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 customer interaction
Refinery Overview

Atmospheric distillation

- Crude oil
- Gas, LPG
- Naphta
- Kero
- Gas oil

HDT

- Vacuum distillation
- Vacuum Gas oil
- HDT MHC
- FCC
- HC
- SRU

Alkylation

- Spent/fresh H₂SO₄
- H₂S
- SRU Tailgas
- Gasoline, jet fuels

Fuel Oils

- Lubricating oils

Visbreaker Delayed coker

Topsoe WSA plant

Topsoe SNOX™ plant

Steam

H₂SO₄

Power

H₂SO₄
What to do with $\text{H}_2\text{S}$?

The traditional way

$\text{H}_2\text{S} \rightarrow \text{Claus plant} \rightarrow \text{Sulfur} \rightarrow \text{Sulfuric acid plant} \rightarrow \text{Sulfuric acid}$

Other uses of sulfur

$\sim 10\%$

$\sim 90\%$ 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
-2 0 +4 +6 +6 +6
Limitations when producing sulfur in a Claus plant

• Minimum H₂S content in feed gas of 20 vol.-%

• Other combustibles than H₂S (like NH₃ and hydrocarbons) make air control more complex

• Ammonia requires very high furnace temperature

• Hydrocarbons give risk of carbon formation and catalyst deactivation

• COS and CS₂ 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></td>
<td>USD</td>
<td>Production/day</td>
<td>USD/year</td>
</tr>
<tr>
<td>Sulfur, MT</td>
<td>80</td>
<td>306</td>
<td>100</td>
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<tr>
<td>Sulfuric acid, MT</td>
<td>40</td>
<td>710</td>
<td>225</td>
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<tr>
<td>HP steam, MT</td>
<td>20</td>
<td>4,040,000</td>
<td>4,690,000</td>
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<tr>
<td>MP steam, MT</td>
<td>12</td>
<td></td>
<td></td>
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<tr>
<td>Production revenues, USD/year</td>
<td></td>
<td>8,730,000</td>
<td>3,530,000</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</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>
<td>6,100</td>
<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>
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<tr>
<td>Waste water, MT</td>
<td>10</td>
<td>57</td>
<td>188,000</td>
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<tr>
<td>Production cost, USD/year</td>
<td></td>
<td>985,800</td>
<td>920,000</td>
<td></td>
</tr>
<tr>
<td>Net income, USD/year</td>
<td></td>
<td>7,740,000</td>
<td>2,600,000</td>
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</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.
What is WSA - Wet gas Sulfuric Acid
A process for cleaning sulfur containing streams under production of concentrated sulfuric acid

- 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.

Lean H₂S gas
Rich H₂S gas
SRU tail gas
SWS gas
SO₂
SO₃
Elemental sulfur
CS₂ / COS
Spent H₂SO₄
WSA process lay-out

H₂S gas

Reaction:
H₂S + 1½O₂ → SO₂ + H₂O + heat

Reaction:
SO₂ + ½O₂ → SO₃ + heat

Reaction:
SO₃ + H₂O → H₂SO₄ (g) + heat

Reaction:
H₂SO₄ (g) → H₂SO₄ (liq) + heat
**WSA process lay-out**

**H₂S gas + SWS gas**

Additional reaction:

\[ \text{NH}_3 + 1.25 \text{ O}_2 \rightarrow \text{NO} + 1.5 \text{ H}_2\text{O} + \text{heat} \]

Reaction:

\[ \text{NO} + \text{NH}_3 + 0.25 \text{ O}_2 \rightarrow \text{N}_2 + 1.5 \text{ H}_2\text{O} + \text{heat} \]
WSA process lay-out
Spent acid regeneration

Superheated steam
Combustion air
SO\(_2\) converter
WSA condenser
Cleaned gas

BFW
Combustor
Steam drum
Spent acid
H\(_2\)S gas
Atom. air
Fuel gas

Air
Blower

CW
Acid cooler
Product acid

Interbed cooler
Interbed cooler
Gas cooler
ESP
Dust
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

SO$_3$ gas inlet

Hot air outlet

Sulfuric acid
WSA condenser – modular construction
WSA condenser design
WSA/SNOX™ references
March 2018

Acid production: 4 – 1,140 MTPD
155+ references
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
Too good to be true??
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.