Field experience in biomass cofiring on SCR catalyst technology

IEA Clean Coal 8th Workshop – Copenhagen 11-13 September 18
Dipl.-Ing. Teresa Hitzke
# Outline

<table>
<thead>
<tr>
<th>01</th>
<th>Johnson Matthey Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>02</td>
<td>Selective Catalytic Reduction of NOx</td>
</tr>
<tr>
<td>03</td>
<td>Catalyst types and selection</td>
</tr>
<tr>
<td>04</td>
<td>Fuel characteristics</td>
</tr>
<tr>
<td>05</td>
<td>Catalyst deactivation mechanism</td>
</tr>
<tr>
<td>06</td>
<td>Field experience</td>
</tr>
<tr>
<td>07</td>
<td>Erosion</td>
</tr>
</tbody>
</table>

Field experience in biomass cofiring on SCR catalyst technology / Teresa Hitzke et al. / 11-13 September 2018
Johnson Matthey Group

A speciality chemicals company and a world leader in sustainable technologies

Origins date back to 1817, floated 1942, FTSE 100 company since June 2002, ranked 79

Gross R&D spend £193.0 million

£3,846 billion revenue and underlying profit before tax* of £525.0 million for year ended 31st March 2018

Operations in over 30 countries with around 14,000 employees

Leading global market positions in all its major businesses

* Before amortisation of acquired intangibles, major impairment and restructuring charges, profit or loss on disposal of businesses, significant tax rate changes and, where relevant, related tax effects
Selective Catalytic Reduction of NOx

Flue Gas from boiler → Ammonia/Air-Mixture → Flow Rectifier → Soot Blower

SINOx® Reactor

**NOx, NH₃, O₂, SOₓ, H₂O, N₂, CO₂**

Desired reactions:
1) 4NO + 4NH₃ + O₂ → 4N₂ + 6H₂O
2) 2NO + 2NO₂ + 4NH₃ → 4N₂ + 6H₂O
3) Hg + 2HCl + ½O₂ → HgCl₂ + H₂O
4) Dioxin + O₂ → CO₂ + HCl + H₂O
5) CH₂O + ½O₂ → CO + H₂O

Undesired reactions:
6) SO₂ + ½O₂ → SO₃
7) NH₃ + SO₃ + H₂O → NH₄HSO₄
8) 4NH₃ + 3O₂ → 2N₂ + 6H₂O

Cleaned Flue Gas:
N₂, H₂O, (SO₃)
Catalyst types and selection – Honeycomb Catalysts

- High specific surface area
- High SCR activity, low SO2 oxidation
- Optimized pressure drop
- Variable length and number of cells (6-300 cpsi)
- Low to medium-dust flue gas applications (high-grade coal, oil, gas, diesel or WtE applications)
Catalyst types and selection – Plate Catalysts

- Variable pitch, minimal dust deposition
- High SCR activity, low SO2 oxidation
- High erosion and poison resistance
- Low pressure drop
- Plate-to-plate clearance, variable Specific Surface Areas
- High-dust flue gas and special applications (coal-fired, biomass incineration, industrial processes & refinery power plants)
## Fuel characteristics

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Coal (Bituminous)</th>
<th>Cofiring (10-20% Biomass)</th>
<th>Biomass (straw, wood)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorific value [MJ/kg]</td>
<td>25</td>
<td>17 – 22</td>
<td>9.5 – 17.5</td>
</tr>
<tr>
<td>Water content [%]</td>
<td>10</td>
<td>9 – 28</td>
<td>8 – 45</td>
</tr>
<tr>
<td>Ash content [wt%]</td>
<td>5 – 32</td>
<td>4 – 30</td>
<td>0.1 – 12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ash composition</th>
<th>Coal (Bituminous)</th>
<th>Cofiring (10-20% Biomass)</th>
<th>Biomass (straw, wood)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca [wt%]</td>
<td>0 – 3.5</td>
<td>1 – 9</td>
<td>2 – 18</td>
</tr>
<tr>
<td>K [wt%]</td>
<td>1 – 2.5</td>
<td>1 – 20</td>
<td>1.5 – 20</td>
</tr>
<tr>
<td>Na [wt%]</td>
<td>0 – 1</td>
<td>0 – 2</td>
<td>0 – 2</td>
</tr>
<tr>
<td>P [wt%]</td>
<td>0 – 0.5</td>
<td>0 – 2</td>
<td>0 – 2</td>
</tr>
<tr>
<td>S [wt%]</td>
<td>0 – 7</td>
<td>0 – 7</td>
<td>-</td>
</tr>
</tbody>
</table>
Influence of fuel characteristics on catalyst performance

<table>
<thead>
<tr>
<th>Coal</th>
<th>Cofiring</th>
<th>Biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% bituminous coal</td>
<td>10 – 20% biomass</td>
<td>100% biomass</td>
</tr>
<tr>
<td>Catalyst deactivation</td>
<td>Small increases in K$_2$O, P$_2$O$_5$. Minor impact on catalyst design.</td>
<td>High levels K, Na, P. Chemical deactivation. Determining catalyst design.</td>
</tr>
<tr>
<td>determined by As / Ca</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As - Ca dominant</td>
<td>Na, K, P</td>
</tr>
<tr>
<td></td>
<td>K - P (secondary effect)</td>
<td></td>
</tr>
</tbody>
</table>
Catalyst deactivation mechanism

**Fresh Catalyst**

**Masking**
Reactive particles grow on the catalyst surface
Promoting conditions: CaO in ash > 20%, high SO$_2$, dew point conditions, excessive humidity

**Plugging**
Fly ash particle diffusion into catalyst pores
Catalyst micropore system is plugged mechanically

**Poisoning**
Two kinds of catalyst poisoning:
1) Reaction of alkaline metals with acidic sites
2) Reaction of phosphorus with active centers
Field experience #1
100% biomass plant (80% wood pellets, 20% agro fuel) – 3000 oph

-40% loss in catalyst activity

• uptake of K$_2$O in catalyst bulk
• uptake of K$_2$O, P$_2$O$_5$, SO$_3$ and CaO on catalyst surface
• catalyst poisons first adsorb on catalyst surface, some further penetrate into pore system (bulk)
Field experience #2
Comparison 100% biomass plant vs. changing fuel regime (coal/biomass)

100% biomass (80% wood pellets, 20% agro fuel)
- Operating hours approx. 3000h

Changing fuel regime (wood pellets, hard coal)
- Operating hours approx. 5400h

-40% loss in catalyst activity

no catalyst deactivation
Field experience #3
Catalyst deactivation caused by cofiring biomass

- Originally the unit burned coal only
- Since the unit burned wood (approx. 3% heat rate) and olive residues (approx. 2% heat rate), trace elements from cofiring caused higher deactivation
Field experience #4

Catalyst deactivation with 100% biomass and coal fly ash (up to 3 wt%)

- Catalyst deactivation strongly depends on alkalis accumulated on catalyst
- Measured deactivation consistent with designed deactivation
Erosion

**Influence on fly ash particle size**

Large particles have large erosion impact – also on standard high dust suitable plate type catalyst.

**Lignite ash / ~30 µm particles**

- ~ 55 wt.-% SiO₂
- ~ 30 wt.-% Al₂O₃

**Lignite ash / ~250 µm particle**

- ~ 58 wt.-% SiO₂
- ~ 15 wt.-% CaO

- Small particles → blocking
- Large particles → high erosion
Erosion

**Typical ash composition and particle size with biomass firing**

100% biomass ash / ~180 µm particles

- ~13 wt.-% SiO$_2$
- ~23 wt.-% CaO
- < 2 wt.-% Al$_2$O$_3$

Cofiring biomass ash / ~40 µm particle

- ~17 wt.-% SiO$_2$
- ~44 wt.-% CaO
- ~10 wt.-% Al$_2$O$_3$
Erosion

New plate catalyst development with high erosion resistance

**JM standard plate catalyst**
- high erosion resistance compared to honeycombs

**JM Low Erosion – highly erosion resistant catalyst**
- Erosion resistance boosted significantly
- Formulation optimized for high mechanical resistance

Accelerated test was developed to achieve within one hour similar erosion as years in application
Erosion

New plate catalyst development with high erosion resistance

New catalyst shows superior erosion resistance even at large particle size (simulated ash particle)
Thank you for your attention!

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