Dealing with Aromatics in the Sulfur Recovery Unit

A Comprehensive Summary

Eric Roisin
Content

- Introduction
- Review of litterature from Saudi Aramco
- Development of Axens’ solution
- Industrial feedback
- Conclusion
Influence of AG concentration at thermal stage

<table>
<thead>
<tr>
<th>H₂S Content (%)</th>
<th>90</th>
<th>80</th>
<th>70</th>
<th>60</th>
<th>50</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace Temperature (°C)</td>
<td>1240</td>
<td>1175</td>
<td>1110</td>
<td>1045</td>
<td>970</td>
<td>890</td>
</tr>
<tr>
<td>Fraction of S in COS/CS₂</td>
<td>1.1</td>
<td>2.45</td>
<td>3.55</td>
<td>4.4</td>
<td>5.1</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Simulations using Sulsim, all flows at 35°C, 1% CH₄, 4% H₂O, bal CO₂

Low H₂S content results in:
- Low furnace temperature
- High COS and CS₂ formation

The leaner the acid gas, the lower the recovery of S. High recovery targets require converting COS/CS₂.
Thermal destruction of aromatics

Decomposition temperature of aromatics:
- Benzene: 1050°C
- Toluene: ~ 950°C
- Xylene: 925°C

Source: B. Klint, LRGCC 2000
Effect of Aromatics on Claus Catalyst

- Aromatics famous for poisoning Claus catalysts via “carsul” formation
- Several industrial cases already published

Figure 9.25  Catalyst Deactivation in a Split-Flow Plant’s First Converter

Reprinted from Gas Conditioning and Processing, Campbell Petroleum Series, 1998
Middle Eastern feedback (2011)

First converter

DeltaT (°C)

Days in operation

Axens
IPF Group Technologies
Long split-flow configuration for ultra-lean cases

Increased flame temperature allowing operation
BUT:
Feed gas contaminants (BTX) reaching the catalyst
Problem of Shedgum and Uthmaniyah SRUs
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The different effects of aromatics

Source: « Quantifying the Effect of Individual Aromatic Contaminants on Claus Catalyst »; P. Crevier, LRGCC 2001
The different effects of aromatics

Main Conclusions from this article:

- Benzene, Toulene and Xylene have a different impact on the catalyst
  - Xylene is the main cause to deactivation. It shall be largely removed or destroyed
  - Benzene has a relatively minor effect
- Deactivation rate is proportionnal to the aromatics concentration
- Deactivation rates depend upon the temperature

Source: « Quantifying the Effect of Individual Aromatic Contaminants on Claus Catalyst »; P. Crevier, LRGCC 2001
Available engineering solutions

Conclusions on the Saudi Aramco study cases:

- **O₂ enrichment**: split flow required if < 38% H₂S,
- **Fuel gas co-firing**: need for larger furnace and converters; produces additional CS₂
- **Change of the upstream amine**: not acceptable due to the CO₂ impact on downstream process
- **Condense BTX in the acid gas**: too warm climate
- **Strip BTX out of rich amine**: too expensive
- **Acid gas enrichment**: 6 times too costly
- **BTX Removal using activated carbon bed** is viable

Source: « Evaluating Solutions to BTX Deactivation of Claus Catalyst in Lean Feed SRUs »; P. Crevier, Brimstone 2002
The effects of aromatics on Alumina and Titania

For TiO$_2$ at 310°C (results at 80% conversion):

- Xylene = 4.2 * Toluene
- Toluene = 17.6 * Benzene

* Catalyst life time prediction model *

No need for drying and cooling the carbon beds after regeneration due to the minor impact of Benzene

All catalysts available on the market are not equivalent.

Source: « Performance of Commercial Titania and Titania Hybrid Catalysts in the Presence of Aromatic Contaminants »; P. Crevier, LRGCC 2005
Carbon bed absorption process

Carbon bed absorption process

Benefit:
- Removing TX and part of B solves the poisoning
- Recovered BTX can be valorized

Inconvenient:
- Requires installing additional major equipment
- Large steam requirements
- BTX contaminated water to be treated
- Long term reliability of carbon beds exposed to water?
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Towards a catalytic solution?

Typical BTX content outlet of reaction furnaces: 0-100 ppm

Aromatics split should be mainly Benzene, more than Toluene and Xylene

We looked for a catalytic solution to deal with BTX contaminated lean acid gases, able to provide sufficient COS and CS$_2$ conversion
The lean acid gas problem

Dealing with lean acid gases implies:

- A reduced furnace temperature: Aromatics (Benzene) breakthrough?
- High quantities of COS and CS$_2$ to be hydrolyzed in the first converter

The catalyst to be loaded in the reactors need to be very efficient in hydrolysis, and resistant towards BTX poisoning
Lab testing

Automated pilot test dedicated to this study
Testing conditions

The following gas composition has been used for this study:

- 6 % H₂S, 4 % SO₂, 1 % CS₂,
- 10 % H₂O, 25% CO₂, 1% H₂, N₂ balance
- 5000 ppmv Toluene

- Tests performed on ~150 ml of catalyst
320°C with CR-3S

- Quick deactivation of CR-3S
- Insufficient conversion of CS$_2$
- Continuous catalyst poisoning

![Graph](image)
320°C with CRS 31

- High initial activity
- Quick deactivation at 320°C
- Conversion reaches a “plateau”
300°C with CRS 31

- Lower initial activity
- Similar slope deactivation
- Conversion reaches a "plateau"
280°C with CRS 31

- Lower initial activity
- Acceptable deactivation
- Conversion reaches a "plateau" at 60%
Effect of temperature on CRS 31

- Detrimental influence of temperature
- Operating at 280°C is more favorable
### Comparison of Catalyst Performances

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CR-3S</th>
<th>CRS 31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Initial CS₂ conv.,</td>
<td>88 %</td>
<td>98 %</td>
</tr>
<tr>
<td>Deactivation, %/h</td>
<td>3.1</td>
<td>4.4</td>
</tr>
<tr>
<td>60% conv. After</td>
<td>9h</td>
<td>9h</td>
</tr>
</tbody>
</table>

CRS 31 at 280°C same performances than CR-3S at 320°C, but lasts 3 times longer!
CSM 31 purposes

1. Increases H$_2$S/SO$_2$, increased furnace temperature
   \[ \text{SO}_2 + 3 \text{H}_2 \rightarrow \text{H}_2\text{S} + 2 \text{H}_2\text{O} \]

2. Converts nasty Toluene and Xylene to “catalytically friendly” Benzene (hydrodealkylation)

3. Uses Water gas shift conversion which produces H$_2$ continuously:
   \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \]
1/3 CSM 31 + 2/3 CRS 31 at 280°C

- Deactivation slope very low
- Better than pure CRS 31 after 5 testing hours
1/3 CSM 31 + 2/3 CRS 31 at 320°C

- Protection by CSM 31 has limitations
- Always keep catalyst bed below 300°C
Best strategies for TiO$_2$ – Option 3

When aromatics are present

» Operate as cold as possible (<280°C)

» Load CSM 31 on top half of R1

» Load TiO$_2$ in R2 to satisfy high COS/CS$_2$ conversion requirements

CSM 31 + CRS 31 = lifetime*3
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Definition of a complete feedback

CSM31/CRS 31 combination has been loaded in 15 different units since mid 2008 (lifetime up to 5 years).
The ideal operation feedback would contain:

- Details of the operating company and site location
- Unit design capacity and process conditions
- BTX measured at the inlet of the first reactor
- Bed temperature profiles
- COS and CS$_2$ conversion trends
- Comparison with previous catalyst performances

At the time of this presentation we did are not in the position to publish such detailed data.
Feedback from North American SRU

Lean Acid Gas concentration, approx. 45%
Split Flow configuration
Usual catalyst lifespan: 6 months
No information on BTX content in the feed
High carsul contamination of previous alumina: 8% C

First catalyst bed loading: 70/30 CSM 31/CRS 31
Loaded in June 2009
No sign of deactivation after 1 year…
untill a sulfur fire killed the catalyst!
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Conclusions

Aromatics drastically effect the performances of Claus catalysts. Their concentration shall be minimized by all practical/economical means.

Saudi Aramco’s work is a major source of information. Large BTX concentrations (>100ppm) can be removed from AG using activated carbon absorbers.

Axens’ catalytic solution (CSM 31 + CRS 31) allows processing low BTX concentrations (<100ppm) at catalytic stage.

- No additional equipment required
- No extra operating cost
Driving Sulfur Recovery Towards Excellence

Axens pioneered every evolution in sulfur recovery catalysis over the past 50 years

- $\text{Al}_2\text{O}_3/\text{TiO}_2$ hybrid: CRS 21 (1972)
- Fe Oxygen scavenger: AM (1976) & AMS
- Pure TiO$_2$: CRS 31 (1984) & CRS 31 TL
- Optimized Alumina: CR-3S (1994)
- BTX management: CSM 31 (2007)
- Low turndown: CR-3S LG (2014)

Focussing on the benefits of our customers made us Sulfur recovery catalyst World leader
Axens Sulfur Complete Portfolio

**Claus Catalysts**
- CR: Claus alumina
- CR-3S: Improved Claus alumina
- DR Series: Active bed supports
- CRS 31: Titanium dioxide catalyst
- CRS 31 TL: Low density titanium dioxide catalyst
- AM & AMS: Oxygen scavengers
- CSM 31: BTX management

**Tail Gas Treatment Catalysts**
- TG 103: TG hydrogenation catalyst, spherical
- TG 107: Low temperature TG hydrogenation catalyst, spherical
- TG 203: Low density TG hydrogenation catalyst, spherical
- TG 136: Low temperature TG hydrogenation catalyst, extrudate