With the increasing environmental concerns, sulfur recovery has become one of the leading issues in emissions reduction in industry. For gas processing and refining facilities sulfur recovery requirements range from 97.5% to 99.8%. The well-known Claus process with some form of tail gas cleanup or special processing capability can meet these requirements with the help of high performance process analytics. Siemens Analytical Products and Solutions, a leader in process analytics, has proven over decades its competence to plan, engineer, manufacture, implement and service analyzer systems for use in Claus plants.

This Case Study provides details about the Claus process and related analyzer tasks.

**Sulfur recovery**

The relatively high sulfur content of the still available crude oil and natural gas reserves and the more stringent standards for sulfur emissions from oil, gas, and chemical processing facilities demand reliable and cost-effective technologies for sulfur recovery. Sulfur recovery refers to the conversion of hydrogen sulfide (H₂S) as by-product of natural gas plants and crude oil refineries to elemental sulfur.

The most common conversion method is the Claus process. Approximately 90 to 95% of recovered sulfur is produced by the Claus process.

First invented over 100 years ago, the Claus process has undergone a continuous evolution in attempts to increase the sulfur recovery efficiency of the process. In the 1930s, a thermal stage was added to the two catalytic stages, which increased the recovery efficiency from 95% to approximately 97%. In the 1970s, a hydrogenation/hydrolysis plus amine separation was added to treat the tail gas from the Claus process. In 1988, Super Claus was introduced, which added a selective oxidation reactor to the end of the Claus process, increasing the efficiency to approximately 99%.

Sulfur recovered in Claus plants is e.g. used for manufacturing of medical products, cosmetics, fertilizers and rubber products.

Chemical analysis of the process streams is required for controlling and monitoring the Claus process. Process gas chromatography together with continuous gas analyzers has proven to be a very reliable and cost-efficient method.

Siemens Analytical Products and Solutions provides efficient solutions for this demanding analysis tasks.
Claus process for H₂S removal

Hydrogen sulfide (H₂S) is commonly found in natural gas and products from oil refineries, especially if the crude oil contains a lot of sulfur compounds. Typical sources are:

- Gas from natural gas fields
- Sour refinery gas
- Sour water stripper gas
- Sour gas from chemical plant
- Sour gas from salt production plant
- Sour gas from coal gasification

H₂S is a smelly, corrosive, highly toxic gas, which also deactivates industrial catalysts. Therefore it is converted to non-toxic and useful elemental sulfur at almost all locations where it is produced. The process of choice is the Claus sulfur recovery process.

Most sulfur plants comprise two conversion stages: one non-catalytic, thermal conversion stage and two or more catalytic conversion stages in series (fig.1). The Claus reaction is highly exothermic, releasing a great deal of heat energy that can be recovered by generating steam in heat exchangers following the conversion stages.

**Thermal conversion stage**
The H₂S containing gas (sour water stripper - SWS - gas, amine acid gas) is fed to the thermic converter where it is partially oxidized with air in a reaction furnace at high temperatures (1 000 to 1 400 °C). Combustion air is fed to the burner, with the amount of air controlled to combust only ¹/₃ of the H₂S to SO₂ (reaction 1).

\[
\begin{align*}
(1) & \quad 3 \text{H}_2\text{S} + \frac{1}{3} \text{O}_2 \rightarrow 2 \text{H}_2\text{S} + \text{SO}_2 + \text{H}_2\text{O} \\
(2) & \quad 2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 2 \text{H}_2\text{O} + 3 \text{S}
\end{align*}
\]

²/₃ of the H₂S remain unreacted due to lack of oxygen. Additionally air may be fed to combust also ammonia and hydrocarbons entering with the acid gas streams.

The furnace acts as a thermal conversion stage, as the high temperature in the furnace will cause part of the H₂S and SO₂ to react with one another via reaction (2). Thus sulfur is formed, but some H₂S and SO₂ remain unreacted.

The hot combustion products from the furnace enter the waste heat boiler and are partially cooled by generating steam. The gas is further cooled in the first sulfur condenser, to condense the sulfur formed in the furnace, which is then separated from the gas and drained to a collection pit.

**Catalytic conversion stage**
The gas leaving the sulfur condenser is heated again to avoid forming liquid sulfur in the downstream catalyst bed and enters the first catalytic converter. There, the remaining H₂S reacts with the SO₂ at lower temperatures over a conversion catalyst (mostly alumina-based) to make more sulfur. Unfortunately the reaction does not go to completion even with the best catalyst. Typically, about 70 % of the H₂S and SO₂ in the gas will react via reaction (2) to form sulfur, which leaves the reactor with the gas as sulfur vapor. The hot gas is cooled in the second sulfur condenser, where more sulfur is formed, separated, and drained to the collection pit. This is usually followed by one or two more heating, reaction, and condensing stages to react most of the remaining H₂S and SO₂.

**Tail gas treatment stage**
A small amount of H₂S and SO₂ remains in the tail gas. The tail gas is routed to either a tail gas cleanup unit (modified Claus process with tail gas cleanup) for further processing, or to a tail gas thermal oxidizer to incinerate all of the sulfur compounds in the tail gas to SO₂ before dispersing the effluent to the atmosphere.

Fig. 1: Generic flowsheet of the Claus process, simplified
Claus process versions
Increasingly stringent standards for sulfur emissions have caused further developments of the Claus process with the objective of higher recovery rates. Table 1 shows a selection.

<table>
<thead>
<tr>
<th>Claus process versions (selection)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Claus process</td>
<td>This original Claus process uses only the catalytic reaction.</td>
</tr>
<tr>
<td>Modified Claus process</td>
<td>This process uses the additional thermal conversion stage where 1/3 of the ( \text{H}_2\text{S} ) is converted to ( \text{SO}_2 ) and ( \text{S} ). The modified Claus process is generally limited to a sulfur recovery efficiency of 94 ... 97 %. Higher recovery rates are achieved by adding a tail gas treatment unit.</td>
</tr>
<tr>
<td>Oxygen Claus process</td>
<td>This process uses an air/oxygen mixture to reduce the nitrogen content in the process flow for better plant efficiency.</td>
</tr>
<tr>
<td>Super Claus</td>
<td>This process uses a special catalyst material in the last catalytic reactor.</td>
</tr>
</tbody>
</table>

Table 1: List of Claus process versions

Analysis tasks
The continuous development of sulfur recovery processes has increased the demand in efficient process analytical techniques for process and emission control. Stringent requirements are placed on the process analyzers and especially on the tail gas analyzer to determine process parameter air demand.

Various measuring points with different tasks are located along the process route (fig. 1 and table 2). The most important task is the determination of the concentrations of hydrogen sulphide (\( \text{H}_2\text{S} \)) and sulfur dioxide (\( \text{SO}_2 \)) in the desulfurized gas (tail gas, MP 5 in fig. 1) and following from this the calculation of the \( \text{H}_2\text{S}/\text{SO}_2 \) ratio. This ratio is the only parameter for direct process control through the amount of combustion air fed to the furnace at the thermal stage. The ratio should be kept to 2:1 to run the process at optimum efficiency.

Challenges
There are two major analysis challenges that must be considered when choosing the measuring principle of the analyzer:

- Other gaseous components may be present in the sample gas such as \( \text{CO}_2 \), hydrocarbons, \( \text{COS} \) and \( \text{CS}_2 \) with varying concentration levels. So the analyzer principle should be free from cross-interferences.
- The sample gas is saturated by sulfur vapor or even elementary sulfur may be produced that may amongst others block sample lines. So the entire sampling system must be heated to a temperature that prevents reliably from sulfur condensation.

Solution from one hand
Siemens Analytical Products and Solutions is able to supply turnkey analyzer systems for Claus plants including CEM system (see table 2, MP 7), along with planning, engineering, start-up, commissioning and training services.

MAXUM edition II "Claus Analyzer"

MAXUM edition II represents the top technology in process gas chromatography with outstanding features resulting in a high versatility to solve any given application task with best possible analytical results at highest cost efficiency. Instrumental reasons for that are:

- Multiple analytical tools such as ovens, detectors, valves etc.
- Single and independent dual oven concept minimizing the number of analyzers
- Airbath and airless oven to reduce utility costs
- Valveless column switching to reduce maintenance
- Parallel chromatography for fast analysis, system simplification and increase of reliability
- Complete networking capabilities and powerful processing software

Fig. 2: Claus plant

Table 2: Analysis measuring tasks and suitable Siemens analyzers

<table>
<thead>
<tr>
<th>Sampling point (MP)</th>
<th>Measuring components</th>
<th>Suitable Siemens analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Process gas feed</td>
<td>( \text{H}_2\text{S}, \text{SO}_2, \text{CO}_2, \text{HC} )</td>
</tr>
<tr>
<td>2</td>
<td>Inlet of first catalytic converter</td>
<td>( \text{H}_2\text{S}, \text{SO}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>Outlet of first catalytic converter</td>
<td>( \text{H}_2\text{S}, \text{SO}_2 )</td>
</tr>
<tr>
<td>4</td>
<td>Outlet of last catalytic converter</td>
<td>( \text{H}_2\text{S}, \text{SO}_2 )</td>
</tr>
<tr>
<td>5</td>
<td>Tail gas downstream the last condenser</td>
<td>( \text{H}_2\text{S}, \text{SO}_2, \text{COS}, \text{CS}_2, \text{N}_2, \text{H}_2\text{O}, \text{O}_2 )</td>
</tr>
<tr>
<td>6</td>
<td>At the sulfur collection pit</td>
<td>( \text{H}_2\text{S}, \text{SO}_2 )</td>
</tr>
<tr>
<td>7</td>
<td>Before / at the stack (CEM)</td>
<td>( \text{SO}_2, \text{CO}, \text{NO}, \text{O}_2 )</td>
</tr>
</tbody>
</table>

Measurements at MP 3, 4 and 5 can be performed with just one analyzer using sample stream switching.
MAXUM edition II configured for Claus analysis

Process gas chromatography has generally proven to be a reliable and cost effective method to solve the demanding task of Claus tail gas analysis. Especially MAXUM edition II, because of its double oven concept and outstanding modularized design, can be designed a very efficient Claus gas analyzer.

The two separately heatable ovens with airless mass heating (fig. 3) are used to clearly separate the functionalities required for the analysis task:

- The right oven contains the analysis system including the separating columns, circuit and detectors.
- The left oven contains sample conditioning, calibration media dosing and the dosing valve. To prevent from blockages by solid or plastic sulfur the sample line is purged with nitrogen or air.

Heated sampling and dosing

Sulfur becomes solid or semi-liquid when the sample temperature drops below 135 °C or rises above 150 °C. Therefore, the sample temperature must be kept at 145 °C continuously from the sampling point to the analyzer. Steam heated sampling lines (tube-in-tube technology, fig. 4) and sample conditioning components mounted in a high temperature environment (left oven) meet this requirement.

User benefits

- Proven technology with high reliability, long term stability
- Reliable operation through backpurge to clean analyzer and sample lines in case of temperature variations or power failure and during maintenance
- Easy operation, remote operation
- Low maintenance efforts
- No UV-lamp, long-time stability
- No expensive spare parts regularly needed
- High accuracy through use of chromatographic separation (no interferences by sulfur, COS, CS₂)
- High reliability due to comprehensive self diagnosis
- Extended analysis to other components possible such as N₂, CO₂, COS, H₂O
- Network with other GCs on plant
- Very cost-efficient

Fig. 3: MAXUM edition II Claus analyzer

Fig. 4: tube-in-tube technology (left) and isolated sampling lines (right)