large reheater with a residence time of 0.5 seconds or more. The other limiting case prevents the Claus reaction from occurring at all, representing a small reheater with a residence time of 0.1 second or less. The behaviour of a real reheater is bounded by these two extremes.

Effect on flame temperature

The most immediate result of differing air-to-fuel ratio in the reheater is on the adiabatic flame temperature (see **Figure 2**). As expected, the hottest temperature is at the stoichiometric air-to-fuel ratio since deviation from this ratio implies the presence of additional unreacted gas which will act as a heat sink. The Claus reaction is endothermic at flame temperatures, so models which inhibit the Claus reaction show slightly higher flame temperatures. Note that for this case study, air-to-acid-gas ratios above 50% lead to flame temperatures that can result in refractory and burner damage.

Effect on sulphur recovery

Perhaps the most important observation from this study is that the reheater burn strategy can affect the overall recovery of the conversion section of the SRU. As **Figure 3** shows, changing the reheater burn strategy can lead to an almost 0.5% loss in sulphur recovery, forcing a larger work load onto the TGTU. (Recall that the TGTU has to handle all of the unrecovered sulphur. Dropping sulphur recovery from 97.3 to 96.9% means an increase from 2.7 to 3.1% not recovered, or 15% more sulphur load to the TGTU.) The cause of this effect is that unconverted and unburned acid gas passing through the reheater is fed to the third sulphur converter which then has more work to do. In the unusual circumstance where the reheaters are large enough to allow the Claus reaction to come to equilibrium this will not be a significant effect, as shown by the converging lines at the right-hand side of both **Figure 3** and **Figure 4**. As discussed, most real plants will lie somewhere between the two extremes shown in these plots.

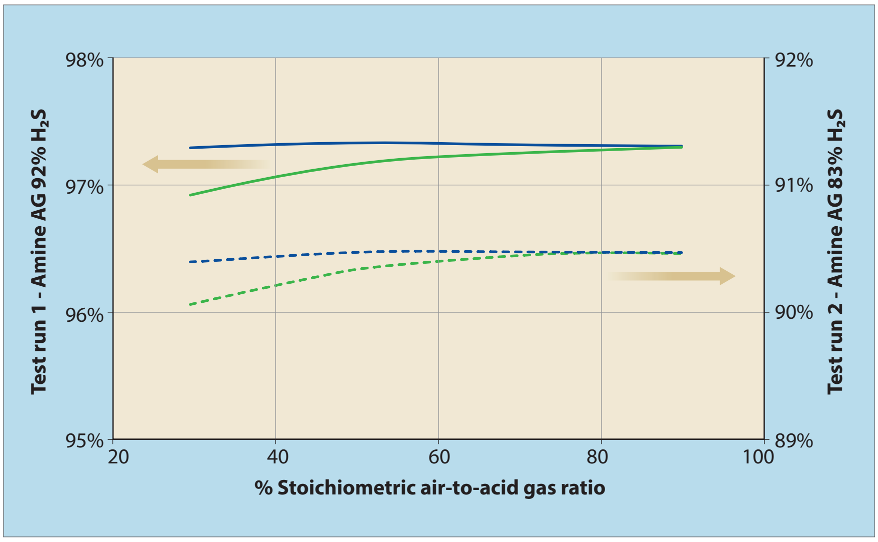

Figure 3 Sulphur recovery changes with burn strategy. Green lines represent cases with no Claus reaction. Blue lines represent cases with Claus reaction proceeding to equilibrium. Solid lines represent Test Run 1 with higher H_2S concentration in amine acid gas. Dashed lines represent Test Run 2 with lower H_2S concentration

Effect on COS sent to TGTU

A final conclusion relates to the amount of COS that reaches the TGTU. In sulphur plants, COS is an undesired by-product created when hydrocarbons are present while acid gas is being burned. Depending on catalyst and operating conditions, an appreciable amount of COS – but not all – is destroyed in the sulphur converter beds. For example, in this case study the three converters destroyed 92%, 45%, and 27% of the COS fed to them. The amount of COS sent to the TGTU here is small relative to the most prevalent sulphur-bearing species (H_2S, SO_2, Sx). Despite its relatively small concentration, the amount of COS sent to the TGTU is important because it is much harder to remove from the tail gas – therefore it disproportionately contributes to emissions.

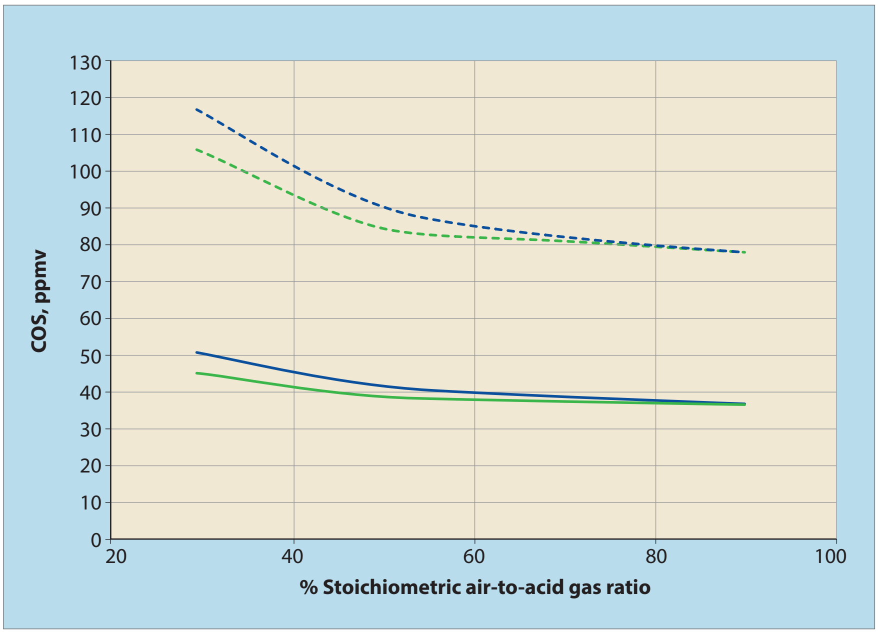

Figure 4 COS sent to TGTU changes with burn strategy. Green lines represent cases with no Claus reaction. Blue lines represent cases with Claus reaction proceeding to equilibrium. Solid lines represent Test Run 1 with higher H_2S concentration in amine acid gas. Dashed lines represent Test Run 2 with lower H_2S concentration

Since burn strategy has a strong influence on reheater flame temperature, it also has a strong influence on the amount of COS generated in the reheater. Lower flame temperatures favour the formation of COS. This relationship is borne out in **Figure 4** which shows that the amount of COS being sent to the TGTU increases when the reheater gets more acid gas than is stoichiometrically required.

Conclusion

Two directional observations have been shown which demonstrate that, from a process chemistry perspective, operating close to the stoichiometric air-to-fuel ratio is beneficial for acid gas fired reheaters.

In a typical reheater, where residence time is too short to allow the Claus reaction to come to equilibrium, any unburned acid gas from the reheater will place an additional load on the following converter bed. When this happens in the last converter, this leads directly to lower overall conversion and recovery across the sulphur plant and a larger load on the TGTU.

Since there is less unburned acid gas passing through the burner, the flame temperature is higher and this has the benefit of inhibiting COS production.

Despite the favourability of stoichiometric operation for process chemistry, mechanical constraints on refractory and equipment often limit the maximum allowable flame temperature.

There are many other parameters which can influence the performance of a particular unit. For example, ageing of the Claus catalyst, lower temperatures in the TR, and shorter residence times without oxygen enrichment. Also, the nature of the Claus process makes it difficult or impossible to directly measure some important performance parameters in the field. For example, the exothermic transition from S2 to S8 will spontaneously occur as samples cool. For these reasons, a high-quality simulation tool is one of the best ways to study the details of sulphur plant operation.

It should be noted that this has been a simplified study structured to provide general learnings about choosing a burn strategy for AGFRs. There are many practical implications of choosing an operating philosophy that were not discussed in this article, including controllability, utility requirements of the unit, and mechanical design of the reheaters themselves.

References

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