The Pursuit of Low Emissions
The Development of Catalytic Options for High Sulfur Recovery

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Important

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Agenda

• Comprimo® Sulfur Solutions
• SO$_2$ Regulatory Developments
• Development of Catalytic Sulfur Recovery Technologies
• Solutions and Cost for High Sulfur Recovery Requirements
Jacobs Comprimo® Sulfur Solutions

- A Dutch company Comprimo® in business since 1924
- Since 1959, have licensed, engineered and constructed over 550 gas treating and sulfur recovery plants globally
- Global Licensor Leader in gas treating and sulfur technology
  - Patents (SUPERCLAUS®, EUROCLAUS® and NH₃ Destruction)
  - Licensor for Shell Technologies, including LT-SCOT, LS-SCOT, Sulfur Degassing and Amine Treating Processes (ADIP and Sulfinol)
  - Expertise in Amine Treaters, SWS and Caustic Scrubbers
  - Continually seeking new technologies and third-party relationships
- Jacobs purchased Comprimo® (1999) and Delta Hudson (2000) and their technology portfolios
Regulatory SO$_2$ Developments

Three different levels of Sulfur Recovery Efficiency

- **<98%** : Conventional Claus
  - Typically only for small SRUs

- **98-99.5%** : Claus-like Solutions
  - Some European Countries/Canada/Middle East
  - South America

- **>99.5%** : Tail Gas Treatment Technologies
  - North America/Western Europe/China

- **Worldbank Standard for SOx**: $150 \text{ mg/Nm}^3 = 99.9+\%$
  - Program will be stopped in 2019
Development SUPERCLAUS® Process

\[ 2 \text{H}_2\text{S} + \text{SO}_2 \rightleftharpoons 3 \text{S} + 2 \text{H}_2\text{O} \]

\[ \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} \]
Characteristics of SUPERCLAUS®

- Claus Type Process
- Sulfur recovery efficiency of more than 99%
- Low energy consumption
- Low investment cost
- No waste streams
- Simple revamp
- Improved Combustion Air Control
  - Advanced Burner Control (ABC)
SUPERCLAUS® Catalyst Characteristics

- More than 85% conversion of H$_2$S to S
- Limited Sensitivity for excess O$_2$
- Not sensitive for high H$_2$O concentrations
- No Claus reaction
- No CO/H$_2$ oxidation
- No COS/CS$_2$ formation
- Long lifetime

![Graph showing sulfur yield vs. temperature](image)

Temperature (°C) vs. Sulfur Yield

- 1st
- 2nd
- 3rd
Analysis: Where do the Recovery Losses Occur:

- Formation of COS / CS$_2$ in the Thermal Reactor
- Slip of SO$_2$ from final Claus reactor
- Slip of SO$_2$ from SUPERCLAUS® reactor
- Slip of H$_2$S from SUPERCLAUS® reactor
- Slip of sulfur vapor/ mist in tail gas
- Process upsets due to varying acid gas quality
The EUROCLAUS® Process

Principles:

• Reduction of SO$_2$ in process gas from Claus Reactors
• No reduction of Sulfur vapor to H$_2$S
• Limited COS production in hydrogenation step
• Improved performance Selective Oxidation

\[
\begin{align*}
2H_2S + SO_2 & \leftrightarrow 3S + 2H_2O \\
2H_2S + SO_2 & \leftrightarrow 3S + 2H_2O \\
SO_2 + 3H_2 & \leftrightarrow H_2S + 2H_2O \\
SO_2 + 2H_2 & \leftrightarrow S + 2H_2O
\end{align*}
\]
Targets Further Developments

• High recovery efficiency, ≥ 99.5 %
• Maximum four catalytic stages
• Fully continuous process
• Low investment cost
  – Minimal equipment modifications/additions
• Claus type operation
• No additional chemicals (like H₂) required
The STRATACLAUS™ Process

• Principles:
  – Taking advantage of two layers of catalyst
    • High activity for both layers
    • High activity for lower layer at higher temperatures
  – Improvement of yield of the Selective Oxidation Catalyst
    • Lower SO₂ formation and slip
Further Improvements:

- Longer Final Condensers
- Titania in first and second Claus Reactor
- Installation of Oxygen Analyzer in Tail Gas from Selective Oxidation Reactor
- Improvement of sulfur vapour removal from tail gas
- Feed Forward Air Demand Control via ABC+
ABC+ Control Benefits

• Units with fluctuating feed compositions
• Complex refineries with multiple upstream units
• Units with (varying) high concentration of HC components
• Units with varying CO₂ concentrations
• Units with SWS gas
• 10 units designed
Deep Sulfur Removal

• Industry Standard:
  – Amine Based Tail Gas Treatment Unit (SCOT)
  – Hydrogenation of tail gas and absorption in Amine
  – Recycle of acid gas to Thermal Stage of Claus unit
  – Developments in solvent for improved operation and economics
Deep Sulfur Removal

- Viable alternative to Amine based TGTU
- Very high sulfur removal, very low sulfur emissions (down to 20 ppm SO$_2$ if required)
- Less capital cost
- Small plot footprint
- Simplified operation
# Summary of Technologies for Sulfur Recovery

<table>
<thead>
<tr>
<th>Type of Process</th>
<th>S-recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Stage Claus</td>
<td>95 – 96.5%</td>
</tr>
<tr>
<td>3 Stage Claus</td>
<td>96.5 – 98.0%</td>
</tr>
<tr>
<td>2+1 SUPERCLAUS®</td>
<td>98.5 - 99.2%</td>
</tr>
<tr>
<td>3+1 SUPERCLAUS®</td>
<td>99.0 - 99.4%</td>
</tr>
<tr>
<td>3+1 EUROCLAUS®</td>
<td>99.2 - 99.6%</td>
</tr>
<tr>
<td>3+1 STRATACLAUS®</td>
<td>99.3 - 99.7%</td>
</tr>
<tr>
<td>Claus + SCOT (TGTU)</td>
<td>99.8 – 99.95%</td>
</tr>
<tr>
<td>2+1 SUPERCLAUS® + Caustic Scrubber</td>
<td>99.9 - 99.99%</td>
</tr>
</tbody>
</table>
Cost Comparison

- CLAUS (2R) + LS SCOT
- CLAUS (2R) + Add on LT SCOT
- SUPERCLAUS® (3+1)
- EUROCLAUS® (3+1)
- SUPERCLAUS® (2+1)
- PAQELL

Cost Index % vs. Sulfur Recovery %
CO₂ Footprint Comparison

CO₂ Footprint for 300 TPD SRU

- SUPERCLAUS
- SUPERCLAUS + SCRUBBER
- Amine based TGTU
- SO2 Flue Gas Recovery

99.50%  99.90%  99.98%
Conclusions

• Long way from simple Claus technology
• Possible to meet up to 99.5% SRE with catalytic options only
• Above 99.5%, different options are available with wide range of cost and environmental footprint
  – All options shall be evaluated during conceptual to determine optimal solution for Client taking into account capital cost, operating cost, operability and environmental footprint
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