Reformate Desulfurization for Logistic SOFC Power Systems

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IntraMicron Inc is a small business company located at Auburn, AL. Its R&D covers: (1) Filtration; (2) Desulfurization; (3) Fischer Tropsch Synthesis; (4) CO oxidation.
Desulfurization Sorbents/Adsorbents

Low Temperature Gas Phase
Desulfurization Sorbent: Cu-ZnO/\text{SiO}_2, (Patent Applied for)

Liquid Phase Desulfurization Adsorbents:
Ag_2O/TiO_2 for JP-5

Current capacity: ~6 mg S/g adsorbent

After Desulfurization
Ultralow Sulfur Diesel Sample

- Proprietary and business Sensitive -
Outline

• Sulfur Issue
• Reactor Design and Bed Configuration
• Desulfurization & Regeneration Performance
• Desulfurizer Construction
• Conclusion
• Acknowledgements
Sulfur Issue

• Typical Fuel Cells Have Low Sulfur Threshold:
  – 0.1 ppmv most for PEM Fuel Cells
  – 2~3 ppmv for typical Solid Oxide Fuel Cells

• Sulfur Content in Logistic Fuels (ca. JP-5, JP-8)
  – i.e. 500~3000ppmw, equivalent to 50~300 ppmv after converted to reformates in reformers.

• Sulfur Removal Techniques
  – Pre Reformer Desulfurization
  – Post Reformer Desulfurization

• Post Reformer Desulfurization Using Reactive Sorbents
  – ZnO, CuO, Fe$_2$O$_3$ etc.
  – High sulfur capacity (i.e. 392 mg S/g ZnO), compared to adsorbents for liquid phase desulfurization.
Objectives

• To build a desulfurizer able to
  – Reduce total sulfur concentration to less than 3 ppmv
  – Provide a continuous run of 200 hours
  – Have a good low temperature performance for cold
    startup and transient operations
  – Small bed size: ~1 foot long
  – Low pressure drop ca. 1-2 psi
Cyclic Arrangement and Transition Operation

Start with heating

Time balance

Desulfurization

Regeneration

Purging

\[
\text{Time balance} = 5\text{ hours} = 4\text{ hours} + 1\text{ hour Transition}
\]
Preferred desulfurization temperature: 400 C
Preferred regeneration temperature: 600 C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>0.8~1.4 mm</td>
<td>Regn &lt;5 hour</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>6”</td>
<td>60 cm/s</td>
</tr>
<tr>
<td>Bed length</td>
<td>12”</td>
<td>L/D=2</td>
</tr>
<tr>
<td>Pipe /valve size</td>
<td>2”</td>
<td>6 m/s</td>
</tr>
</tbody>
</table>

**Note:**

The system works at 400 C during desulfurization and 600 C during regeneration. Therefore the valves are required to work at high temperature in the presence of oxygen during regeneration.

**Sulfur input: 300 ppmv**
Design Challenges

Reformates:
Flow rate: 17 kg/hr.
Temperature from reformer: 850°C
Reformate Composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>24.9%</td>
</tr>
<tr>
<td>CO₂</td>
<td>10.2%</td>
</tr>
<tr>
<td>WATER</td>
<td>6.9%</td>
</tr>
<tr>
<td>H₂</td>
<td>25.0%</td>
</tr>
<tr>
<td>N₂</td>
<td>33.0%</td>
</tr>
<tr>
<td>H₂S</td>
<td>300 ppmv</td>
</tr>
</tbody>
</table>

High CO and CO₂ concentration, COS formation.

\[
\text{CO}_2 + \text{H}_2\text{S} = \text{COS} + \text{H}_2\text{O}
\]
\[
\text{CO} + \text{H}_2\text{S} = \text{COS} + \text{H}_2
\]

Breakthrough Concentration: 2~3 ppmv
Run time: 200 hours
Regenerable
Small Reactor
Good Low Temperature Performance for Cold
Pressure Drop: < 2 psi
Startup and Transient Operations.
Desulfurization Performance
COS Equilibrium Analyses

\[
\begin{align*}
\text{CO(g)} + \text{H}_2\text{S(g)} &= \text{COS(g)} + \text{H}_2(g) \quad \text{(slow homogeneous reaction)} \\
\text{CO}_2(g) + \text{H}_2\text{S(g)} &= \text{COS(g)} + \text{H}_2\text{O(g)} \quad \text{(fast heterogeneous reaction)}
\end{align*}
\]

(1) Experimental results suggest the COS formation via CO is slow, the outlet COS concentration is about 6 ppmv at test conditions in a blank tube.

(2) COS formation via CO\(_2\) requires catalysts such as ZnS.

(3) COS is difficult to be captured by ZnO sorbent. Hydrolysis is required.

Reformate composition: 25% CO, 25% H\(_2\), 10% CO\(_2\), 7% H\(_2\)O and 33% N\(_2\).

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- Proprietary and Business Sensitive -
Effects of CO and CO₂

Need sorbents for COS removal or conversion

\[
\begin{align*}
CO + H_2S &= COS + H_2 & K = 0.0363 & C_e = 10.4 \text{ ppmv;} \\
CO_2 + H_2S &= COS + H_2O & K = 0.0029 & C_e = 1.2 \text{ ppmv}
\end{align*}
\]

Breakthrough curves of layered beds tested with 300 ppmv H₂S-25% H₂-25% CO-10% CO₂-7% H₂O-33% N₂ at a face velocity=100 cm/s at 400 C. Bed length: 22 cm
Bed Configuration
Layered Bed Design

- Low outlet sulfur concentration (as low as 0.3 ppmv)
- Less weight
- Short regeneration time
- Low temperature function
- Bed Configuration
  - Down flow direction
  - (in desulfurization)
  - Diameter: 2.14 cm
  - Particle size: 0.8~1.4 mm
  - Supported sorbent: ZnO/SiO₂ and supported Cu doped ZnO sorbent which has a better low temperature performance.
Layered- Bed Performance

Desulfurization was carried out at 400°C in the presence of reformates containing 300 ppmv H₂S-25% H₂- 25% CO-10% CO₂-7% H₂O-33% N₂ at a face velocity of 60 cm/s.

(1) Allow multiple stop and resume
(2) Run time can be extended if necessary.
Cyclic Test
(Layered Bed of ZnO-ZnO/SiO$_2$)

Desulfurization was carried out at 400 C in the presence of reformates containing 300 ppmv H$_2$S-25% H$_2$- 25% CO-10% CO$_2$-7%H$_2$O-33% N$_2$.

2 beds
30 cycles/bed
5 hrs/cycle
Total is 300 hours.
Reduced Regeneration Time

Sorbent can be regenerated in a shorter time;
Sorbent bed can be stop and resume multiple times during the run.
Sorbent bed can provide a longer service time.

Tested with challenge gas containing 300 ppmv, 30% CO, 32% H₂, 30% N₂ and 8% H₂O at a face velocity of 1.0 m/s at 400 C. The sorbent bed contains 56 g of 1.2 mm ZnO particles with a bed length of 10 cm, and ZnO/SiO₂ of 12 cm. Spent sorbent was regenerated in air-steam mixture containing ~14% O₂ for 4 hours.
Desulfurization was carried out at 150 C in the presence of reformates containing 300 ppmv H₂S-25% H₂- 25% CO-10% CO₂-7%H₂O-33% N₂.
Off-Site Regenerable Desulfurizer
(Sulfur Cartridge)

- Single reactor provides a run time of 200 hours.

Desulfurization was carried out at 400 C in the presence of reformates containing 300ppmv H2S-25% H2- 25% CO-10% CO2-7%H2O-33% N2 at a face velocity of 60 cm/s.
Conclusion

• The layered bed made of commercial ZnO and supported ZnO based sorbent demonstrated a wide operational temperature window (150~400 °C).

• The layered bed are highly regenerable. It can be regenerated for 30 cycle without significant changes in desulfurization performance.

• The designed desulfurizer can provide a continuous run with regeneration or 200 hours run as a sulfur cartridge.
Acknowledgements

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Thank you for your attention

Questions?