Overcoming operational issues in a Claus tail gas hydrogenation unit

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What is the typical reason for shutting down a Claus tail gas unit? A or B?

A: Shut down because of catalyst deactivation?

B: Shut down because of operational upset?
The cause of the problems
European refinery suffering from pressure drop problems
Reactions in a tail gas unit

The purpose of the tail gas catalyst is to convert all sulfur species to $\text{H}_2\text{S}$. The following reactions take place:

1) $\text{S}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{S}$
2) $\text{SO}_2 + 3\text{H}_2 \leftrightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}$
3) $\text{COS} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2\text{S}$
4) $\text{CS}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{S}$
5) $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
The problems in tail gas treatment
Problems

Soot, CO and $O_2$

Corrosion

Milling

Contaminant pressure drop issues

Premature shutdown
Potential operational problems

• Carbon formation on the catalyst leading to **accelerated deactivation**
• Soot formation from the burner leading to **pressure drop build-up**
• Temperature excursions as a result of excess air (over-stoichiometric) leading to **loss of catalyst activity/surface area**
• Thermal sintering of the active sites due to temperature and age leading to **accelerated deactivation**
• Sulfidation of the alumina, $\text{Al}_2(\text{SO}_4)_3$ leading to **catalyst decomposition**
Problems caused by CO and O$_2$

The following reactions may occur in the tail gas catalyst when the air/fuel ratio is too low and CO and soot is formed:

1. $\text{SO}_2 + 3\text{CO} \leftrightarrow \text{COS} + 2\text{CO}_2$
2. $\text{S}_2 + 2\text{CO} \leftrightarrow 2\text{COS}$
3. $\text{H}_2\text{S} + \text{CO} \leftrightarrow \text{COS} + \text{H}_2$

COS is more difficult to hydrotreat.

The following reactions may occur if excess oxygen from the burner reaches the tail gas catalyst:

1. $\text{O}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{O}$
2. $\text{O}_2 + 2\text{SO}_2 \leftrightarrow 2\text{SO}_3$
3. $3\text{SO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2(\text{SO}_4)_3$ (sulfidation)
4. $2\text{FeS} + 9/2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_3$

$\text{Al}_2(\text{SO}_4)_3$ leading to catalyst decomposition, and $\text{Fe}_2\text{O}_3$ giving pressure drop problems.
Solution: Burner operation

• Burner control and operation are key to the unit operation

• The preferred operating range is between 70% and 90% of the required stoichiometric oxygen concentration

• If the air/fuel ratio is too high (> 90%), oxygen will reach the tail gas catalyst

• If the air/fuel ratio is too low (< 70%), soot and CO can be formed. Soot will plug the catalyst pores.

• The optimum air/fuel ratio is dependent on the burner design
Potential operating problems
Corrosion

- Iron scales and particles from corrosion leading to **pressure drop build-up**
**Milling**

Top layer

- Milling is catalyst particles being caught by the vortexes of the inlet stream and then being “tossed” around in the reactor
  - Results in a crust of catalyst dust

- Milling of catalyst can occur if:
  - Catalyst is loaded too close to the inlet distributor
  - Too high inlet flow or poor inlet distributor
Grading is the solution
Solution: Grading
Concept of grading

The principles:
• Shape-optimized
• Void
• Particle size
• Catalyst activity

Background:
• Grading products are used for all hydrotreating purposes
• We have more than 40 years experience in developing grading
• So far, we have sold more than 4000 charges for 600 different unit
• We know it works!
Solution

Corrosion

- TK-26 TopTrap™ is inert macro porous material designed to pick up iron scale, coke fines, and other inorganic particulates

- TK-26 TopTrap™ is produced in 1/2” QL with three center holes

- TK-26 TopTrap™ should be loaded below TK-10 or TK-15 high void topping material
Solution: Grading
TK-10 High void topping

Traps impurities leading to pressure drop problems

- Size: 16x11 mm
- Void fraction: ~55
- Bulk density: 800 kg/m$^3$
Solution: Grading
High void topping

Our TK-15 is specifically developed as a grading product with a hold down function and should replace ceramic balls

- Size: 1.5”
- Void fraction: ~65
- Bulk density: 1190 kg/m³
Selection of the right catalyst
The Claus tail gas catalysts
Optimal performance with TK-220, TK-222, and TK-224

High activity + Low pressure drop + High physical strength + Good thermal stability = Optimal performance
Relative pressure drops
Claus tail gas catalysts

- TK-222, 1/8" ring: 0.27
- TK-220, 1/10" quadralobe: 0.91
- TK-224, 1/8" sphere: 1.00

Low pressure drop
Catalyst pressure drop and capacity

• Clean pressure drop in the tail gas unit is determined solely by the catalyst’s size and shape.

• TK-222 1/8” ring has the highest void fraction of any tail gas catalyst in the market today and will provide the refiner with the lowest possible SOR pressure drop.

• Lower pressure drop means:
  • Possible higher feed rate
  • Increased crude capacity and consequently increased profitability
  • Debottlenecking of sulfur recovery unit
Benefits of low pressure drop
Calculation example

<table>
<thead>
<tr>
<th></th>
<th>TK-220</th>
<th>TK-222</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>1/10” Quadralobe</td>
<td>1/8” Ring</td>
</tr>
<tr>
<td>Relative ΔP</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Relative gas flow</td>
<td>100</td>
<td>180</td>
</tr>
</tbody>
</table>

80% higher capacity at same pressure drop
Physical strength
Claus tail gas catalysts

High physical strength prevent breakage of particles and creation of fines during catalyst handling and unit upsets.

<table>
<thead>
<tr>
<th></th>
<th>TK-220</th>
<th>TK-222</th>
<th>TK-224</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>1/10” Quadralobe</td>
<td>1/8” Ring</td>
<td>1/6” Spheres</td>
</tr>
<tr>
<td>Side crush strength, kp/mm</td>
<td>&gt;1.5</td>
<td>&gt;0.7</td>
<td>13.6 kp</td>
</tr>
</tbody>
</table>

High physical strength
Thermal stability
Claus tail gas catalysts

A sample of TK-220 was heated in an oven to the below listed temperatures, and the Side Crush Strength (SCS) and surface area were measured after the heat treatment.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>SCS, kp/mm</th>
<th>Surface area, m²/g*</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.85</td>
<td>297</td>
</tr>
<tr>
<td>540</td>
<td>1.94</td>
<td>300</td>
</tr>
<tr>
<td>650</td>
<td>2.12</td>
<td>281</td>
</tr>
</tbody>
</table>

Haldor Topsoe’s tail gas catalyst exhibits a temperature stability.
Conclusion: Overcoming operational issues

Pressure drop
- Follow the guidelines for burner operation
- Installing a grading solution

Increasing capacity
- We recommend taking advantage of the very low pressure drop of TK-222 by combining it with TK-220 or TK-224 to increase capacity