Sulfur Plant Process Control Analyzers

TECHNICAL PAPER

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Sulphur plant process control analyzers

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Process and Process Control Basics

The Claus process, although simple to describe, is more complex than it appears. What sets it apart from many unit operations in the refinery or gas processing plant is that, unlike the treatment and processing of hydrocarbons, it is a chemical process. In order to define the control requirements, an understanding of the process fundamentals is required. To implement advanced control techniques, knowledge of both analytical methods and process mechanisms is required.

The following discussions are based on experience gained through the development of analytical techniques and process testing procedures for Claus sulphur recovery units, and from applying and refining those techniques and procedures while carrying out over 400 in-depth sulphur plant tests around the world. The analyses of those test results led to good understandings of the process, of sampling systems and of the capabilities and limitations of continuous process gas analyzers. Indeed, the knowledge gained from such intensive process evaluations of many diverse sulphur plants was used to develop analyzers for use in controlling the Claus process. Currently, there are 400 units installed world-wide at over 200 locations.

Fundamental Chemistry and Process Configuration

The original Claus process produces elemental sulphur in a single step by partial oxidation of H_2S over a catalyst according to the reaction:

$$(1) \qquad H_2S + \frac{1}{2}O_2 \rightleftarrows \frac{1}{x}S_x + H_2O.$$

Because the reaction is very exothermic, only low volumes of gas could be processed without overheating the catalyst. A major breakthrough was achieved in the 1930s; the reaction was split into two steps. The first step is a free-flame oxidation of 1/3 of the H_2S

to SO_2 in a reaction furnace, followed by the second step of reacting the remaining H_2S with the SO_2 at lower temperatures over a catalyst[1]:

(2) $$3H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + 2H_2S + H_2O,$$ and

(3) $$2H_2S + SO_2 \rightleftarrows \frac{3}{x}S_x + 2H_2O.$$

This two-step process was formally referred to as the modified-Claus process and is the process generally used for modern sulphur recovery units. However, the single-step Claus process is still used occasionally in some cases. The difference between the two processes is obscured by the fact that the single term, *Claus Process*, is carelessly applied to either process. If optimized, either process is capable of sulphur recovery efficiencies as high as 98 percent.

The string of vessels comprised of the reaction furnace, condensers, reheaters and converters (catalytic reactors) is referred to as the *sulphur recovery train, sulphur recovery unit (SRU), Claus plant,* or just the *sulphur plant.* Although a number of different configurations are used for special handling of some feed streams, the dominant configuration is the straight-through configuration shown in Figure 1. In this configuration, which is applicable to acid gas streams with high H_2S concentrations (rich feeds), all of the feed stream passes through all process vessels. The term *acid gas* as used here is reserved for the H_2S-containing stream feeding a sulphur plant, even though the stream may contain a substantial quantity of NH_3. In general, the balance of the acid gas stream is primarily CO_2 with varying amounts of H_2O, hydrocarbon compounds and other trace species that depend upon the source of the acid gas. *Acid gas* and *feed gas* are used synonymously.

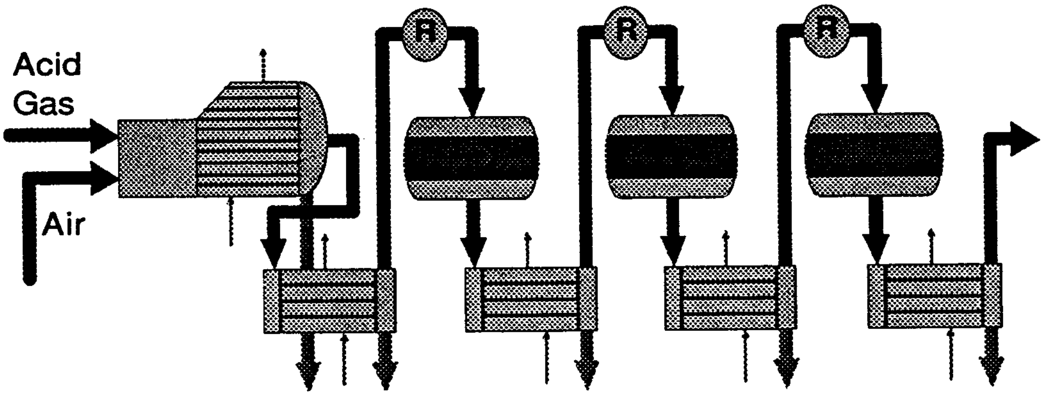

Figure 1: Modified-Claus process, straight through configuration.

NH_3-burning Configurations

Many refineries must dispose of a sour water stripper (SWS) overhead stream that contains both NH_3 and H_2S. While in the distant past it was allowable to incinerate this relatively small volume of H_2S-bearing gas, it is now generally required that the sulphur be recovered which is usually done by sending it to the SRU. The reaction furnace and air blower must then be designed to establish the necessary conditions to destroy the associated NH_3 because breakthrough of NH_3 from the reaction furnace will cause plugging in the cooler, downstream process vessels. There are two common approaches for achieving this. One method burns the SWS gas with part of the amine-generated acid gas in the front, high temperature zone of the reaction furnace, followed by injection of the rest of the amine-generated acid gas into the back section of the reaction furnace (Figure 2). The other method mixes the SWS and amine-generated acid gas streams prior to combusting with an extremely efficient burner using a sophisticated control strategy (Figure 3) for the process air.

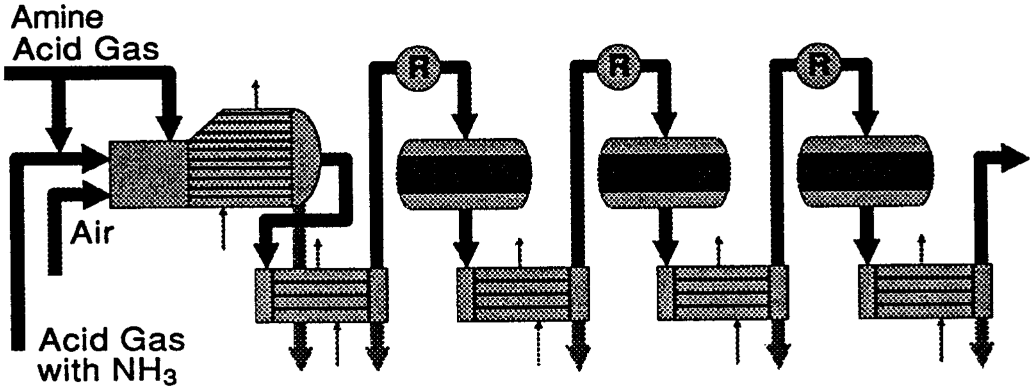

Figure 2: NH_3-burning modified-Claus process using the dual-chamber reaction furnace.

Control Parameters

As with any chemical process, the most important aspect of sulphur plant operation is to ensure that the reactants come together in the correct stoichiometric ratio. A deficiency in either of the reactants will limit the conversion of the other reactant. In the case of the sulphur plant, control is achieved by regulating the ratio of total air (O_2) to total acid gas (H_2S) entering the plant[2].

The objective of the control strategy is to ensure that, for a given flow rate of acid gas, the correct amount of air is introduced to maintain two parts of H_2S for every part of SO_2 in the downstream converters. This is, as indicated by Equation 3, a precondition for

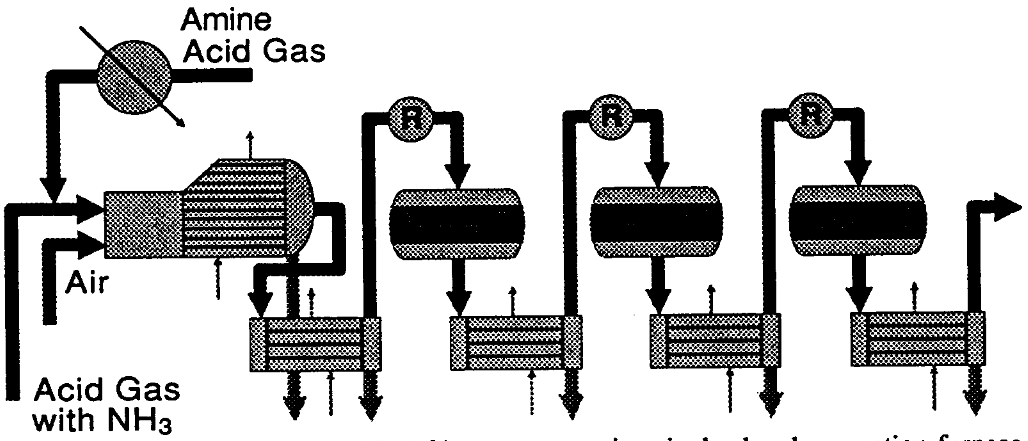

Figure 3: NH_3-burning modified-Claus process using single-chamber reaction furnace.

achieving maximum sulphur conversion.

To avoid confusion, it should be pointed out that there are two distinct *ratios* used in discussions of the Claus processes. The *air to acid gas ratio* refers to the amount of air introduced into the process in relation to the acid gas flow rate. The $H_2S:SO_2$ *ratio* (sometimes called the *tail gas ratio*) refers to the ratio of H_2S and SO_2 concentrations in the tail gas stream.

The use of the $H_2S:SO_2$ ratio to express the stoichiometric condition in the Claus process has been superseded by the concept of *air demand,* which is defined by:

$$\text{(4)} \qquad \text{Air Demand} \equiv K\{2[SO_2] - [H_2S]\},$$

where [*X*] denotes the concentration of species *X* in the process stream and K is a constant for a given plant.

Air demand is a linear function: when it is equal to zero the process is optimized with respect to the air to acid gas ratio. Compared to the tail gas ratio, this concept is simple to implement in a control loop, easy for the operator to understand and is independent of the conversion efficiency. Moreover, it can be used to eliminate the low levels of analytical interferences from sulphur vapour (S_V), which will be discussed later.

Tail Gas Analysis

As implied by the foregoing, analysis of the tail gas can be used to control the SRU. The species of major interest are H_2S, which is used as an indicator of the acid gas rate, and SO_2, which is used as an indicator of the air rate.

It is now generally accepted that a continuous, on-line tail gas analyzer is required for efficient operation of an SRU. Plants that operate without the benefit of an on-line analyzer sometimes attempt to control the air to acid gas ratio using manual methods such as Draeger® tubes (stain tubes) or a Tutweiler apparatus. This is considered marginally acceptable[3] only for very small plants (<10 t/d). For any SRU associated with a refinery, however, the stringent emission guidelines preclude the manual methods as viable options.

There is no substitute for tail gas analysis and a feedback control loop. A plant that does not have one can realize between a 1 and 5 percent increase in conversion efficiency by installing a continuous feedback control system to fine tune the ever-present feed-forward flow ratio control system.

Detection Principles

The gas chromatograph (GC) was the first analyzer applied to the on-line analysis of an SRU tail gas. Analysis intervals of 6 to 8 minutes were possible, which was a marked improvement over the 4 to 8 hour intervals that were prevalent with the manual wet chemical methods. Developmental work on columns and temperature-programmed ovens reduced the analysis time to 2 minutes, but this is still quite long compared with the usual process lag time of 15 to 30 seconds for a plant at full load. The fact that a GC can provide the concentration of additional components in the tail gas is of minor benefit compared to the problems associated with handling two condensible species in a reactive sample and the resultant analytical lag time. GCs are most suited for laboratory conditions and require frequent servicing when used on line in the SRU environment. This is the major reason that GCs are now commonly not used in SRU control systems.

Currently, ultraviolet (UV) spectrophotometry is considered to be the best detection principle for SRU tail gas analysis. The major components in the tail gas (N_2, CO_2 and H_2O) do not absorb mid-range UV radiation and the species of interest have some relatively strong absorptions[4] (Table I).

Table I
Molar Absorptivities of Sulphur Species

Wavelength (nm):	228	280
Used for measuring:	H_2S	SO_2
H_2S	140	0
SO_2	60	205
S_V	4785	2722
COS	74	0
CS_2	43	0

From Table I it is evident that S_V strongly absorbs at the wavelengths used for measuring H_2S and SO_2. Since the tail gas is saturated with S_V at the final condenser outlet temperature (130 to 150°C, 266 to 302°F), and often contains liquid sulphur in the form of mist, analyzing for 2 percent H_2S and 1 percent SO_2 includes potentially large interferences from S_V.

The sample can be conditioned with an in-line mist eliminator so that only sulphur as S_V is present. Then, from knowledge of the system pressure, sulphur vapour pressure and the sulphur saturation temperature, the absorption due to S_V can be subtracted electronically from the measured absorptions at the two measuring wavelengths to obtain the H_2S and SO_2 signals. In practice this correction would be implemented as a constant correction determined at the initial set up of the analyzer. Unfortunately, this approach leaves residual background interferences and, further, renders the analyzer insensitive to small changes in the H_2S and SO_2 concentrations. Moreover, this approach is totally frustrated if sulphur condenses within the sampling system because it would change the amount of S_V in the sample, which would require a different correction factor! Condensation of sulphur in such systems is frequent, especially at measuring-cell windows.

A different approach was taken to solve this problem[5]. An air-cooled condenser is used to lower the sample temperature to approximately 107°C (225°F) which reduces the S_V concentration to the 25 to 50 ppm (v/v) range. Then the absorption due to S_V is only about 4 percent of the total absorption at the two measuring wavelengths. Under this condition, advantage can be taken of the relative absorptivities of S_V at the two measuring wavelengths. The magnitude of the S_V absorptivity at the H_2S-measuring wavelength (4785) is nearly twice the S_V absorptivity at the SO_2-measuring wavelength (2722) so that the effects of S_V on H_2S and SO_2 are effectively cancelled when the air demand equation (Equation 4) is used to process the signals. The use of the sulphur condenser, using a single cell single beam spectrophotometer for both gases, the judicious choice of measuring wavelengths and the use of the air demand equation collectively make it unnecessary to quantify the S_V interferences to obtain an accurate signal for controlling the SRU. If the absolute H_2S and SO_2 concentrations are required for other reasons, appropriate corrections must be applied to remove the residual S_V interferences and also the interferences from CS_2 and COS.

The interferences from CS_2 and COS are significantly less than that from S_V. Both CS_2 and COS absorb only at the H_2S-measuring wavelength and the absorptivities are less than half the absorptivity of H_2S. Under normal Claus plant operation, the concentrations of these two species are typically in the 100 to 500 ppm (v/v) range and can be treated as constant. If catalyst deactivation in the first converter, or some other process change, produces higher concentrations of CS_2 and COS in the tail gas, correction factors can be applied. However, the more appropriate course of action is to correct the process conditions that caused the higher concentrations of CS_2 and COS.

Sample System

The application of on-line analyzers has always been limited by the capability of the sampling system to transport a representative sample from the process to the analyzer. An accurate analysis of a non-representative sample is meaningless, and is of no use to the operator. The tail gas analyzer is no different in this respect. Claus tail gas is a wet, highly reactive, corrosive, toxic mixture saturated with sulphur vapour, that is sampled at a temperature relatively close to the freezing point of sulphur. Obtaining and conditioning a representative sample from such a stream is not an easy task.

The first element of the sampling system to consider is the heating mechanism. Because of the potential problem with condensing sulphur, the sampling line must be heated and insulated, from the point of extraction from the process to the analytical cell, through to the point of return of the sample to the process. Steam is usually readily available and would seem to be the ideal choice. However, experience has shown that the use of steam for this application created many of the subsequent problems. The temperature within the sampling system is critical and the quality of steam delivered to outlying areas of the processing complex usually deteriorates during transit. The low pressure steam provided is often not high enough pressure (550 kPa; 5.5 bar; 80 psi) to yield sufficient heat. On the other hand, if liquid sulphur is present (as in a condenser), medium pressure steam (1 200 kPa; 12 bar; 175 psi) provides too much heat. Liquid sulphur held at a temperature between 160 and 185°C (320 and 365°F) exhibits an anomalous, 10- to 10,000-fold increase in viscosity that will cause plugging of the lines[6].

Electrical heat tracing is the preferable heating mechanism for sampling systems in the SRU. Electrical heat tracing is easily controlled, provides consistent temperature control, is not affected by upsets in any process units and does not rely on field fabrication by tradesmen not familiar with sampling systems. For installations in locations classified as hazardous, the temperature rating is normally T-3 (CENELEC) in Europe and in North America the Group D specification is normal.

The connection between the process pipe and the sampling system is a critical juncture. When plugging does occur, it usually occurs here. Because electrically-heated valves are not practical, this is one place where steam is used. A steam-jacketed (**not** steam-traced) ball valve is an ideal connection to the process piping, provided that the steam pressure is kept between 550 and 1 000 kPa (5.5 and 10 bar; 80 and 145 psi). To keep the surface area and thermal mass to minima, screwed connection is preferred. In those cases where flanged fittings must be used, the flange must be as small as possible and close-coupled to the pipe. A custom-made insulating jacket should be provided for the valve because it is necessary periodically to inspect the valve and connections. It frequently has been observed that if rigid (permanent) insulation is removed "temporarily" to do an inspection, rarely is it replaced properly and this leads to chronic plugging problems.

The reason the aforementioned ball valve was specified is that a probe must be used to extract the gas sample from the mid section of the process stream. The gas sample must not be drawn from next to the inner wall of the process pipe for two reasons. First, consistently it has been observed that the composition of the "boundary-layer" gas next to the mild steel pipe is not the same as the composition of the bulk, inner portion of the gas stream, as shown in Table II. The analysis without the probe indicates the process is deficient in air by 1.34 percent whereas the proper analysis shows the process is deficient by only 0.71 percent. Thus, without a probe in this case, a control system would add too much air to the process, by a factor of 2.

Second, for any number of reasons including failure of an upstream demister pad or the fact that the mild steel is usually cooler than the gas stream, liquid sulphur flows along the wall of the pipe. If a probe is not used, this liquid sulphur is drawn into the sampling line and overloads the sampling system. When a probe is used with a low sampling rate (< 3 L/min), problems with liquid sulphur in the sampling system are eliminated.

Table II
Effect of Using a Probe to Obtain Sample
Condenser 3 Outlet

	No Probe	With Probe
	(Mole Percent, dry basis)	
H_2	1.696	1.673
Ar	0.940	0.940
O_2	0.000	0.000
N_2	78.587	78.588
CO	0.542	0.527
CO_2	16.976	16.797
H_2S	0.893	0.942
COS	0.068	0.067
SO_2	0.133	0.305
CS_2	0.165	0.161
Total	100.000	100.000

The ideal location for the analyzer is above the connection of the sampling line to the process pipe so that if sulphur does condense, it will drain back to the process. Of course, the sampling line must not contain any loops or "pockets" in which liquid sulphur could collect. If it is impossible to position the analyzer in the ideal location, the analyzer must be less than 6 m (20 ft) below the highest point in the sampling system so that any liquid sulphur can be returned to the process by the sampling system aspirator.

The length of the sampling line should be as short as possible. At normal sampling rates, the gas speed in the normal 3/8 in (10 mm) OD sampling line is between 1.0 and 2.0 m/s (3.25 and 6.5 ft/s). If the sampling line is kept as short as possible, the sample transport time will be small compared to the process lag time so that the overall response time of the system is not influenced significantly.

All components of the analyzer through which the sample passes must be heated, preferably using electricity. This includes the analytical cell of the analyzer, the sulphur knockout/condenser and aspirator. This can be accomplished by housing all these components in an insulated enclosure maintained above the sulphur dewpoint temperature. The sulphur knockout/condenser is then cooled with air to control the amount of S_V in the sample entering the analytical cell. In this manner the analytical cell is kept under controlled conditions and special provisions for maintaining the optical components are not required. Finally, provision for automatically back purging the sampling system if the temperature falls below 140°C (284°F) should be included. This prevents the freezing of sulphur in the sampling system in the event of a power failure.

Sample Point Location

For normal Claus plants, the primary requirement with respect to sample point location is that it **must** be after all acid gas and all process air have been introduced into the plant. Thus, if direct-fired reheaters are used in the plant, the sample point must be after the last such reheater. However, the SUPERCLAUS process, which is an exceptional version of the process, does require modification to this rule[7].

The second requirement is that the sample should be obtained from the point in the process where the measured parameters ([H_2S] and [SO_2]) are the most sensitive to change in the total air to total acid gas ratio. As illustrated by Table III, this condition occurs at the same point as the highest conversion efficiency, which is at the final condenser outlet, the tail gas. Moreover, it has been shown that the most accurate determination of excess process air is obtained when the measurements are made at the same point[3]. The exception

Table III
Changes in H_2S and SO_2 Concentrations as Functions of Excess Air and Position in the Process

Excess Air (Percent)	-1.0	0.0	+1.0
Converter 1 Outlet			
H_2S - (mole percent)	1.957	1.856	1.761
- (percent change)	+5	0	-5
SO_2 - (mole percent)	0.849	0.928	1.009
- (percent change)	-9	0	+9
Converter 2 Outlet			
H_2S - (mole percent)	0.534	0.426	0.351
- (percent change)	+25	0	-18
SO_2 - (mole percent)	0.135	0.213	0.306
- (percent change)	-36	0	+43
Converter 3 Outlet			
H_2S - (mole percent)	0.392	0.271	0.204
- (percent change)	+45	0	-91
SO_2 - (mole percent)	0.064	0.136	0.233
- (percent change)	-53	0	+71

Sulsim® simulation for rich feed plant also processing a SWS stream containing NH_3 (3 indirect reheaters).

to this rule is the MCRC process in which, during normal operations, the ordinal positions of all *except* the first converter are periodically changed[8]. In this case, the sample point must be after the first converter. The sensitivity and accuracy can then be maintained by incorporating a special catalytic converter within the sampling/analyzer system.

Output Signals

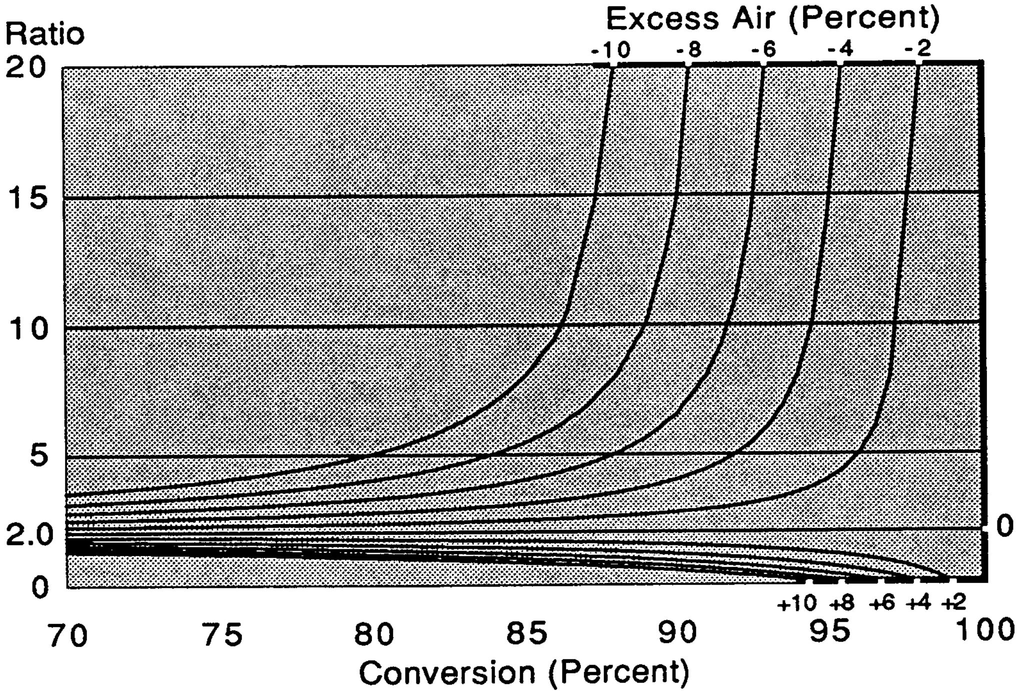

Figure 4: $H_2S:SO_2$ ratio as a function of conversion efficiency and excess air.

As mentioned previously, expressing the control signal in terms of *air demand* rather than the $H_2S:SO_2$ ratio is preferable. The $H_2S:SO_2$ ratio is a nonlinear function of both excess air and the conversion efficiency, as shown in Figure 4. On the other hand, the air demand signal is linear and more easily implemented in the feedback control loop. It is independent of the efficiency of the process and is therefore unaffected by continued reaction between H_2S and SO_2 in the sampling system[3]. The single *air demand* parameter replaces two other commonly used expressions. A positive air demand is equal[9] to *excess* SO_2 and a negative air demand is equal to *excess* H_2S. There is a humane benefit to using the control signal in this form. The operator can tell immediately in which direction the control action should be and how much change is required.

Table IV
Control Signal Scaling
Air Demand = K{2[SO_2] - [H_2S]}

Air Demand (Percent)	Output (mA)	Control Action
-5	4	Increase Air (Process is air-deficient)
0	12	None (Null, Setpoint)
+5	20	Decrease Air (Process is air-excess)

In practice, the control output is scaled as shown in Table IV. The air demand is expressed in terms of the total stoichiometric air required by the process. When the air demand is equal to zero, the correct amount of process air is entering the SRU, the SRU is said to be "on-ratio" and no control action is required.

The feedback control loop is usually set up to handle 10 percent of the total air requirement, covering the range from -5 to +5 percent air demand. Experience shows that this is sufficient for control purposes and yet will not result in catastrophic disturbance of the process if the control system fails. If special circumstances require it, this range can be changed or the output from the controller can be biased to run at slightly "off-ratio" conditions[10]. Although the control range is -5 to +5 percent, the analyzer provides a wider (-20 to +20 percent) display range which is useful to operators during start-ups, shutdowns or severely upset conditions.

A common misconception is that the tail gas analyzer can be used to approximate the total emission from the Claus plant. Although additional outputs for indicating H_2S and SO_2 are available, they are not reliable as absolute concentrations. The reasons for this are that fixed saturation conditions are assumed for applying the corrections for S_V interferences, the H_2S is not corrected for the interferences from CS_2 and COS and the outputs normally are not compensated for variations in analyzer cell pressure. Further, the tail gas vented to the incinerator or tail gas clean-up unit (TGCU) usually also contains liquid sulphur. The quantities of these four species are normally constant since they are not affected by changes in the air to acid gas ratio. However, decayed performance in certain process units can cause these species to contribute more to the SO_2 emission than the SO_2 and H_2S, without producing a conspicuous difference in operations. Indeed, in extreme cases these other four species can cause 4 to 8 percent of the total sulphur feed to become SO_2 emission as compared with 2 to 3 percent for the H_2S and SO_2[1,11].

Shelter

The tail gas air demand analyzer should be housed in a proper walk-in shelter. It is a complex instrument with many subsystems which must be maintained in a controlled environment. The ambient air in and around a Claus unit is hostile to electronic components and an ordinary instrument cabinet simply does not provide adequate protection.

Usually it is possible to install the tail gas analyzer along with other instruments, such as a stack gas analyzer or a gas detection control panel, in a single shelter.

Feed Analysis

Analysis of the SRU feed gas stream(s) for use in feed-forward control of the air to acid gas ratio has not been common. The reasons for this are that the Claus feed stream composition is usually relatively constant and, in practice, a complete real-time qualitative or quantitative analysis is currently not possible with a single analyzer. There are cases, however, in which control of the SRU will benefit from the use of an analyzer in the feed-forward flow ratio control loop. When an analyzer is incorporated into the feed-forward flow ratio control loop, it must be tuned to work with, rather than fight, the analyzer in the feedback loop.

Feed Analysis for H_2S

Normally, H_2S is the major combustible component in the feed stream, comprising 60 to 90 percent of the total feed for a typical SRU in a refinery. The amine acid gas composition is relatively constant and any small or gradual changes cause similar small and gradual changes in the tail gas. Such changes are within the range of the tail gas analyzer and good control of the air to acid gas ratio is easily maintained. If, however, the changes in H_2S concentration in the acid gas are rapid or exceed 5 percent, then incorporating the output from an acid gas H_2S analyzer into the feed-forward flow ratio control loop should be considered.

The best detection principle for measuring H_2S in the acid gas is UV spectrophotometry because the other significant components (CO_2, H_2O and hydrocarbons) in the acid gas do not absorb mid-range UV radiation. An analyzer in this service is capable of achieving ±1 percent of full scale accuracy[3] but ±2 percent is more realistic[12] and certainly is adequate.

Feed Analysis for H_2S and Hydrocarbons

Although hydrocarbon concentrations in the feed gas are normally steady, sudden changes due to upsets in the amine treater are not uncommon. Heavier hydrocarbons and aromatics are especially troublesome: they compete favourably with H_2S for available O_2 and their demand for O_2 is so high that even small quantities can severely disrupt the $H_2S:SO_2$ in the SRU.

A recent development[13,14] is an analytical system that uses indirect methods to determine the H_2S content and the O_2 requirements for hydrocarbons and other oxidizable components. A metered, aliquot sample is oxidized with excess O_2 and the concentrations of both produced SO_2 and residual O_2 are measured in the combustion-product stream. The SO_2 concentration is used to infer the initial H_2S concentration which is then used with the measured O_2 concentration and the input O_2 flow rate to determine the consumption of O_2 by all other oxidizable components. It is claimed that a change in the composition of the feed gas can be detected, analyzed and responded to within 10 seconds[15].

If the concentrations of H_2S, hydrocarbons and other oxidizable components fluctuate widely and rapidly, an analytical system of this type might be considered, especially if it could accommodate multiple feed streams, including a SWS overhead stream. In effect, this analytical system attempts to simulate the reaction furnace so that changes in feed composition can be counteracted by the feed-forward flow ratio control loop. Unfortunately, laboratory and field studies on incinerators[16] and reaction furnaces[17] have shown that accurate simulation of these units is not possible. Side reactions in the reaction furnace make it imperative that any SRU using such a system also must have a feedback control loop using a tail gas analyzer[13,14].

Feed Gas Sampling System and Sample Location

Because the feed gas is much easier to handle, the sampling system is not as difficult to design and is easier to maintain than a tail gas sampling system. The feed gas sample is usually saturated with H_2O at about 40°C (104°F) so that steam tracing is sufficient to prevent condensation. The analyzer may be installed in an insulated cabinet which is maintained 5 degrees above the sample H_2O dewpoint temperature; purging the cabinet to protect the electronic components from contaminants in the ambient air would be prudent. A knockout drum should be included in the sampling system to protect the analyzer from any slugs of liquid in the gas sample. In some cases, a filter for solid particles may be appropriate.

To maximize the lead time, the sampling point should be as far upstream of the reaction furnace as is practical, but should follow the process liquid knockout drum. The sampling line should be as short as possible. With the foregoing requirements and constraints, the maximum lead time will be only a few seconds, at best.

For SRUs processing more than one feed stream such as, say, an amine acid gas and a SWS overhead gas, it would be preferable to sample the resultant combined stream. However, this is not usually possible because of the process configuration. This is certainly true for the dual-chamber NH_3-burning scheme (Figure 2), because the two streams are completely mixed only at the exit of the reaction furnace, and is also true for the single-chamber NH_3-burning scheme (Figure 3) because the two streams are mixed in the burner. Even if sampling the combined stream was possible, the shortened lead time could destroy any usefulness of the analytical result as a feed-forward control parameter.

An Alternative View

The addition of an analytical system into the feed-forward flow ratio control loop of a Claus plant is not always simple. The usual reasons it is considered are rapid fluctuations of the compositions and flow rates of the feed streams. Since the streams come from upstream processes, the upstream processes should be investigated. Operating deficiencies in those processes are likely the causes of the problems with the Claus feed. For example, sudden hydrocarbon carryover from an amine treater may be the result of foaming, caused by poor level control in an inlet separator or by failure of the solution filtering system. Or, the surge volume for the SWS may be too small. Correcting all the operational deficiencies in upstream processes may obviate the need for an analytical system in the feed-forward flow ratio control system for the Claus plant. If the Claus plant feed streams are not completely stabilized by adjustments in the upstream processes, then the analytical system for the feed-forward flow ratio control loop should be chosen carefully.

Even after optimizing all upstream processes, the H_2S concentration of the amine acid gas can vary because of changing feed to the refinery or gas plant. In this case a simple H_2S analyzer can be an effective addition to the feed-forward flow ratio control loop.

If optimization of the upstream processes does not stabilize the concentrations and flow rates of hydrocarbons and other oxidizable components to the Claus plant then the aforementioned oxidation analytical system may be considered. But, if more than one feed stream is involved, this is only a partial solution. An alternative to the oxidation analytical system might be the use of a second tail gas analyzer, re-scaled for the higher H_2S and SO_2 concentrations, and placed just after the wasteheat exchanger. This analyzer would quickly detect changes in the air demand caused by any side reactions and by any species entering the reaction furnace from any source. The signal from such an analyzer would be used in the feed-forward flow ratio control loop and the tail gas analyzer would still control the feedback loop. The overall control system would require careful tuning.

Feedback and Feed-forward Control

The reliability of tail gas analyzers has increased to the point where they can be used in closed-loop control systems. Together with the normal feed-forward flow ratio control loop and sophisticated features available from digital control systems, the tail gas analyzer can limit the efficiency loss of an optimized SRU to less than 0.3 percent[2].

Feed-forward Control

Every SRU has a feed-forward flow ratio control loop that sets the air flow rate based on the compositions and flow rates of the feed streams. Feed-forward control is theoretically capable of achieving perfect control. In practice, its performance is limited by the accuracy of the measurements, computations and controlled devices. Given a relatively constant H_2S concentration in the acid gas, the best that can be expected is control of the process air to within ±3 percent of the correct amount[3,12]. The error arises primarily from dead band, sensitivity and calibration errors in the sensors, ratio station, controller, main air valve and actuator.

As discussed in the previous section, the addition of a feed gas analyzer can help with compositional changes in the feed gas but it cannot predict what will happen in the reaction furnace or downstream vessels. The reaction furnace is kinetically limited and produces varying amounts of H_2, CO, COS and CS_2, none of which can be predicted accurately from a feed gas analysis. All of these components affect the air demand of the process. Some of the COS and CS_2 is hydrolysed to H_2S in the first converter but the degree of hydrolysis is dependent upon catalyst activity[1,11,12]. The overhead gas stream from a SWS often has a highly variable hydrocarbon content in addition to the NH_3 and an analyzer suitable for these components in this stream is currently not available. If direct-fired reheaters are used in the SRU, the deviation from Claus stoichiometry and generation of CO and H_2 in these units must be accounted for.

The only way to correct for all of these factors is to obtain appropriate measurements at a point where no further change can occur -- the tail gas. It is for this reason that the control strategy for SRUs has evolved into using the feed-forward flow ratio control loop to establish the proximate air to acid gas ratio and then using a feedback loop controlled by a tail gas analyzer to fine tune to a more exact ratio. The addition of an analytical system to the feed-forward loop has generally been an attempt to correct for deficiencies in upstream processes or to handle truly uncontrollable fluctuations in the feed streams. As noted previously, the addition of an analytical system to the feed-forward loop cannot replace the tail gas analyzer.

Feedback Control

Because the tail gas analyzer feedback loop "fine tunes" the feed-forward loop, it does not need full control of the total air into the process. Experience has shown that control of 10 percent of the process air is sufficient to provide trim adjustment over a wide range of conditions without the risk of destabilizing the reaction furnace if the control loop fails.

The feedback controller output can be used to bias the setpoint on the main air controller (cascade control) or it can be used to position a separate trim air valve. In either case, the feedback signal should have a dedicated controller. Note that when based on the air demand algorithm (Equation 4), the analyzer output is expressed in terms of what is happening in the process but which must be corrected. Thus, the controller must be reverse-acting -- a positive air demand indicates excess air in the process so the air valve should be closing.

Process lag time is approximately 15 to 30 s for a three-stage SRU at full load. Extreme turndown can increase process lag time to 4 to 5 minutes. For this reason, the gain setting during steady-state operation at or near an air demand of zero has to be low, typically 0.5 or less. Integral and derivative settings are also set to meet these conditions. Analyzer lag time is about 5 s for a typical tail gas analyzer with a 3 m (10 ft) sampling line.

Trim Air versus Main Air Valve Control

Whether control is applied to a separate trim air valve or is applied directly to the main air valve depends upon the size of the main air valve. Under steady-state operation near or at an air demand of zero, the analyzer output will continuously vary by ±0.5 percent air demand (±5 percent of full range or ±0.8 mA). If the process is to remain optimized, the main air valve must be capable of making these small adjustments. Experience has shown that if the main air valve is larger than 20 cm (8 in), such small changes are not possible and the ability of the control system to use the analyzer's sensitivity to optimize the process is negated.

Therefore, if the main air valve is larger than 20 cm (8 in), a separate trim air valve is recommended. It should be sized with a ratio of 1:8 in cross-sectional area relative to the main air valve. This is slightly more than 10 percent of the process air. A simple butterfly

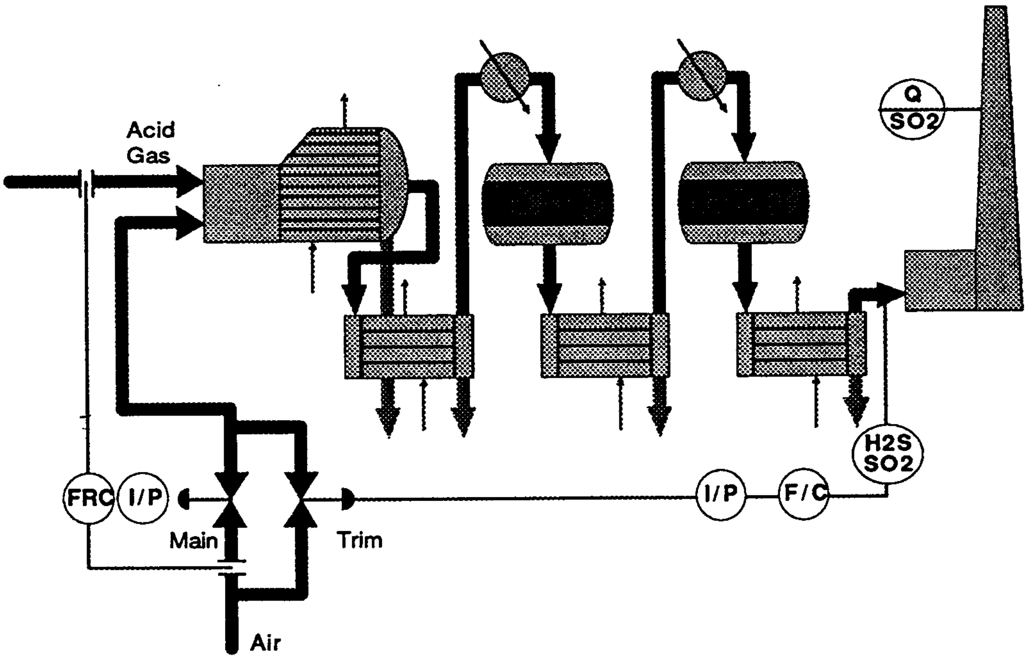

Figure 5: Claus plant with trim air line and a simple control system.

valve is adequate. It is important, however, to ensure that the trim air line take-off is upstream of the main air flow meter and the re-entry point is downstream of the main air control valve as shown in Figure 5 .

If the feedback signal is used to bias the main air to acid gas ratio setpoint in the feed-forward flow ratio control loop, the feedback control action must be limited to a similar 10 percent range to prevent complete disruption of the process if there is an equipment failure in the feedback control loop.

Advanced Control Techniques

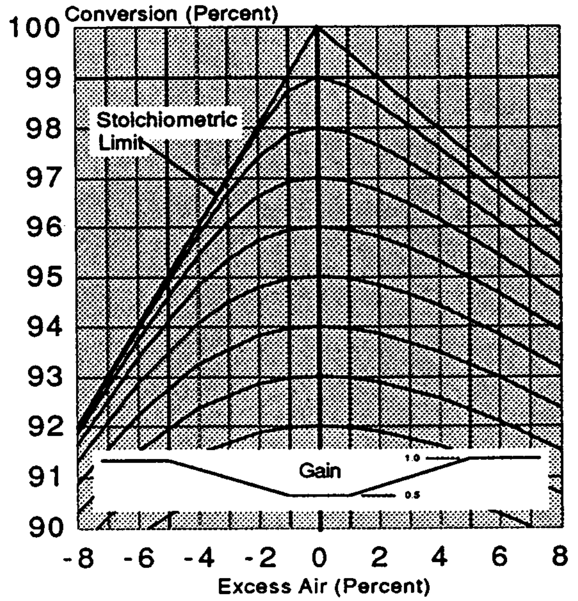

Figure 6: Efficiency as a function of excess air showing use of adaptive gain.

The behaviour of the SRU is usually quite different between steady-state operation at or near the correct air to acid gas ratio and operation during severely upset conditions.

Under steady-state operation with proper feedback control near the setpoint, the process air requirement (and hence the air demand) will vary by ±0.5 percent. In this case, optimal control of the air is achieved with low gain setting on the controller. Quite often an SRU must adjust to large changes in load or to changes in the amount of other combustibles (hydrocarbons, NH_3) in the feed streams. In these cases, the process is under upset conditions and the process air can be in error by ±20 percent or more. Quick control response is then required to avert severe loss of recovery efficiency and possible damage to the catalyst. If the feedback control loop is left in a low gain setting, such severe excursions from the setpoint can last 30 minutes or longer.

For this reason, the process is well suited for the application of adaptive gain or "smart" controllers. It is recommended that as soon as the control output exceeds ±1 percent of air demand (±10 percent of full scale or ±1.6 mA), the controller gain should be increased to give effective feedback control during the upset conditions (Figure 6). The gain is normally increased by a factor of 2, but does depend upon the programmable features of the controller. While slower, fine control action during operation near the setpoint optimizes recovery efficiency, quick control action during upset conditions provides a faster recovery from the upset condition.

Whereas an adaptive gain type control loop can handle momentary changes in feed streams, a smart controller can re-tune itself for varying load changes and this is well suited to SRUs that must handle different loads on a day-to-day basis. Another feature worth considering in advanced control is a remote input from the acid gas meter to adjust the gain in the feedback loop (Figure 7). If the SRU frequently must operate at high turndown, adjustment for the increase in process lag time can then be done automatically.

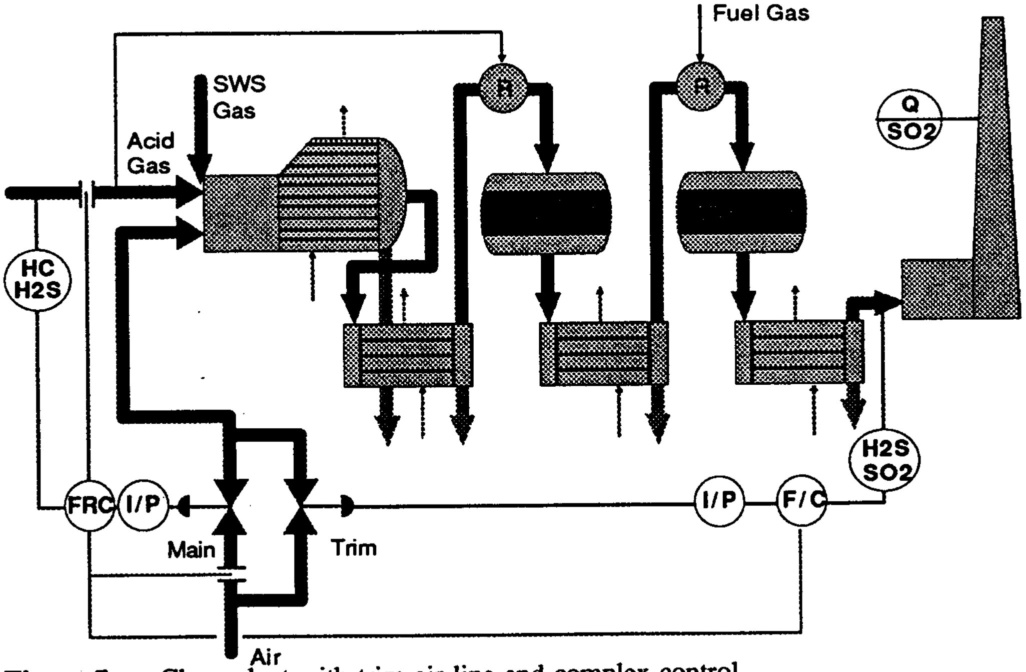

Figure 7: Claus plant with trim air line and complex control.

These advanced control features are available in most DCS or discrete controllers and are best integrated into the overall plant control system. The Foxboro 760 is an example of a self-tuning, smart controller that can be completely configured for most process conditions. Separate and distinct from the advanced control functions, there is an interface between the analyzer and the closed-loop control system to provide fail-safe action in case of analyzer failure or abnormal outputs. A built-in set of diagnostics in the analyzer locks out the control loop during malfunction or calibration, stabilizes control action and alerts the operator that service is required. In order to use this feature, the plant DCS controller must have a remote (auto/manual) input function.

Related topics and SRU Analyzer Applications

Area Classification

The classification of the area in which the SRU tail gas analyzer is installed depends upon the upstream processes. For SRUs associated with gas processing plants with relatively large site plots, the distances from adjacent unit operations are relatively large so that the areas are usually, but not always, classified as non-hazardous. This makes the packaging and specification of electrical heating components relatively easy.

However, this is not the case for refineries where the area surrounding the SRU is usually classified as hazardous. The site plots are much more crowded and the materials and processes present higher risks during normal operations. Because of recent catastrophic explosions in refineries and off-shore platforms, the worldwide regulations concerning safety are becoming more stringent. As a result, the specifications of equipment for use in hazardous areas are being upgraded and enforced.

Where required, the tail gas analyzer is given protection by purging the entire walk-in shelter. In other cases, it is installed in hazardous areas using a combination of purged and flame-proof (explosion-proof) cabinets for the various components so that a large purged housing or cabinet is unnecessary. The system temperature classification is usually T-3 in Europe and Group D in North America. Both allow a maximum temperature of at least 200°C (392°F) for surfaces exposed in the hazardous area.

There are two points worth noting about the tail gas sample. First, the pressure of the sample is usually lower than atmospheric pressure so that if a leak develops in the sampling system, air will enter the sampling line rather than tail gas vent to the atmosphere. Second, the normal concentration of H_2S is well below the lower explosive limit.

The electrical design of an analyzer for use in a feed-forward control loop is not as difficult. Since the water dewpoint temperature of the sample is usually lower than 40°C (104°F), the analyzer is easily packaged in a flame-proof (explosion-proof) housing.

Measurement of SO_2 Emission Rate

The mass emission rate of SO_2 is given by,

$$E = K_1 Q_S [SO_2], \tag{5}$$

where K_1 is a units conversion constant, Q_S is the flow rate of stack gas and $[SO_2]$ is the concentration of SO_2 in the stack gas. From the equation, it can be seen that two measurements are required for the determination of the mass emission rate: the concentration of SO_2 in the stack gas and the stack gas flow rate.

For a continuous emission monitoring (CEM) system, the concentration can be measured with a suitable UV analyzer and the flow rate can be measured by a number of methods, including an S-type pitot tube and by hot wire or ultra-sonic techniques. The mass emission rate of SO_2 is monitored continuously by such systems at most SRUs in Alberta, Canada.

For a Claus plant, a CEM has two functions. The first is obviously the policing function. The second is to provide process information to the operator. During normal operation or during optimization tests, an operator can easily evaluate any changes in process conditions by noting whether the SO_2 emission rate increases or decreases after the change is made. This is especially true if the incinerator and stack are dedicated to a single sulphur recovery train. Further, using the measured sulphur production with the measured mass emission rate of SO_2 is an accurate method for determining sulphur recovery efficiency[18]. For these reasons, it is preferable for any CEM installed on an SRU to provide mass emission rate as its output rather than just the SO_2 concentration.

Measurement of O_2 in Process Streams

Until recently, there has not been a pressing need for an on-line O_2 analyzer for use on conventional SRU process streams. The sub-stoichiometric operating conditions of the

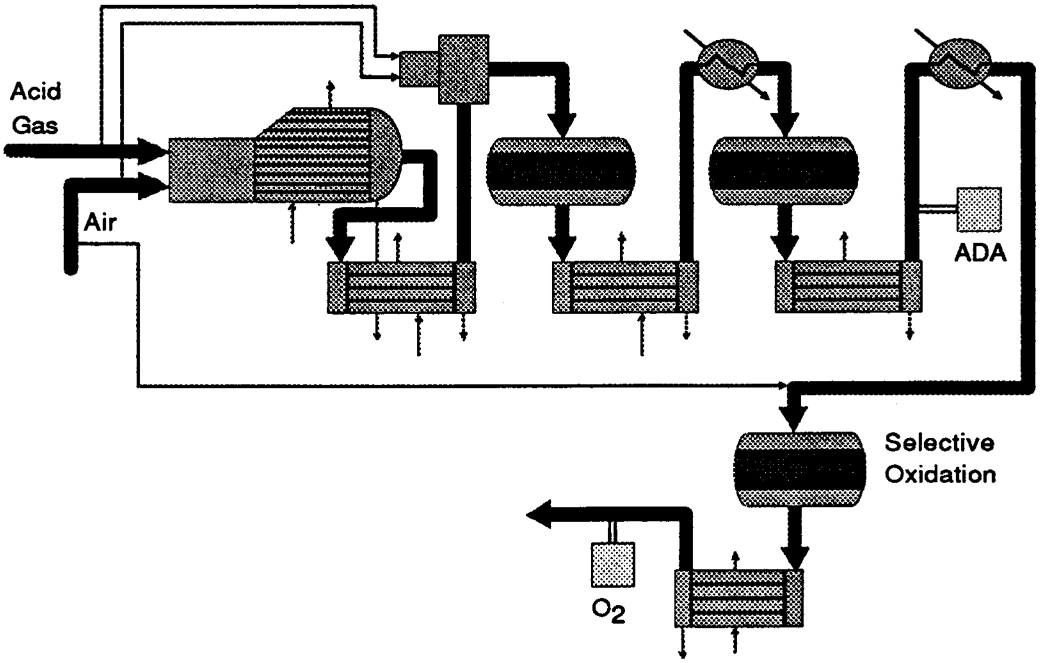

Figure 8: SUPERCLAUS-99 process showing locations of the air demand analyzer (ADA) and the O_2 analyzer.

process mean that free O_2 should not be present downstream of the reaction furnace. The new SUPERCLAUS-99 process[7] not only requires an O_2 analyzer but also requires a different control strategy. SUPERCLAUS-99 uses a selective oxidation catalyst in the final converter to increase recovery efficiency to 99 percent or better. Control of the process requires a modified air demand analyzer at the outlet of the final Claus converter and an O_2 analyzer at the outlet of the SUPERCLAUS converter (Figure 8). The process is operated such that the H_2S concentration at the outlet of the final Claus converter is between 0.6 and 3 mole percent (the SO_2 concentration is then minimal) and additional air is added just ahead of the SUPERCLAUS converter which contains a catalyst that selectively oxidizes H_2S directly to elemental sulphur. The O_2 analyzer is required at the outlet of the SUPERCLAUS converter to ensure the necessary excess of O_2 is present for the selective oxidation reaction.

The on-line analysis of O_2 in the SRU tail gas stream is difficult. It is currently being done successfully with an analyzer which employs the paramagnetic property of O_2 as the detection method. The sampling system used for the O_2 analyzer is the same as for the air demand analyzer whereby S_V is removed with an air-cooled condenser. An alternate sample-conditioning procedure is the use of a water wash to remove S_V. This approach must be used with caution because the water wash also removes other gases, including H_2O, O_2, SO_2, H_2S, which yields hard-to-handle, acidic washings and also requires that the output of the O_2 analyzer be corrected accordingly.

Measurement of Reaction Furnace Temperature

The measurement of the reaction furnace temperature in a conventional SRU is considered by many to be important only during the start-up procedure. The reason for this is that the temperature in the reaction furnace of a conventional straight-through SRU is determined by the composition of the acid gas which cannot be changed by the operator. However, for plants having the split-flow configuration, or plants with straight-through configurations that are processing a SWS stream or any plant using an O_2-enrichment scheme, the reaction furnace temperature is an important operating parameter. In the past, the measurement of the reaction furnace temperature has been very difficult. Even noble metal thermocouples do not have acceptable lifetimes in the hostile high temperature (up to 1500°C, 2725°F) environment.

The development of a non-intrusive infrared optical pyrometer[19] specifically for this application has solved the problem. The device is in service in a large number of SRUs worldwide and has proven to be accurate and reliable.

Measurement of H_2S in Liquid Sulphur

Produced liquid sulphur from the Claus SRU contains a certain amount of dissolved H_2S in the form of polysulphides. It is becoming more common that the produced sulphur must be "degassed" to meet customer's specifications, and the H_2S from the degassing process must be monitored.

The degassing process causes the gaseous H_2S to accumulate in the vapour space of the pit, where it is normally removed by a fresh air sweep educted to the incinerator or stack. To prevent an explosive mixture from accumulating, the vent gas is analyzed for H_2S and alarmed at 50 % of the LEL (2 mole %).

The analyzer in this case is very similar to the tail gas application, although sample conditions are not quite as severe. The sample temperature is at $\approx$ 100 °C and can be saturated with sulphur vapour. For this reason all the usual precautions to prevent sulphur plugging must be taken. If the analyzer has the capability, it is also desireable to monitor for SO_2 simultaneously. High SO_2 readings would indicate a smoldering sulphur fire.

Advanced Photometric Techniques for Tail Gas Analyzers

Recent developments by vendors of UV photometric analyzers for sulphur plant applications include multiwave UV photometers and process diode array (PDA).

The principal objective is to try and quantify the interferences in the sample stream (S_V, COS, CS_2) that affect the H_2S and SO_2 outputs. As well components of minor interest (COS, CS_2) can be made available as secondary outputs.

Both diode array and multiwave photometers are capable of these determinations, but their value as control parameters is limited.

The best way to minimize interference is to reduce the S_V concentration by conditioning the sample. It is acceptable to try and further quantify the remaining interference, but removing the bulk of it, optimizes the primary analysis of H_2S and SO_2.

Certainly COS and CS_2 are of interest, as they can be related to catalyst activity. However, given that the absorbance for COS/CS_2 is only 20 - 40 % compared to the absorbance of H_2S/SO_2 and that there is normally an order of magnitude difference in concentration (COS/CS_2 < 1000 ppm, H_2S/SO_2 $\approx$ 1 %) the information is at best an indication, as they are below the threshhold limit. Once COS and CS_2 reach significant levels (>1000 ppm), a decrease in catalyst activity is readily apparent from decreased catalyst bed temperatures.

At the same time as new analytical principles have been applied, there have been changes made to some sampling systems. These sampling techniques have placed the analyzers on, and close coupled to the process pipe. The claimed advantage is elimination of the sample line, but complications arising from access to the sample system and poor environment for the analyzer easily negate this. A properly designed extractive sample line is not a source of problems.

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