Eliminating the Burner and Thermal Reactor from the Sulfur Recovery Unit

GT-CataFlame™ replaces the conventional burner and thermal reactor of the “modified Claus” process with a catalytic combustor that uses a patented catalyst which is highly selective to the conversion of H₂S to Sulfur. The GT-CataFlame catalytic combustor achieves, in a fraction of the volume, near equilibrium H₂S conversion with fewer operating issues than a conventional Claus thermal reactor.

Some of the advantages of this technology include:

- Higher reaction efficiency
- Lower turn-down capabilities
- Lower COS and CS₂ formation
- Smaller Claus reactor beds
- Reduction of soot formation
- Near seamless switching between acid gas/fuel gas
- No oxygen breakthrough during start-up or shut-down activities

GTC Technology US, LLC has integrated the GT-CataFlame equipment with the other equipment of the Claus Sulfur Recovery Process and licenses the complete process technology under the name GT-SPOC™. The GT-SPOC process may utilize the GT-CataFlame equipment in a conventional horizontal arrangement or in a single vertical tower arrangement.

In the vertical arrangement GT-CataFlame is coupled to a waste heat boiler followed immediately by the first Claus converter bed, first Sulfur condenser, gas reheater, second reactor bed and second Sulfur condenser in a single vertical tower arrangement. The vertical arrangement reduces the interconnecting piping, Sulfur rundown piping and the overall plant footprint of the process which in turn reduces capital cost. The molten Sulfur produced also contains a lower concentration of dissolved H₂S and sulphanes.

GTC Technology offers a full range of solutions in the refinery and gas processing industries including acid gas removal, dehydration, liquids recovery and Sulfur recovery from a variety of process gas streams. In addition, GTC offers to refining, polyester, chemical and petrochemical industries more than 25 licensed technologies to increase capacity, improve efficiency, maximize production of valued-added products and reduce environmental impact.
Introduction

Producers and processors in the refining, gas processing, petrochemical and other industries have a growing focus on technologies that will not only improve the quality of their product streams but will also enable them to comply with the more stringent environmental regulations being imposed by governmental agencies. They face the additional challenge that conventional fuel sources are becoming increasingly sour and environmental regulatory agencies are consistently taking steps to improve emission standards with a desire for a cleaner environment. A process that is used widely by producers and processors for controlling Sulfur-containing emissions is the modified Claus Sulfur Recovery Unit (SRU). The SRU has a very low operating cost and could in some circumstances have a positive return, depending upon the market value of Sulfur and the utilization of the produced steam. Oftentimes however, the value of an SRU is defined by the lost opportunity cost associated with downtime of the associated hydrocarbon processing unit as well as by its cost of operation. Therefore a more reliable unit has significant value as it allows the producers and processors increased “on stream” factor. For the producers and processors, it is important to understand the various Sulfur removal and recovery technologies available so that the most reliable, lowest cost processes can be selected and used in their facilities.

Over the past decade, researchers at Phillips 66 developed a catalytic combustor that can be used to replace the burner and thermal reactor in modified Claus units to improve the operation and reliability of the SRU [1-10]. GTC Technology US, LLC, has acquired the exclusive licensing rights to the catalytic combustion technology and markets it under the name GT-CataFlame™. GTC markets the complete SRU process of GT-CataFlame integrated with the downstream Claus converters under the name GT-SPOC™ (Sulfur Partial Oxidation Catalysis). The ultimate design of GT-SPOC is a single vertical vessel that contains all the components of GT-CataFlame, followed by the Claus converters and Sulfur condensers.

Background

Conventional Claus

The Claus process was patented by Carl Friedrich Claus in the 1880’s, and introduced in the middle 1930’s by I.G. Farbenindustrie. The process as introduced included the addition of a furnace upstream of the Claus catalyst beds, and is referred to as the “modified Claus” process. It is the most successful commercial method for Sulfur recovery. In the modified Claus SRU, the reaction of $\text{H}_2\text{S}$ with oxygen is separated into two stages: (1) a highly exothermic thermal stage where any hydrocarbons and combustibles in the sour gas are burned and approximately one third of $\text{H}_2\text{S}$ present in the sour gas stream is converted to $\text{SO}_2$ and (2) moderately exothermic catalytic stages where the remaining $\text{H}_2\text{S}$ in the sour gas stream reacts with $\text{SO}_2$ to produce elemental Sulfur. The reactions are reversible, and conversions are highly temperature, Sulfur content and moisture
content dependent. To achieve Sulfur conversions of greater than 60-70%, the thermal stage is followed by Sulfur condensation and separation which is followed by reheating upstream of a catalytic stage operated at temperatures higher than the Sulfur dew point. Additional catalytic stages may be added to increase Sulfur removal efficiency.

The flame stability of the combustion section is a critical parameter in Claus operations. At H$_2$S content of above 50%, the acid gas can be sent directly to the burner. Between 30 – 50% H$_2$S, the acid gas or combustion air (or both) may need to be preheated. At acid gas concentrations below 30% H$_2$S, the Claus unit operates in a “split flow” mode with preheat, and if the H$_2$S content drops below 10%, fuel gas may need to be added.

A 2-stage Claus unit can deliver 90 – 95% Sulfur recovery efficiency, with a 3-stage configuration delivering 95 – 98% recovery. The tail gas is generally sent to an incinerator if 96 – 97% Sulfur recovery efficiency is acceptable. If Sulfur recovery in the 99 – 99.5% range is required, tail gas operations based on a continuation of the Claus reaction under sub-dew point is generally undertaken either on a solid bed, or in the liquid-phase. If Sulfur recovery efficiencies of 99.9% are required, the Sulfur compounds in the tail gas are converted to H$_2$S by hydrogenation and hydrolysis; then the H$_2$S is captured by an amine solution and after stripping it out of the amine solution the H$_2$S is recycled to the inlet of the Claus unit.

Modified Claus units may be very challenging to operate reliably, and are particularly prone to problems during startup and shutdown. The burner is usually started up and shut down by burning fuel gas rather than the acid gas. For example, during a shutdown when the feed is switched from acid gas to predominantly fuel gas a higher temperature and/or soot formation may result in addition to other undesirable consequences. The soot has a tendency to foul and plug the Claus catalyst downstream of the thermal reactor.

The operating cost associated with Sulfur removal for a Claus unit with tail gas cleanup is in the range of $100 per ton of Sulfur produced considering utilities and maintenance costs. The Sulfur that is recovered is generally bright yellow and preferred in the marketplace. Depending upon the commodity value of Sulfur the unit may achieve a net positive annual return.

**GT-SPOC Technology: Process Description**

GT-SPOC Technology uses a patented, durable catalyst in a “short-contact-time” reactor, GT-CataFlame, to achieve near equilibrium H$_2$S conversion and Sulfur selectivity in one-tenth of the volume used by a conventional Claus burner and thermal reactor [10, 11]. The GT-CataFlame catalyst also contains components that eliminate classic Claus catalyst deactivation mechanisms of
Sulfur poisoning and coke deposition of the catalyst in the first Claus converter during normal Sulfur recovery operation and start-up / shut-down activities using fuel gas.

Figure 1 shows a block flow diagram for GT-SPOC Technology and the GT-CataFlame combustor equipment integrated with the Waste Heat Boiler (WHB), and the remainder of the typical downstream equipment as expected in a conventional 3-stage Claus SRU. This diagram shows the horizontal configuration of GT-CataFlame where the GT-CataFlame is installed in place of the Claus burner and thermal reactor.

In the GT-SPOC process, the air and the acid gas are preheated to approximately 220 °C (428 °F) before they are mixed. The gases are blended in a specially designed chamber to thoroughly mix the two gases upstream of the GT-CataFlame combustor catalyst. The mixed gases enter the GT-CataFlame and pass through the catalyst bed in less than 1 second and immediately after the catalyst bed enter the WHB. In the GT-CataFlame combustor approximately 1/3rd of the H$_2$S is converted to SO$_2$ and H$_2$ or H$_2$O, most of the hydrocarbons are converted to H$_2$, CO, CO$_2$ and H$_2$O, and any ammonia is converted to N$_2$ and H$_2$ or H$_2$O. A portion of the remaining 2/3rd of the H$_2$S reacts with the 1/3 of the formed SO$_2$ to form elemental Sulfur, and a portion of the H$_2$S splits to form H$_2$ and Sulfur. As a result of those reactions, approximately 70% of the inlet H$_2$S is converted to Sulfur in the GT-CataFlame combustor and is removed by the first Sulfur condenser. In the conventional Claus SRU as well as in the case of GT-SPOC, the gas exiting the WHB may be sent to the first Sulfur condenser where elemental Sulfur is removed, and after the condenser the gas may be reheated to pass into the first Claus converter. Alternately, in GT-SPOC, the gas exiting the WHB may pass directly into the first Claus converter and the previously mentioned first Sulfur condenser and
re-heater may be eliminated; passing directly from the WHB into the first Sulfur condenser the process effectively “jumps” the Gamson and Elkins curve and 90% Sulfur recovery occurs after the first Claus converter [12]. The process that includes sending the gas directly from the WHB into

### Table 1 Conditions for Comparison of GT-CataFlame to a Claus Burner and Thermal Reactor.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Acid Gas From Amine Unit</th>
<th>Sour Water Stripper Gas</th>
<th>Combustion Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Flow, kg/h</td>
<td>4,050</td>
<td>730</td>
<td>10,900</td>
</tr>
<tr>
<td>Flow Rate, Nm₃/h</td>
<td>2,671</td>
<td>675</td>
<td>8,500</td>
</tr>
<tr>
<td>Composition, Mole %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>0.403</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂</td>
<td>0.604</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C₃</td>
<td>0.998</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C₄</td>
<td>0.503</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.998</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.398</td>
<td>19.960</td>
<td>1.423</td>
</tr>
<tr>
<td>H₂S</td>
<td>94.096</td>
<td>39.920</td>
<td>0.000</td>
</tr>
<tr>
<td>Hexene</td>
<td>0.000</td>
<td>0.133</td>
<td>0.000</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.000</td>
<td>0.067</td>
<td>0.000</td>
</tr>
<tr>
<td>N₂</td>
<td>0.000</td>
<td>0.000</td>
<td>77.892</td>
</tr>
<tr>
<td>O₂</td>
<td>0.000</td>
<td>0.000</td>
<td>20.685</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.000</td>
<td>39.920</td>
<td>0.000</td>
</tr>
</tbody>
</table>

A conventional Claus burner and thermal reactor unit was compared to a GT-CataFlame combustor unit, both were designed for the same acid gas application, and the conditions used to design both units are summarized in Table 1. Comparing the designs indicates that the Claus burner and thermal reactor are 10 times the size of the GT-CataFlame for the same application. The savings in metal, footprint and amount of refractory material required for GT-CataFlame is significant. In this
comparison the GT-CataFlame refractory volume is 1/40th that of the refractory volume required for the thermal reactor.

The ultimate design intended for GT-SPOC is a vertical arrangement, i.e., the GT-CataFlame integrated with WHB and the downstream Claus unit equipment all combined in a single vertical tower. A simplified diagram of the vertical GT-SPOC with two Claus converter stages is shown in Figure 2. The acid gas and air are first preheated as was previously mentioned in the process description above. The preheated gases are then combined at the top of the GT-SPOC unit in the mixing chamber. The well-mixed gas then travels downward to the GT-SPOC catalyst where 1/3rd of the H₂S is converted to SO₂. In the GT-SPOC process, the gas passes from the GT-CataFlame directly into the first Claus converter without first passing through a Sulfur condenser, i.e., the Sulfur condenser located

![Figure 2](image-url)
between the WHB and the first Claus converter is removed. The WHB is designed so that the operating
temperature of the gas out of the first Claus converter remains above the Sulfur dew point temperature;
the heat rise from the reaction in the first Claus converter is accounted for in the design of the WHB.
After the first Claus converter, the gas is cooled in the first Sulfur condenser and molten Sulfur forms
as it does in the conventional Claus SRU. The molten Sulfur collects on a chimney-type separation
tray where the liquid Sulfur exits the side of the unit or through an internal downcomer, and the gas
passes down through the chimney. After this molten Sulfur separation tray, the gas is reheated and the
remainder of the process has the same steps as a conventional SRU except that they are arranged in a
vertical configuration.

The process that includes removing the first Sulfur condenser, i.e., the condenser located after the
WHB and upstream of the first Claus converter, is patented by Phillips 66 and licensed by GTC.
This step has the advantage of reducing the number of pieces of equipment, the overall SRU footprint,
and reducing the cost of the SRU. This configuration may be applied to a conventional Claus SRU
with or without a GT-CataFlame in addition to being used in the vertical GT-SPOC SRU.

GT-SPOC: Operating Data
Phillips 66 conducted a large number of tests on a catalytic combustor that could be used to replace
the conventional Claus burner and thermal reactor with the goal of providing improved operation of
Claus SRU’s. After extensive development, a robust catalyst formulation and a combustor design were
attained that delivered results which could be used to model and design commercial facilities. The
GT-SPOC summary results presented in Table 2 are from tests using the catalytic combustor compared
to measurements taken at the SRU’s of four refineries. The results showed significant improvement
in hydrogen and Sulfur yields over what was typically observed in conventional refinery Claus SRU’s.
Higher Sulfur and hydrogen yields resulted from direct oxidation and subsequent splitting of H₂S
at high reaction temperature [11]. The results were gathered with no hydrocarbons in the inlet gas
therefore the hydrogen must come from NH₃ and H₂S.

<table>
<thead>
<tr>
<th>Unit</th>
<th>GT-CataFlame</th>
<th>Refinery A</th>
<th>Refinery B</th>
<th>Refinery C</th>
<th>Refinery D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃ present?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>% S yield</td>
<td>74.0</td>
<td>63.4</td>
<td>48.1</td>
<td>54.9</td>
<td>68.2</td>
</tr>
<tr>
<td>% H₂ yield</td>
<td>7.0</td>
<td>6.3</td>
<td>3.5</td>
<td>5.4</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 2 Results for GT-CataFlame compared with Sulfur and H2 Yields at Four Refinery Claus SRU’s.
Operating Results

Shown in Figure 3 is a GT-CataFlame unit built by the researchers at Phillips 66 and installed at a refinery location in the U.S. The horizontally configured GT-CataFlame is shown in the red-dashed line circle in the figure.

![GT-CataFlame Equipment Installed at a Refinery in the United States.](image)

The GT-CataFlame operated successfully, and testing was performed to identify the operating parameters and catalyst formulation that resulted in:

1. The highest $\text{H}_2\text{S}$ conversion to Sulfur,
2. Producing the necessary amount of $\text{SO}_2$ for the downstream Claus converters,
3. The least amount of unwanted byproduct formation, primarily COS and CS$_2$,
4. The destruction of ammonia, and
5. Formation of $\text{H}_2$ and CO, rather than any unwanted hydrocarbon byproducts.

The results in Figure 4 show the performance of the catalyst that was evaluated for an extended period of time in the GT-CataFlame unit. During this period, air-to-$\text{H}_2\text{S}$ ratios and gas velocities were being evaluated, so throughout the duration of the testing these parameters were varied to observe the
effects and to arrive at optimum operating conditions. However, even though conditions were changed
H₂S conversion and selectivity towards forming elemental Sulfur remained high throughout the
period. At certain points the data reflect operating conditions that achieve the best H₂S conversion
and Sulfur yield so those operating conditions will be used for commercial unit design and operation.
Throughout the test period the range of gas composition was approximately 80 - 82 mol% H₂S, 11
- 12 mol% CO₂, 5 - 6 mol% water, and 1 mol% hydrocarbon content; the remaining 1 - 2 mol% is
nitrogen and the typical analytical measurement error.

The results indicate that over 80% of the H₂S was converted with approximately 69-70 % yield of
elemental Sulfur, the remainder was as unreacted H₂S and SO₂, and less than 1% formation of COS
and CS₂ combined. In addition there was an average 7% yield of H₂. This performance was better
than that of a conventional Claus burner and thermal reactor where 50–70% of the inlet H₂S is
converted and the elemental Sulfur yield is 40 – 65% of the inlet Sulfur.

Figure 4 Results of H₂S Conversion, Sulfur Yield and Hydrogen Concentration in the Outlet Gas for
900 Hours of Testing at Various Operating Conditions for the GT-CataFlame Unit.
GT-CataFlame and GT-SPOC Advantages

Based upon the results of the GT-CataFlame unit that have been presented here and previously [10], several process and economic advantages have been identified from having a short-contact-time catalytic combustor versus a Claus burner and thermal reactor. The advantages are summarized below and explained in more detail in the following sections.

Process Advantages

• Since the reactants are pre-mixed prior to passing through the GT-CataFlame combustor, the reaction is uniform through the cross section of the high-temperature catalyst eliminating the problems of post-combustion mixing in the Claus thermal reactor for contaminant destruction.
• Close-coupling of the GT-CataFlame catalyst zone and the WHB improves overall Sulfur yield and reduces the air requirement due to rapid reaction quenching. This eliminates the oxygen breakthrough problems that routinely occur in Claus units.
• No flames, fire-eyes, nor burner management systems are required. A small retractable burner or access to a hydrogen containing fuel is all that is needed to trigger the catalyst at startup.
• Fuel gas oxidation for warm up takes place at 25% air stoichiometry eliminating oxygen breakthrough to downstream Claus converter beds during startup and shutdown.
• Low molecular weight hydrocarbons are converted to reduction Tail Gas Unit (TGU) friendly H₂ and CO by catalytic partial oxidation. Soot formation is eliminated. Air/fuel ratios for fuel gas oxidation are very close to the acid gas/air ratios making switching between the two nearly seamless.
• COS and CS₂ formation are significantly reduced.
• The Sulfur product contains only 25-33% of the dissolved H₂S and sulphanes of normal Claus Sulfur, reducing the need for large Sulfur degassing units.

Economic Advantages

• GT-CataFlame requires significantly less refractory lining compared to the conventional Claus thermal reactor.
• Small GT-CataFlame combustor volume and reduction of byproducts allows for design changes reducing overall SRU footprint.
• The Claus plant can be constructed in a vertical orientation where the unit is self-draining.
• The vertical GT-SPOC design eliminates some interconnecting piping and Sulfur rundown piping and equipment.
• Because GT-CataFlame is smaller than a typical burner and thermal reactor, there is less refractory and catalyst mass to heat up or cool down; this in turn reduces the time required for shutdown or startup.
• The first Sulfur condenser and re-heater that is located downstream of the WHB may also be eliminated, so that the gas stream exiting the WHB flows directly to the first Claus reactor stage. Eliminating this equipment is a significant capital reduction.
COS and CS$_2$ Reduction and Implications for Claus Converter Bed Design

The best method to minimize the effects of hydrocarbon contamination of acid gases in any SRU is to prevent hydrocarbon absorption in the acid gas removal system (by using slug and drop catching drums, aerosol droplet removal, and lean amine /sour gas differential temperature control) and mitigate hydrocarbon accumulation (by using rich flash drums with skimming and gas removal, carbon filtration, and regenerator reflux purge). Despite these efforts, hydrocarbon may get into the acid gas leading to a production of the undesired byproducts, COS and CS$_2$. Nominally the byproducts result from reacting after the flame mixing zone where hot, oxygen-free flame byproducts can mix with unburned hydrocarbons and form sulfur, e.g., CH$_4$ and S$_2$, in the acid gases as in a typical 1/3-2/3 split flow burner and thermal reactor for leaner H$_2$S content gases. [14] Since the gases flowing to the GT-CataFlame combustor are pre-mixed and preheated the temperature is hotter than that of a thermal reactor (CataFlame is approximately 2200 to 2300 °F). Also, since the residence time from the catalyst reactor to WHB is a fraction of a second, less COS and CS$_2$ will form as compared to a conventional Claus unit. Data from the GT-CataFlame unit operations confirms a significant reduction in the amount of byproduct COS and CS$_2$.

A study of 24 gas plants with a broad range of inlet H$_2$S concentration in the gas passing to the Claus burner and thermal reactor showed that the COS and CS2 concentration in the gas exiting the WHB was in the range of 0.06 – 1.7 mol% for COS and 0.01 – 1.1 mol% for CS$_2$. [13] At the optimized operating conditions for the GT-CataFlame unit, 0.12 – 0.18 mol% COS and 0.36 – 0.48 mol% CS$_2$ were measured in the gas leaving the catalytic combustor.

Also, since COS and CS$_2$ formation is significantly decreased, and the first Claus converter conditions will be hotter than a conventional Claus SRU design, the Claus converter following the GT-CataFlame combustor can be much smaller helping to reduce the Claus catalyst bed size and allowing for a more compact footprint. In GT-SPOC the first Claus converter may be hotter than in a conventional Claus design if the gas out of the WHB flows directly to the Claus converter without being cooled first in a Sulfur condenser.

Acid Gas Concentration Requirement

Stable operation of the GT-CataFlame catalyst was demonstrated at acid gas concentrations as low as 25% H$_2$S using only preheated air and preheated acid gas. A wide range of tests were conducted on lean H$_2$S streams containing CO$_2$ or nitrogen diluents and typical light hydrocarbon components. Sulfur yield varied with H$_2$S concentration, but the yield was still close to equilibrium computations, unlike lean acid gas Claus units that produce little to no Sulfur from the thermal stage. The GT-CataFlame unit located at the refinery in the U.S. confirmed the results obtained in the laboratory.
Turndown
Testing showed that operations were stable down to 25% turndown when operating with just acid gases. Hypothetically, the GT-CataFlame unit is capable of operating with any mixture between pure natural gas and pure H₂S since the stoichiometric ratio for air-to-reactant is in the range of 2.2 – 2.5 for both natural gas and acid gas. The plant data was run at as low as 12% turndown with minimal effect on performance. Because of the ability to operate with nearly any ratio of fuel gas to acid gas, even lower turndown rates can be achieved.

Air Demand and Related Operational Improvements
While the overall recovery of Sulfur will fluctuate significantly with air-to-acid gas ratios in both the Claus and GT-SPOC processes, the GT-CataFlame catalyst selectivity for Sulfur does not vary significantly over a wide range of air-to-H₂S ratios.

The combination of pre-mixing before reaction and close coupling of the reactor to the WHB aids both hydrogen formation reactions (partial oxidation and dissociation) and inhibits the main hydrogen consumption reaction (recombination of H₂ and S). As the flow rate increases in the GT-CataFlame unit, improved heat transfer due to higher Reynolds number and thermal conductivity of the gas (due to higher hydrogen content) appear to aid in inhibiting recombination of H₂ and S. This translates to more capacity with less overall pressure drop.

Startup and Shutdown Operating Improvements
Most of the time starting up a Claus plant is spent heating up the large amount of refractory in the thermal reactor chamber and catalyst in the catalyst beds. The GT-CataFlame combustor is very compact and in close proximity to the waste heat boiler entrance, so there is a minimum amount of refractory to be dried and heated to operating temperature.

The small amount of catalyst and support materials in the GT-CataFlame combustor is easily heated up by a small preheater such as a STACKMATCH® eliminating one of the biggest problems in starting up or recovering from a shutdown, i.e., relighting the main burner. It was shown that hydrogen rich gases (~40% H₂) and air mixtures can be catalytically ignited by the GT-CataFlame catalyst potentially bypassing the need for any type of fired preheater.

Minimizing the formation of contaminants such as COS and CS₂ and operating the first catalyst bed directly after WHB makes it possible to reduce the amount of Claus catalyst needed speeding up both the shut-down process (Sulfur removal or heat soak) and the start-up process (warm up). Elimination of the Sulfur condenser following the WHB and subsequent reheater eliminates cool down or warm up of equipment and interconnecting piping, again speeding up the shut-down or start-up process.
When heating up or cooling down a Claus plant, fuel gas is used at near the stoichiometric ratio with air. When the Claus catalyst is Sulfur-laden, it needs to be “heat soaked”, i.e., operated at a 15 – 30 °C higher temperature, to vaporize any condensed sulfur and thus regenerate the catalyst bed. During these periods that are oftentimes planned to coincide with a startup or shutdown, unreacted excess oxygen may pass through the furnace and cause damage to the catalyst bed by overheating the bed or causing sulphation of the catalyst. Sulphation results in the need to regenerate the Claus catalyst by operating it at an even higher temperature of near 475 °C. The air-to-fuel gas ratio for most natural gas streams range from (9.5-10)-to-1, while the air-to-acid gas ratio is typically in the (1-2.5)-to-1 range depending on acid gas concentration. This makes for difficult switching from one feed gas to another while maintaining accurate air flow control. At the stoichiometric ratio the adiabatic flame temperature (~3500 °F) for most fuel gas is well above the temperature limit of thermal reactor refractory (~2800 °F) and ferrules requiring the incorporation of steam or nitrogen diluent to hold the flame temperature to a safe operating range. GT-CataFlame eliminates these problems with its air-to-fuel ratio in the range of 2.2 – 2.5, which is the same range as for its air-to-acid gas ratio.

A slightly sub-stoichiometric flame in the Claus burner has a tendency to form soot which can rapidly plug the catalyst bed downstream of the burner. GT-CataFlame catalyst can convert fuel gas via partial oxidation with an air-to-fuel ratio in the range of 2.2-2.5 so that no soot is formed. In addition the catalyst contains components that resist the formation of coke on the catalyst surface which results in less production of soot. GT-CataFlame eliminates the difficulties of switching between operating with fuel gas and operating with acid gas.

Firing near stoichiometric with air can result in some oxygen passing through to the Claus converters causing unwanted catalyst exotherms damaging both the catalysts and the vessels. Since GT-CataFlame catalyst does not have to be operated near the stoichiometric air-to-fuel ratio, the exotherms that would normally damage the downstream Claus catalysts are eliminated.

In general, the more frequent the shutdown and startup of a Claus unit, the more problems that can be expected. During the GT-CataFlame unit’s long-term catalyst evaluations the unit was shut down and started up over 30 times. Through all of the startups and shutdowns the GT-CataFlame catalyst retained its original activity.
Reduction of H$_2$S and Sulphanes in the Produced Sulfur

The results from the GT-CataFlame operating data show that the Sulfur produced in the first downstream Sulfur condenser contains less dissolved H$_2$S and sulphanes (H$_2$Sx) than is typically measured in a conventional Claus SRU. The results in Table 3 show the difference in H$_2$S and H$_2$Sx content as the Sulfur from the Sulfur condenser immediately following GT-CataFlame contains five to six times more dissolved H$_2$S and H$_2$Sx as Sulfur from the condenser that follows both GT-CataFlame and the first stage Claus converter.

As previously discussed, in GT-SPOC the Sulfur condenser immediately following the WHB has been eliminated as well as the first re-heater immediately following that condenser. Therefore, the gas exiting the WHB flows immediately into the first Claus catalyst bed where more H$_2$S is converted to Sulfur so that approximately 90% of the H$_2$S is converted by the time the gas reaches the first Sulfur condenser. At the point where the first molten Sulfur is produced there is a significantly lower H$_2$S partial pressure in the gas than would normally be found in the first Sulfur condenser in a conventional Claus SRU, resulting in reduced H$_2$S dissolved in the produced molten Sulfur. In essence, in GT-SPOC the H$_2$S partial pressure that is measured in the gas in the first condenser is what would normally be found at the second condenser of a conventional Claus unit.

Capital Cost Comparison

An independent engineering firm performed a cost study that compared the capital cost of a two stage GT-SPOC unit to a conventional two stage Claus unit with a burner and thermal reactor. The GT-SPOC SRU was designed in the single, vertical tower arrangement as shown in Figure 2. The amine unit, the TGU and the Sulfur pit were assumed to be similar for both units and were not included in the capital cost estimate. Therefore any cost advantage of the GT-SPOC effects of reduced duty on the TGU and less H$_2$S and H$_2$Sx dissolved in the Sulfur are not included in the comparison. The cost study was prepared using the standard engineering cost factors based on U.S. Gulf Coast prices.

Design Basis

The composition of the acid gas flowing to the GT-CataFlame or to the Claus burner is shown in Table 4. For purposes of presentation in the Table, the acid gas and Sour Water Stripper (SWS) off gas are added together and reported as the composition of one stream as they would be in the case of the feed gas to the GT-SPOC SRU. However, in the case of a conventional Claus stream the SWS off gas is added to the burner and the acid gas is operated in split flow.

The flow rate of the combined acid gas and SWS off gas is 4,290 Nm3/h (3.8 MScfd) and the Sulfur production rate is approximately 100 MTPD.
Cost Comparison Results
The results of this cost estimate indicated that the GT-SPOC unit is approximately 20% less than the capital cost of a conventional Claus unit. A few major differences between the two processes are the reasons for the savings:

- The GT-CataFlame combustor is approximately 20% of the volume of an equivalent Claus burner and thermal reactor;
- GT-CataFlame requires much less refractory (as little as 1/40th the amount required for a conventional Claus burner and thermal reactor);
- The Sulfur condenser located after the WHB and before the first Claus converter in a conventional Claus SRU is eliminated in either the vertical or horizontal GT-SPOC SRU designs;
- The first reheater that follows the first Sulfur condenser in a conventional Claus SRU is also eliminated as it is unnecessary in GT-SPOC; and
- Interconnecting piping is reduced in GT-SPOC as the stages are close coupled in a vertical arrangement as compared the conventional Claus SRU.

Summary
Conventional “modified Claus” technology with a free-flame thermal section is well known to have a number of operating challenges associated with the reactions that occur in the flame and the thermal reactor. An alternate, proven approach was presented here, where the free-flame thermal section is replaced with a catalytic combustor that utilizes a durable catalyst that enables Sulfur partial oxidation catalysis. This change at the front end of a conventional Claus process results in significant

<table>
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<tr>
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<table>
<thead>
<tr>
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Table 4 Composition of the Acid Gas Flowing to the GT-CataFlame Combustor for the Capital Cost Comparison of GT-SPOC and Conventional Claus SRU’s.
process and economic advantages including improved Sulfur yield, reductions in COS and CS$_2$ formation, reduced impact of hydrocarbons on air demand, improved start-up and shut-down operations, and reductions in the Claus converter catalyst bed sections. Overall, GT-CataFlame allows upgrades of aging Claus burners and thermal reactors, and enables a 20 – 30% reduction in capital costs associated with Claus plants, while reducing the Tail Gas Unit load due to its higher conversion efficiencies. GT-SPOC provides the additional advantages of reducing the number of pieces of equipment and reduced interconnecting piping in the vertical arrangement.

In addition to GT-CataFlame and GT-SPOC, GTC Technology is also the exclusive licensor of GT-DOS™ a direct oxidation technology for removal of H$_2$S from dilute H$_2$S-containing gas streams. GTC’s gas processing and Sulfur technology portfolio is focused on delivering solutions for acid gas removal, Sulfur recovery, dehydration, and liquids recovery from a variety of process gas streams to meet very specific customer needs. GTC utilizes these technologies to deliver robust and reliable custom solutions for challenging applications across multiple industries. These technologies are delivered in a variety of ways including license with a basic engineering package or via an Engineering, Procurement and Construction management (EPCm) project. Our broad portfolio of products and extensive experience enables clients to seamlessly integrate our processes across business lines.

References
1. US 6,403,051 Recovery of Sulfur from H2S and Concurrent Production of H2 Using Short Contact Time Reactors.