Refinery SRU’s Tail Gas Handling Options

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Refinery SRU tail gas handling options

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1. Introduction
Refinery standard sulphur management

Crude → Refinery Processing Units → Products

- Amine Regeneration (ARU)
  - $\text{NH}_3 + \text{H}_2\text{S}$

- Sour Water Stripping (SWS)
  - Stripped Water

→ Sulphur Recovery Unit (SRU)

- Flue Gas
  - $\text{H}_2\text{S}$

- Sulphur
Refinery standard sulphur management

- **Refinery SRUs are designed to process**
  - Acid gas feedstock from amine regeneration unit(s) (AAG), containing mainly \( H_2S \) with limited \( NH_3 \) content
  - Acid gas feedstock from sour water stripping (SWSAG), containing both \( NH_3 \) and \( H_2S \)

- **Facts impacting the sulphur management**
  - Increasingly stringent emission regulations dictate the sulphur recovery efficiency of the refinery
  - Increasing \( NH_3 / H_2S \) ratio due to the quality of the crude
  - Debottlenecking SRU capacity may be required to meet new products specifications or crude slates
  - A number of refinery off-gases contribute to SOx emissions, that cannot be economically processed in the SRU
Ammonia : a constraint for refineries SRU

- **Design constraints**
  - Increased air demand for \( \text{NH}_3 \) destruction
  - Increased Claus process gas volume and larger equipment
  - High temperatures and special burner/combustion chamber arrangement in Claus reaction furnace
  - Limitations on maximum \( \text{NH}_3/\text{H}_2\text{S} \) ratio acceptable in the Claus furnace may dictate a two-stage sour water stripping

- **Operating constraints**
  - Risks of incomplete \( \text{NH}_3 \) destruction
  - ammonium salts deposition at the cold spots of the Claus section
  - Fouling, plugging, corrosion
2. Tail Gas Treatment Alternatives for Refineries
Claus Tail Gas Treating Technologies

Two Claus TGT technologies in Shell’s portfolio

- **SCOT®**
  - well known technology applied for decades in both upstream and downstream applications

- **CANSOLV® SO₂ scrubbing**
  - more recent TGT alternative, capable of meeting SO₂ emissions as low as 10 ppmv

Both technologies can be designed to comply with the most stringent environmental regulations, such as the World Bank emissions standards
SCOT® Technology with H₂S recycle

1. Tail Gas from Claus Section
   - Hydrogen from refinery
2. Hydrogenation Reactor
   - Steam
3. Quench Tower
4. Off-Gas to Thermal Oxidizer
5. Amine Absorber
6. Filtration
7. Sour Water blowdown
8. Acid Gas Recycle to Claus RF
9. Regenerator
TGT Section – LT-SCOT®

- Reduction reactor using low temperature catalyst
- Quench column
- TGT amine section using MDEA with stripping promoter
  - Very low content of H₂S and CO₂ in lean solvent
  - Expected H₂S content in the absorber off-gases < 50ppmv
- Solvent storage, filtration and sump drum

Classic refinery TGT design for compliance with World Bank Standard emissions limit
Process Line-up – SCOT® technology

- CLAUS SECTION
  - SWS
  - Amine Acid Gas

- TGT SCOT
  - H₂S recycle
  - Water Blowdown

- THERMAL OXIDISER
  - Flue Gas

- SULPHUR DEGASSING
  - Degassing Off-Gas

- LIQUID SULPHUR
  - Acid Gas
  - Degassing Off-Gas
Cansolv® SO2 scrubbing alternative

- In operation since 2002 to recover SO₂ from flue gases
- Can be applied as the tail gas treatment downstream the Claus section in place of the SCOT® technology
- SO₂ emissions in flue gas as low as 10 ppmv
- The recovered SO₂ is recycled to the Claus section and further converted to sulphur
Cansolv® technology with SO$_2$ recycle

Flue Gas from Claus TG Thermal Oxidizer

Flue Gas Pre-Cleaning Section
- SO$_3$ removal
- Quench tower
- Venturi scrubber
- Droplet removal

SO$_2$ Absorber

Flue Gas to atm

Amine Purification Unit

Caustic

Waste Water

Sour Water blowdown

SO$_2$ Recycle to Claus

Regenerator
Process Line-up – Cansolv® technology

- SWS Acid Gas
- Amine Acid Gas
- CLAUS SECTION
- THERMAL OXIDISER
- CANSOLV SO2 Scrubbing
- SO₂ recycle
- Degassing Off-Gas
- Water Blowdown
- Liquid Sulphur
- Flue Gas
Alternative Concept for Cansolv® line-up

Total or partial bypass of SWS acid gas to the thermal oxidiser

- SWS Acid Gas
- Amine Acid Gas
- SO₂ recycle
- Degassing Off-Gas
- Liquid Sulphur
- Water Blowdown
- Flue Gas
Alternative Concept for Cansolv® line-up

- **Objectives**
  - Divert ammonia from Claus reaction furnace
  - Reduce Claus section process gas volume and equipment size
  - Enhance flexibility toward increased amounts of ammonia

- **Parameters to be evaluated**
  - Combustion of ammonia bearing acid gas in thermal oxidiser
  - Impact of increased $\text{SO}_2$ recycle on Claus reaction furnace
  - Optimum $\text{SO}_2$ injection points in the Claus section
  - CAPEX and OPEX compared to Claus + SCOT® line-up
3. Case Study Basis
Case study for two refinery applications

- Identical sulphur production capacity (230 t/d)
- Two feedstock composition cases (average and high NH₃ content)
- Different configurations for Claus + Cansolv® line-up
- With or without oxygen enrichment
## Design Feedstock

<table>
<thead>
<tr>
<th></th>
<th>Refinery A</th>
<th>Refinery B</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEED</td>
<td>AAG</td>
<td>AAG</td>
</tr>
<tr>
<td>S load</td>
<td>91.1%</td>
<td>68.1%</td>
</tr>
<tr>
<td>S load</td>
<td>8.9%</td>
<td>31.9%</td>
</tr>
<tr>
<td>(\text{NH}_3/(\text{H}_2\text{S}+\text{NH}_3))</td>
<td>15.1 % v/v</td>
<td>24.2 % v/v</td>
</tr>
<tr>
<td>Flow Nm3/h</td>
<td>7040</td>
<td>4842</td>
</tr>
<tr>
<td>Flow Nm3/h</td>
<td>2476</td>
<td>5607</td>
</tr>
<tr>
<td>Mol %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{S})</td>
<td>86.63</td>
<td>94.24</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>7.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>Others (HC, H2O, ...)</td>
<td>6.35</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td>28.21</td>
<td>23.6</td>
</tr>
</tbody>
</table>
## Design Cases  Refinery A

<table>
<thead>
<tr>
<th>CASE</th>
<th>CASE A01</th>
<th>CASE A02</th>
<th>CASE A03</th>
<th>CASE A04</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGT</td>
<td>SCOT®</td>
<td>CANSOLV®</td>
<td>CANSOLV®</td>
<td>CANSOLV®</td>
</tr>
<tr>
<td>SWS Acid Gas to RF Burner</td>
<td>100 %</td>
<td>100%</td>
<td>65 %</td>
<td>0%</td>
</tr>
<tr>
<td>SWS Acid Gas to Incinerator</td>
<td>0%</td>
<td>0%</td>
<td>35%</td>
<td>100%</td>
</tr>
<tr>
<td>Enriched Air Claus Burner</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>FG Co-firing in CLAUS RF</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
</tr>
</tbody>
</table>
### Design Cases Refinery B

<table>
<thead>
<tr>
<th>CASE</th>
<th>CASE B01</th>
<th>CASE B02</th>
<th>CASE B03</th>
<th>CASE B04</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGT</td>
<td>SCOT®</td>
<td>CANSOLV®</td>
<td>CANSOLV®</td>
<td>CANSOLV®</td>
</tr>
<tr>
<td>SWS Acid Gas to RF Burner</td>
<td>100 %</td>
<td>100%</td>
<td>65 %</td>
<td>53%</td>
</tr>
<tr>
<td>SWS Acid Gas to Incinerator</td>
<td>0%</td>
<td>0%</td>
<td>35%</td>
<td>47%</td>
</tr>
<tr>
<td>Enriched Air Claus Burner</td>
<td>YES 25 %VOL</td>
<td>YES 25 %VOL</td>
<td>YES 28 %VOL</td>
<td>YES 28 %VOL</td>
</tr>
<tr>
<td>FG Co-firing in CLAUS RF</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>
Performance Requirements

- **Flue gas to atmosphere**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>≤</td>
<td>150 mg/Nm3</td>
</tr>
<tr>
<td>NOₓ</td>
<td>≤</td>
<td>200 mg/Nm3</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>≤</td>
<td>50 mg/Nm3</td>
</tr>
<tr>
<td>H₂S</td>
<td>≤</td>
<td>5 ppm vol</td>
</tr>
</tbody>
</table>

- **For CANSOLV® line-up, flue gas to Cansolv® absorber**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>≤</td>
<td>1 ppm vol</td>
</tr>
<tr>
<td>SO₃</td>
<td>≤</td>
<td>10 ppm vol</td>
</tr>
</tbody>
</table>

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4. Main design considerations
Claus section – Thermal stage

Design for proper ammonia destruction

- Feed pre-heating for case A2/3/4 and B4
- Fuel gas co-firing for cases A3/4
- Oxygen enriched air for cases B (B1/2 = 25% O₂; B3/4 = 28%O₂)

<table>
<thead>
<tr>
<th></th>
<th>A01</th>
<th>A02</th>
<th>A03</th>
<th>A04</th>
<th>B01</th>
<th>B02</th>
<th>B03</th>
<th>B04</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF temperature (°C)</td>
<td>1240</td>
<td>1290</td>
<td>1290</td>
<td>1300</td>
<td>1430</td>
<td>1390</td>
<td>1310</td>
<td>1290</td>
</tr>
<tr>
<td>RF residence time (s)</td>
<td>1.6</td>
<td>1.5</td>
<td>1.4</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>% SWSAG to RF</td>
<td>100</td>
<td>100</td>
<td>65</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>65</td>
<td>53</td>
</tr>
<tr>
<td>% S recycle / feed</td>
<td>8.9</td>
<td>3.5</td>
<td>6.6</td>
<td>12.9</td>
<td>7.7</td>
<td>6.3</td>
<td>16.1</td>
<td>20.8</td>
</tr>
</tbody>
</table>
Claus section – Catalytic stages

- Sulphur Recovery Efficiency of the Claus section
- Number of Claus reactors
- Catalyst type (promoted alumina, titanium oxide)

<table>
<thead>
<tr>
<th></th>
<th>A01</th>
<th>A02</th>
<th>A03</th>
<th>A04</th>
<th>B01</th>
<th>B02</th>
<th>B03</th>
<th>B04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Claus SRE (%)</td>
<td>92</td>
<td>96.5</td>
<td>96.5</td>
<td>96.5</td>
<td>93</td>
<td>94</td>
<td>96.5</td>
<td>96.5</td>
</tr>
<tr>
<td>Number of Claus reactors</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
SO$_2$ recycle in Cansolv® line-up

Impact on Claus section operation

- Recycle to Claus Reaction furnace
  - Reaction furnace minimum temperature constraint

- Recycle downstream reaction furnace (first Claus condenser)
  - Maximum temperature rise on the first catalytic reactor
  - Minimum approach to sulphur dew point temperature

- Injection device to be carefully engineered for proper mixing without condensation
Thermal oxidiser section

- Selection of combustion temperature function of contaminant type and concentration
- Ammonia combustion in Cansolv line-up cases requires a more complex design for NOx control
  - Double chamber design
5. Results
CANSOLV® – SCOT® comparison - CAPEX

CAPEX is similar with CANSOLV® line-up being up to 17% cheaper
Basis for OPEX (presented normalized)

- Operational expenditure calculated for two utility costs basis:
  - **Asia Pacific (AP)**
    - high energy cost (fuel gas, steam, power), low cooling water cost
  - **Middle East (ME)**
    - low energy cost (fuel gas, steam, power), high cooling water cost

<table>
<thead>
<tr>
<th>Utility, unit</th>
<th>AP</th>
<th>ME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric Power, kWh</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>HP Steam, ton</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>LP Steam, ton</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>CW, ton</td>
<td>0.45</td>
<td>1</td>
</tr>
<tr>
<td>Oxygen, ton</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fuel Gas, MMBTU</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

- Expected catalysts life time: 5 years
- 8000 hours operation per year
- Man labour costs excluded (SCOT equivalent to Cansolv)
<table>
<thead>
<tr>
<th>Case</th>
<th>A01</th>
<th>A02</th>
<th>A03</th>
<th>A04</th>
<th>B01</th>
<th>B02</th>
<th>B03</th>
<th>B04</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCOT</td>
<td>Cansolv no bypass</td>
<td>Cansolv 35% bypass</td>
<td>Cansolv max bypass</td>
<td>SCOT</td>
<td>Cansolv no bypass</td>
<td>Cansolv 35% bypass</td>
<td>Cansolv max bypass</td>
<td></td>
</tr>
<tr>
<td>AP</td>
<td>+100C</td>
<td>+191C</td>
<td>+147C</td>
<td>+71C</td>
<td>+100D</td>
<td>+118D</td>
<td>+63D</td>
<td>+31D</td>
</tr>
<tr>
<td>ME</td>
<td>+100E</td>
<td>+199E</td>
<td>+148E</td>
<td>+58E</td>
<td>+100F</td>
<td>+112F</td>
<td>+36F</td>
<td>+4F</td>
</tr>
</tbody>
</table>

Legend: C>E; D>F.

Both technologies have operational profits instead of costs
Operational profits comparison refinery A

Cansolv’s profits are higher than SCOT, but decrease with SWS acid Gas bypass
Cansolv’s profits are more impacted by the SWS acid gas bypass rate when ammonia content is high.
6. Conclusions
Conclusions

- Both Cansolv® and SCOT® TGT line-up offer advantages for refineries sulphur management on a case by case basis to comply with strict environmental emissions limitations.

- CANSOLV® configuration provides the refinery with a wider flexibility in terms of NH\(_3\)/H\(_2\)S ratio.

- Implementing a SWS acid gas bypass to the thermal oxidiser is favorable to the Claus section operation.
Conclusions

- CANSOLV® line-up is a powerful solution for SRU capacity debottlenecking
  - routing part of the SWS acid gas to a revamped thermal oxidiser reduces the load on the Claus section.
  - Such option makes more sense when only a Claus plant is existing (no TGTU)

- One advantage of CANSOLV® in comparison to SCOT® is the possibility to route other refinery off-gases containing ammonia and/or sulphur directly to the thermal oxidiser while still meeting stringent emissions
Thank you for your attention