Claus Sulphur Recovery Options

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ABSTRACT

Recovery of elemental sulphur from acid gas was first performed via the Claus process over 100 years ago. This article examines some Claus modifications which can alleviate operational difficulties and improve overall sulphur recovery.

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INTRODUCTION

Since its inception, the Claus process has been the standard of the sulphur recovery industry, but limitations and problems relating to composition may restrict its effectiveness. Numerous modifications have been applied to the basic process in an effort to develop the optimum system for a certain set of conditions.

The primary consideration in determining the optimum sulphur removal process is the composition of the acid gas stream to be processed. A typical rich feed gas stream to a Claus plant contains at least 50 percent H_2S by volume (50–60 percent is considered marginal). The traditional Claus plant may be used for primary sulphur recovery from such a rich acid gas stream. Unfortunately, the H_2S content of acid gas is sometimes very low (5–50 percent) with CO_2 making up the bulk of the feed.

This lean feed is not sufficient to sustain combustion in the burner of the traditional Claus reaction furnace, so some modification to the process is required. In addition, acid gas feeds may contain undesirable components such as ammonia and hydrocarbons, which cause problems during processing. Again, the traditional Claus process must be modified to handle these contaminants.

For the purposes of this article, acid gas is classified into three different categories based on composition, and the types of Claus or modified Claus processes that may be used to lower sulphur emissions to an acceptable level are discussed.

The first type of feed gas discussed is rich acid gas, or feed containing greater than 50 mole% H_2S. The second type is lean acid gas, or feed containing less than 50 mole% H_2S. The last type of feed to be considered is acid gas containing ammonia. A process simulator, TSWEET, illustrates how effective various processes are for each of the three acid gas feed types.

CASE STUDIES: 1

Rich acid gas feed – H_2S content above 50 percent

Several options are available for consideration when designing the primary sulphur recovery unit to process a rich acid gas feed. Even though many variations of the standard Claus plant may be suitable, one may have a slight advantage over the others.

Depending on the required sulphur removal, a number of configurations could be used for primary sulphur removal, such as a two or three-bed Claus plant, with or without a direct oxidation bed or cold (sub dew point) bed. These and other variations are compared, based on their ability to effectively process a rich acid gas stream. Figure 1 is a schematic of the basic Claus process. Some of the more common process modifications to the basic Claus, discussed in the following sections, are indicated with dashed lines.

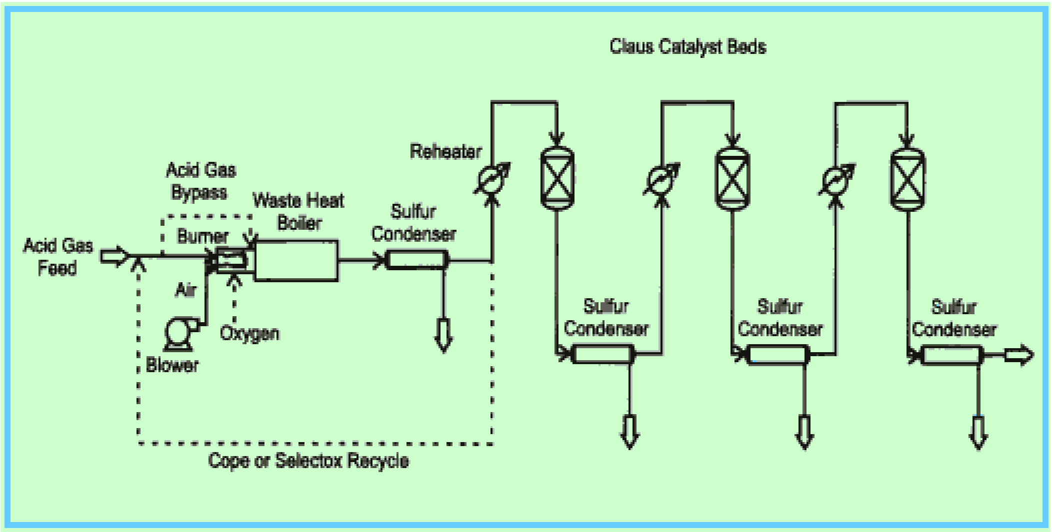

Figure 1. Schematic of the basic Claus process.

A two-bed Claus plant operating in the 1960s with approximately 93 percent H_2S in the feed is used as the base case for this discussion. A process simulator, TSWEET, was used to obtain an initial model by matching plant data. The model was then modified to show how improvements could be made.

A comparison of plant data to TSWEET predictions is listed in Table 1 to provide a basis for the accuracy of the program's predictions for further modifications.

Table 1. Rich acid gas inlet conditions and base case results.

		Composition (mole%)	
Temperature	75°F	H_2S	93.40
Pressure	16.5psia	CO_2	5.64
		H_2O	0.96

	Base Two-Bed		Modified Two-Bed
	Data	TSWEET	TSWEET
Reactor furnace temperature	2230°F	2258°F	2221°F
1st sulphur condenser	none	none	320°F
Bed 1 outlet temperature	730°F	727°F	650°F
Bed 1 H_2S conversion	--	9%	51%
Bed 2 outlet temperature	581°F	590°F	450°F
Bed 2 H_2S conversion	--	65%	77%
$H_2S:SO_2$ ratio	1.2:1	1.2:1	2:1

Overall recovery	91.8	90.7%	96.1%

This particular plant achieved an overall sulphur recovery of 91.8 percent, which is low by current industry standards. Upon examination, there are several areas where small operational or design changes could improve recovery. Some of these changes were simulated to show how the plant might operate if it were optimized by today's standards.

The outlet temperature of the waste heat boiler was decreased from 840^oF to 700^oF and a sulphur condenser was added to remove all the sulphur formed in the furnace. The condenser improves recovery because the presence of elemental sulphur in the catalyst beds reduces the efficiency of the Claus reaction. Also, the outlet temperature of the first reheater was controlled to maintain a bed outlet temperature of 650^oF rather than 727^oF.

This lower temperature promotes improved Claus conversion but still ensures destruction of the COS and CS_2 formed in the burner. Similarly, the second reheater was controlled to maintain the outlet temperature of the second bed at 30 degrees above the sulphur dew point. The closer to the sulphur dew point the bed operates, the higher the equilibrium conversion.

One final item to note concerning this case is the ratio control of H_2S to SO_2 in the tail gas. The Claus reaction requires two moles of H_2S for every one mole of SO_2 for optimum conversion according to the following reactions:

$$H_2S + 1\tfrac{1}{2}O_2 \longrightarrow SO_2 + H_2O$$

$$2H_2S + SO_2 \longleftrightarrow 3S + 2H_2O$$

This plant originally operated at a ratio of 1.2:1, but in the simulation the ratio was changed to 2:1 to optimize the performance of the unit. The ratio is controlled by manipulating the flow rate of inlet air from the blower to the furnace. These seemingly minor changes to operating conditions increased sulphur recovery from 91.8 percent to 96.1 percent, a 4.3 percent improvement over the original design, as shown in Table 1. These modifications are used as the basis for comparisons with other process modifications.

Standard three-bed Claus plant

There are numerous technical papers available on the conventional Claus process and its capabilities. Typically, sulphur recoveries in the range of 96–97.5 percent can be expected for a standard three-bed Claus plant with rich acid gas feed. (Emission regulations often necessitate the inclusion of a secondary tail gas cleanup unit to boost recovery as high as 99.9+ percent). For this comparison, a third Claus bed was added to the modified two-bed plant.

A controller maintains a 2:1 H_2S:SO_2 ratio in the tail gas by operating the burner sub-stoichiometrically. The simulation model assumes a 95 percent approach to equilibrium in the Claus reactors and 4lb liquid sulphur entrained in the sulphur condensers per 100 moles of gas.

The first bed is operated at a temperature of 650^oF to ensure destruction of the COS and CS_2. Subsequent beds are maintained at 30 degrees above the sulphur dew point to achieve the highest possible conversion. The overall sulphur recovery predicted by simulation increased to 98.0 percent, a 1.9 percent improvement over the two-bed case, by adding the third catalyst bed, as shown in Table 2. (Table 2 recoveries assume the plant is operating under optimum conditions and are for comparison only. Actual recoveries may be 0.5 to 1 percent lower than those reported).

Table 2. Rich acid gas feed process comparison.

Process Description	**Overall sulphur recovery**

Modified 2-bed Claus	96.1
Conventional 3-bed Claus	98.0
2-bed with direct oxidation bed	98.8
2-bed with sub dew point bed	99.0
4-bed Claus	98.5
3-bed Claus with direct oxidation bed	99.0
3-bed Claus with sub dew point bed	99.3

Two-bed Claus with a direct oxidation catalyst bed

For this case, the third reactor of the previous three-bed case was replaced by a bed representing a direct oxidation process such as Superclaus. Direct oxidation requires a special catalyst which converts H_2S directly to sulphur.

There are two versions of the Superclaus process – the Superclaus-99 and the 99.5. The 99 and 99.5 represent the overall sulphur recoveries that can be expected when the Superclaus catalyst is used in the final bed of a Claus plant. To achieve 99 percent sulphur recovery, the tail gas from the second Claus bed is fed directly to the reactor bed containing the direct oxidation catalyst.

To achieve 99.5 percent sulphur recovery, the process includes a hydrogenation reactor upstream of the direct oxidation bed to convert all remaining sulphur species to H_2S before passing over the direct oxidation catalyst, thus yielding a higher overall sulphur recovery. Direct oxidation without the hydrogenation step has been chosen for comparative purposes in this case. A conversion efficiency of 85 percent was assumed for the direct oxidation bed in the simulations.

The operation of a process which includes a direct oxidation bed is somewhat different from the operation of the traditional Claus process. Instead of maintaining a 2:1 H_2S:SO_2 ratio throughout, the process operates with an excess of H_2S. All sulphur species except H_2S pass over the special catalyst unreacted. Therefore, prior reduction of non-H_2S species results in greater conversion in the direct oxidation bed and greater overall recovery for the plant.

An additional requirement for this process is a source of air upstream of the direct oxidation reactor. The air mixes with the Claus tail gas to promote oxidation of the H_2S to elemental sulphur in the presence of the direct oxidation catalyst. The success of this process depends on the ability to operate with an excess of H_2S and consume all of the SO_2 before entering the direct oxidation reactor.

Simulation results indicate that the overall recovery of this process increased to 98.8 percent by replacement of the third bed with a direct oxidation catalyst bed. This is an increase of 0.8 percent over the original three-bed case shown in Table 2.

Two-bed Claus with a cold bed

The next option explored in the study of rich acid gas feed was the use of a cold bed as the third and final bed. Since the Claus reaction is exothermic, the lower the reaction temperature, the closer the reaction proceeds to completion. The main difference between this process and the traditional Claus process is that the sulphur formed in the bed is actually adsorbed on the catalyst, since the bed is operated below the sulphur dew point.

More than one bed is required for this process because the beds must be regenerated periodically to remove the adsorbed sulphur. Sulphur is condensing on one bed while the other bed is being regenerated. The gas exiting the third condenser is not reheated before entering the cold bed; therefore, the sulphur condenses directly onto the catalyst as it is formed. The H_2S:SO_2 ratio is controlled at 2:1 in the same manner as in the conventional Claus. The overall recovery predicted by the simulator for this configuration was 99.0 percent, as shown in Table 2. If environmental regulations require greater than 99 percent recovery of sulphur species, further processing of the tail gas may be required. An additional bed with or without hydrogenation or a SCOT type tail gas cleanup unit may be required.

In Table 1, we have included expected recoveries for a three-bed Claus with a fourth direct oxidation bed and a three bed Claus with a fourth cold bed. These values represent the optimum recoveries expected for a plant with feed conditions as stated in Table 1. For feed streams of different compositions, all feasible alternatives should be investigated. A process simulator is an excellent tool to aid in determining appropriate design alternatives.

Another option to consider for increasing plant capacity or boosting sulphur recovery is the use of oxygen in a conventional Claus plant. Oxygen enrichment of the air to the combustion chamber can increase capacity of the plant by displacing the amount of inert compounds present in air such as nitrogen. Oxygen enrichment also raises the burner temperature, ensuring complete combustion of all hydrocarbons which might be in the feed, thus preventing carbon or soot deposition in the catalyst beds.

CASE STUDIES: 2

Lean acid gas feed – H_2S content above 50 percent

Processing a lean acid gas requires that special consideration be given to the operation of the burner. A Claus furnace feed containing a relatively low concentration (less than 50 percent) of H_2S may be incapable of producing a stable flame. Also, as discussed previously, incomplete combustion of hydrocarbons in the feed can lead to deterioration of the catalyst in the reactors due to soot or carbon deposition.

There are several processes available to treat lean streams, including some which require only slight modifications to the conventional Claus plant. The focus of this section is directed at how a certain process compensates for low acid gas concentrations rather than the ability of the process to achieve a required recovery percentage.

A comparison of several of these methods follows, including: a four-bed Claus with acid gas preheat and fuel gas burner, the all-catalytic Selectox process, acid gas bypass around the furnace, and oxygen enrichment of the combustion air feed to the Claus plant.

Acid gas preheat

A four-bed Claus plant with approximately 21 mole% H_2S in the feed (Table 3) is used as the base case for the lean acid gas feed discussion. In order to achieve a stable flame in the burner, this plant uses acid gas preheated to 500^{o}F and fuel gas burned separately using a special burner. TSWEET was used to match plant data, and Table 3 provides a comparison of plant data with TSWEET to provide a basis for the accuracy of the program's predictions.

Table 3. Lean acid gas inlet conditions and base case results.

Inlet gas		**Furnace Temp**		**Overall Sulphur Recovery**	
Temperature	100oF	Data:	1684oF	Data:	96.3%
Pressure	20psia	TSWEET:	1695oF	TSWEET:	96.3%
Composition (mole%)	**Acid gas + Fuel gas Data**	**WHB outlet Data**	**TSWEET**	**Tail gas Data**	**TSWEET**
Argon	0	0.51	--	0.55	--
Hydrogen	0	1.22	0.58	1.21	0.60
Nitrogen	1.30	42.47	41.99	45.78	44.52
Carbon Monoxide	0	0.85	0.84	0.81	0.89
Carbon Dioxide	74.41	47.74	49.32	51.2	53.67
Hydrogen Sulphide	21.13	3.37	3.38	0.15	0.10
Carbonyl Sulphide	0	1.08	1.10	0.02	0.07
Carbon Disulphide	0	0.26	0.25	0.08	0.01

Sulphur Dioxide	0	2.50	2.54	0.20	0.14
C1+	3.16	0	0	0	0
Total:	**100**	**100**	**100**	**100**	**100**

This four-bed plant achieved a 96.3 percent sulphur recovery with a burner temperature of 1700^{o}F (94–96 percent recovery can be expected for a conventional three-bed Claus unit with lean acid gas feed). The inlet composition and conditions listed in Table 3 are in all of the simulations in this section.

Selectox

The Selectox process, licensed by UOP, processes lean acid gas with a catalytic burner which oxidizes the H_2S to SO_2 at a temperature of about 700^{o}F. Two versions are available, the "Straight Through Selectox" and the "Recycle Selectox".

The straight through process is typically used for acid gas streams containing a maximum of 5 mole% H_2S. The Recycle Selectox is normally used for acid gas streams containing 5–40 mole% H_2S but can be utilized effectively on streams of 65-70 mole% H_2S. The Recycle Selectox process is used for this case since the feed contains 21 percent H_2S.

The Recycle Selectox is an all-catalytic process meaning there are no flames at any point in the process. A special catalyst bed replaces the acid gas burner in a conventional Claus plant. The Selectox catalyst occupies the top few inches of the first bed, where it promotes the selective oxidation of H_2S to SO_2. The remainder of the bed is filled with Claus catalyst where the Claus reaction occurs to about 80 percent completion. The highly exothermic nature of these reactions requires that the feed gas be monitored for the concentration of H_2S to avoid overheating. The Recycle Selectox process uses a recycle blower to dilute the inlet H_2S concentration to less than 5 vol% by recycling a portion of the effluent gases from the Selectox condenser (Figure 1). This recycle of mainly inert gases limits the outlet temperature of the catalyst bed to a temperature of approximately 700^{o}F. The Selectox bed is followed by two conventional Claus beds. The simulator predicts 96.3 percent sulphur recovery for the Recycle Selectox case.

Acid gas bypass

Another way of attacking the problem of insufficient combustibles in a lean acid gas feed is through bypassing a portion of the feed around the furnace. The bypassed gas is mixed with the burner effluent prior to the waste heat boiler. 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. Ideally, a flame temperature in the range of 1850-2200^{o}F should be maintained.

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. Another consequence is lower Claus thermal conversion due to a decrease in furnace residence time and lower waste heat boiler entrance temperature. At temperatures below 1200^{o}F, H_2S and SO_2 will not react to form elemental sulphur without a suitable catalyst. The sulphur recovery predicted by simulation for this system was 96.2 percent (Table 4).

Table 4. Lean acid gas feed process comparison.

Process	**Features**	**Sulphur Recovery**
Feed preheat	Acid gas and air preheat Addition of fuel gas to a separate burner Burner temperature 1700^{o}F 4 Claus beds	96.3%
Recycle Selectox	Burner replaced by 700^{o}F catalyst bed Recycle gas controls Selectox bed temperature	96.3%

	2 Claus beds	
Acid gas bypass	Burner temperature 1828^oF 55% Acid gas bypassed 2 Claus beds	96.2%
Acid gas bypass with oxygen enrichment	Burner temperature 1865^oF 50% Acid gas bypassed 30% O_2 to the burner 2 Claus beds	96.4%
Acid gas bypass with oxygen enrichment	Burner temperature 1840^oF 35% Acid gas bypassed 100% O_2 to the burner 2 Claus beds	96.6%

Oxygen enrichment

Increasing the concentration of oxygen in the combustion air to the burner is another option to aid in flame stability. The amount of bypass gas may be reduced by enriching the air with oxygen, as shown in Table 4.

As discussed previously, other benefits of oxygen-enhanced combustion air in both rich and lean acid gas feed cases include increased plant capacity and sulphur recovery, increased SCOT tail gas cleanup efficiency, and burner temperatures high enough to prevent carbon or soot formation and resultant poisoning of catalyst beds.

CASE STUDIES: 3

Acid gas containing ammonia

Ammonia in the Claus plant feed can usually be traced to an upstream sour water stripper. The ammonia must be destroyed in the Claus burner to avoid deposition of ammonium salts in down stream catalyst beds. Most process modifications designed to destroy ammonia include oxygen enrichment and/or the use of a specialized burner.

Several examples of process modifications involving the burner which can be used to destroy ammonia are Cope, OxyClaus, and Comprimo. These methods are discussed briefly, but comparative simulation results are not included. The Cope process achieves an elevated burner temperature with oxygen enhanced feed. The burner temperature is limited to 2700^oF and is moderated by a stream of recycle gas originating as the effluent from the first sulphur condenser (Figure 1).

Up to 100 percent oxygen may be fed to the special burner, which handles acid gas, recycle gas, air and oxygen simultaneously. Other similar processes use SO_2 or other streams as the quench instead of the recycle stream.

The OxyClaus process requires no recycle gas, and 80–90 percent O_2 may be fed to the special burner, or it may operate with air only. The burner may bypass part of the amine acid gas while burning all of the sour water stripper acid gas. This front/side split system is not usually required for streams containing less than 5 percent NH_3. The Comprimo process is similar to the

OxyClaus in that it requires no recycle gas to moderate burner temperature. All gas is fed to the special burner which mixes acid gas, air and oxygen, if desired, so that no front/side split of the acid gas is required. The typical burner temperature range is 2200–2350^oF, which is lower than the Cope burner temperature.

It should be noted that ammonia can be fed to a conventional Claus plant if the burner temperature remains at 2700^oF.

CONCLUSION

The basic three-bed Claus process can be used for rich acid gas feeds, but current emission regulations requiring 99+ percent sulphur recovery necessitate a modification to the traditional Claus process or the addition of a secondary tail gas cleanup process. This could mean using a cold bed or a direct oxidation bed as the final bed.

Another type of tail gas cleanup process such as SCOT could be used with a basic three-bed Claus to achieve elevated recoveries.

Lean acid gas feeds require a modification to the operation of the burner to produce temperatures high enough to promote stable combustion. Other methods such as a catalytic "burner" may be used in place of the traditional burner in some instances.

Processing feeds containing ammonia usually requires a higher burner flame temperature to destroy the NH_3 and avoid ammonium salt deposition on the catalyst beds. Either oxygen enrichment and/or a special burner are the usual choices for handling this problem. In all cases involving ammonia, the burner is the key to solving the problem, and much thought should be given to the burner design to ensure proper ammonia destruction.

To achieve the optimum Claus process design for any feed composition, all suitable processes should be fully explored with a process simulator before making design decisions.

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