WSA Technology

a competitive solution for sulfur management

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Agenda

- A few words about Haldor Topsoe
- Handling sulfurous streams
  - the traditional way
  - the WSA way
- Introduction to WSA technology
- WSA process and lay-outs
- References
- Summary
Haldor Topsoe Company

- Established in 1940 by Dr. Haldor Topsoe. Private 100% family owned company
- Global market leader in heterogeneous catalysis with a 75 year long track record
- ~2,700 employees in 11 countries across five continents.
- HQ in Lyngby, Denmark, HT Inc. located in Houston ~250 employees
- Revenue about $1 billion.

Services:
- Catalysts
- Technology/licensing
- Engineering
- Hardware
- Operation assistance
Synergies in the Topsoe business model

• Founded on the belief that applied fundamental research is key to build and retain a leading position in catalysis and technology supply

• Basic research and catalyst characterization done by 300+ world class scientists

• Approx. 10% of revenues annually applied to support R&D efforts

• Bringing science to the market

• Improving our products through costumer interaction
What to do with H$_2$S?
The traditional way

H$_2$S $\rightarrow$ Claus plant $\rightarrow$ Sulfur

Sulfuric acid $\leftarrow$ Sulfuric acid plant $\leftarrow$ Other uses of sulfur

~ 10 %
~ 90 % of all sulfur
What to do with $\text{H}_2\text{S}$?
The direct way

$\text{H}_2\text{S}$

Sulfuric acid

Sulfuric acid plant (WSA)
Four times more energy when producing sulfuric acid instead of sulfur

- Sulfur: 222 kJ/mole
- Sulfuric acid: 804 kJ/mole

Oxidation state of sulfur:

- H₂S (solid) → SO₂ → SO₃ → H₂SO₄ (gas) → H₂SO₄ (liquid)

Eight times more energy when producing sulfuric acid instead of sulfur.
Limitations when producing sulfur in a Claus plant

• Minimum H$_2$S content in feed gas of 20 vol.-%

• Other combustibles than H$_2$S (like NH$_3$ and hydrocarbons) make air control more complex

• Ammonia requires very high furnace temperature

• Hydrocarbons give risk of carbon formation and catalyst deactivation

• COS and CS$_2$ require special design

• Sulfur solidifies below 120°C and gets viscous above 160°C.
## Comparison WSA vs. Claus

### Operating expenses (OPEX)

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit price</th>
<th>Topsoe’s WSA technology</th>
<th>Claus technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, MT</td>
<td>80 USD</td>
<td>Production/day</td>
<td>100</td>
</tr>
<tr>
<td>Sulfuric acid, MT</td>
<td>40 USD</td>
<td>306 USD/year</td>
<td>4,040,000</td>
</tr>
<tr>
<td>HP steam, MT</td>
<td>20 USD</td>
<td>710 USD/year</td>
<td>4,690,000</td>
</tr>
<tr>
<td>MP steam, MT</td>
<td>12 USD</td>
<td></td>
<td>225</td>
</tr>
<tr>
<td><strong>Production revenues, USD/year</strong></td>
<td></td>
<td></td>
<td>8,730,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit price</th>
<th>Consumption/day</th>
<th>USD/year</th>
<th>Consumption/day</th>
<th>USD/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel gas, Nm³</td>
<td>0.28</td>
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<td>6,100</td>
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<td>563,000</td>
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<tr>
<td>Cooling water, m³</td>
<td>0.01</td>
<td>2,800</td>
<td>9,000</td>
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<tr>
<td>Electric power, KWh</td>
<td>0.08</td>
<td>37,000</td>
<td>976,800</td>
<td>6,400</td>
<td>169,000</td>
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<tr>
<td>Waste water, MT</td>
<td>0.01</td>
<td>10</td>
<td>57</td>
<td></td>
<td>188,000</td>
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<td><strong>Production cost, USD/year</strong></td>
<td></td>
<td></td>
<td>985,800</td>
<td></td>
<td>920,000</td>
</tr>
<tr>
<td><strong>Net income, USD/year</strong></td>
<td></td>
<td></td>
<td>7,740,000</td>
<td></td>
<td>2,600,000</td>
</tr>
</tbody>
</table>

3 x more steam and better quality
Comparison WSA vs. Claus

Summary

- WSA offers larger revenues and less CAPEX
- WSA produces 3 times as much steam; this means saving in fuel consumption and CO$_2$ emissions
- WSA produces HP steam; Claus produces mostly MP steam
- WSA handles NH$_3$, COS and hydrocarbons
- DeNOx is conveniently included in the WSA process, when required
- Smaller plot area for WSA than for Claus
- Less equipment is required
- WSA is simple and easy to operate.
A process for cleaning sulfur containing streams under production of concentrated sulfuric acid

What is WSA - Wet gas Sulfuric Acid

Lean H₂S gas
Rich H₂S gas
SRU tail gas
SWS gas
SO₂
SO₃
Elemental sulfur
CS₂ / COS
Spent H₂SO₄

Clean gas
H₂SO₄
HP steam

- No need to dry the gas
- No water consumption
- No need to use chemicals or other additives
- No generation of waste products
- With high energy efficiency.
**WSA process lay-out**

**H\(_2\)S gas**

Reaction:
\[ \text{H}_2\text{SO}_4(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{liq}) + \text{heat} \]

Reaction:
\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4(\text{g}) + \text{heat} \]

Reaction:
\[ \text{H}_2\text{S} + 1\frac{1}{2}\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{heat} \]

Reaction:
\[ \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3 + \text{heat} \]
WSA process lay-out

H$_2$S gas + SWS gas

Additional reaction:
NH$_3$ + 1.25 O$_2$ → NO + 1.5 H$_2$O + heat

Reaction:
NO + NH$_3$ + 0.25 O$_2$ → N$_2$ + 1.5 H$_2$O + heat
WSA process lay-out
Spent acid regeneration
SO$_2$ conversion catalyst series VK-W

- VK-WSX / VK-WL
  9 mm Daisy
- VK-WSA
  25 mm Daisy
- VK-WSA / VK-WH
  12 mm Daisy
WSA condenser

- Clean gas outlet
- Cooling air inlet
- Hot air outlet
- SO$_3$ gas inlet
- Sulfuric acid
WSA condenser – modular construction
WSA condenser design
Refinery WSA plants

Irving Oil Limited, NB, Canada
- Claus plant
tail gas treatment
- 40 t/d sulfuric acid

OSC Slavneft (YaNOS)
Yaroslavl, Russia
- Spent acid regeneration
- 260 t/d sulfuric acid
Conclusions

- Attractive OPEX and CAPEX
- Simple process and easy to operate
- Proven and reliable technology (155+ references)
- Low emissions and no waste materials
- No issues with NH$_3$ and hydrocarbons.