Advanced Technologies for Desulphurisation of Coke Oven Gas

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Alternative Ways of Using COG

Gas Cleaning

1. COG fine cleaning of NH3 and H2S compounds
   2a. Pressure Swing Adsorption
   2b. Steam Reforming

Utilisation

Underfiring in Coke Oven Battery or Steel Work

Utilisation for industrial heat production

Electricity Generation by
- Gas Engine
- Gas Turbine
- HT Fuel Cell

Raw material for the chemical industry
- Fischer-Tropsch-Synthesis

Hydrogen for the mobility sector
- Fuel cell driven cars & buses
- LNG driven vehicles

Hydrogen for the home sector
- Fuel cell appliances

Increase of Valuability

Heat
Electricity
Raw Material
High Grade Fuel
# Purity Requirements for COG

<table>
<thead>
<tr>
<th>Utilisation</th>
<th>NH₃ (mg/Nm³ COG)</th>
<th>H₂S (mg/Nm³ COG)</th>
<th>HCN (mg/Nm³ COG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke Oven Underfiring</td>
<td>&lt; 10 – 200</td>
<td>&lt; 300 – 900</td>
<td>&lt; 500 – 1000</td>
</tr>
<tr>
<td>Industrial Boilers</td>
<td>&lt; 10 – 200</td>
<td>&lt; 300 – 500</td>
<td>&lt; 500 – 1000</td>
</tr>
<tr>
<td>Gas Motor</td>
<td>&lt; 15</td>
<td>&lt; 300 – 500</td>
<td>unspecified</td>
</tr>
<tr>
<td>Low efficient Gas Turbine</td>
<td>unspecified</td>
<td>&lt; 500</td>
<td>unspecified</td>
</tr>
<tr>
<td>High efficient Gas Turbine (e.g. for Combined Cycle)</td>
<td>&lt; 0,3</td>
<td>&lt; 1,2</td>
<td>&lt; 7,0</td>
</tr>
<tr>
<td>HT Fuel Cell</td>
<td>&lt; 0,5</td>
<td>&lt; 2,0</td>
<td>&lt; 150</td>
</tr>
<tr>
<td>Fischer Tropsch Synthesis</td>
<td>&lt; 1 ppmV</td>
<td>H₂S + COS + CS₂</td>
<td>&lt; 1 ppmV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 1 ppmV</td>
<td></td>
</tr>
</tbody>
</table>
Survey of desulphurisation processes

Wet Oxidation Route

**Stretford**

H$_2$S is scrubbed from the coke oven gas by a sodium carbonate solution (Na$_2$CO$_3$) and elemental sulphur (S°) is yielded using vanadate (VO$_3$) as an intermediate. Regeneration of the scrubbing liquid takes place by aeration (O$_2$), using anthraquinone disulphonic acid (ADA) as an intermediate.

Takahax
Thylox
Perox
Fumaks-Rhodacs

Absorption / Stripping Route

**ASK or Diamex**

H$_2$S is scrubbed from the coke oven gas by a NH$_3$ solution. The NH$_3$ solution is derived from the NH$_3$ scrubber. The H$_2$S and NH$_3$ are stripped from the washing liquor by steam stripping and the vapours are led to a Claus plant or a sulphuric acid plant.

Vacuum Carbonate
Sulfiban
DESLUF
General Comparison of both Process Routes

**Wet Oxidation Route**

- Better desulphurisation efficiency of ca. 99.9% achieving residual H₂S concentrations as low as 1 mg/Nm³ in the COG.
- Removal of most of the hydrogen cyanide from the COG forming sodium thiocyanide which are purged by a liquid stream to prevent salting out of the chemicals.
- Wastewater usually to be treated separately owing to the presence of compounds showing detrimental effects on the BET.
- Applicable at new and existing plants.
- Applicable also for low desulphurisation capacities starting from 400 Nm³/h COG.

**Absorption / Stripping Route**

- Absorptive processes usually do not exceed 95% desulphurisation efficiency achieving residual H₂S concentrations in the COG of ca. 300 mg/Nm³.
- The discharge of small wastewater flows to the BET does not require any further treatment.
- Applicable at new and existing plants.
Plant Configuration for TCO

Wet Oxidation Process

COG
6 g H2S / Nm3
6 g NH3 / Nm3

Ammonium-sulphate Unit

Coal Water

Coal Water Stripper Unit

NaOH

H2SO4

(NH4)2SO4

Na2CO3
Vanadate
ADA
Tartrate
Sulphur

Purge stream to special wastewater treatment

COG
2 mg H2S / Nm3
30 mg NH3 / Nm3

Stretford Unit

Absorption / Stripping Process

COG
6 g H2S / Nm3
6 g NH3 / Nm3

ASK* Unit

Coal Water

NaOH

Coal

Wastewater to Biological Treatment

Wastewater to Biological Treatment

Sulphur

COG
300 mg H2S / Nm3
30 mg NH3 / Nm3

Stripper / Deacidifier Unit

Claus Unit
### Assumptions / Parameters of the TCO elaboration (on European basis) – 1/3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Ammonia Sulphate / Stretford</th>
<th>ASK / Stripper Unit / Claus Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>COG production</td>
<td>Nm³/h</td>
<td>42,000</td>
<td>42,000</td>
</tr>
<tr>
<td>Crude COG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>g/Nm³</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>NH₃</td>
<td>g/Nm³</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Clean COG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>mg/Nm³</td>
<td>2</td>
<td>300</td>
</tr>
<tr>
<td>NH₃</td>
<td>mg/Nm³</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>
Assumptions / Parameters of the TCO elaboration
(on European basis) — 2/3

<table>
<thead>
<tr>
<th>Price of Consumables</th>
<th>Parameter</th>
<th>Unit</th>
<th>Ammonia Sulphate / Stretford Unit</th>
<th>ASK / Stripper / Claus Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.90 €/t</td>
<td>Steam</td>
<td>t/d</td>
<td>154</td>
<td>264</td>
</tr>
<tr>
<td>0.34 €/kWh</td>
<td>Electricity</td>
<td>kWh/d</td>
<td>11,900</td>
<td>6,600</td>
</tr>
<tr>
<td>128.00 €/t</td>
<td>H₂SO₄ (98%)</td>
<td>t/d</td>
<td>17.5</td>
<td>---</td>
</tr>
<tr>
<td>7.70 €/kg</td>
<td>ADA</td>
<td>kg/d</td>
<td>24</td>
<td>---</td>
</tr>
<tr>
<td>27.00 €/kg</td>
<td>Vanadate</td>
<td>kg/d</td>
<td>10</td>
<td>---</td>
</tr>
<tr>
<td>5.50 €/kg</td>
<td>Tartrate</td>
<td>kg/d</td>
<td>13</td>
<td>---</td>
</tr>
<tr>
<td>370.00 €/t</td>
<td>Soda</td>
<td>t/d</td>
<td>2.6</td>
<td>---</td>
</tr>
<tr>
<td>110.00 €/t</td>
<td>Caustic Soda</td>
<td>t/d</td>
<td>9.6</td>
<td>9.6</td>
</tr>
</tbody>
</table>
**Assumptions / Parameters of the TCO elaboration**

*(on European basis) — 3/3*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Ammonia Sulphate / Stretford</th>
<th>ASK / Stripper Unit / Claus Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Products</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>t/d</td>
<td>4.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Ammonium Sulphate</td>
<td>t/d</td>
<td>23.5</td>
<td>--</td>
</tr>
<tr>
<td><strong>Revenues</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>€/t</td>
<td>125</td>
<td>250</td>
</tr>
<tr>
<td>Ammonium Sulphate</td>
<td>€/t</td>
<td>180</td>
<td>--</td>
</tr>
<tr>
<td><strong>Annual Debt Service on Capital Costs</strong></td>
<td>%</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td><strong>Annual Maintenance on Capital Costs</strong></td>
<td>%</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Sulphur Quality

Stretford Sulphur
(Solidified Product after Autoclave)

Claus Sulphur
(Solidified Sample after S-Separator)
TCO comparison (incl. costs for steam)

Δ = 0.06 €ct/Nm³ COG
≈ 6.5 %
**TCO comparison** *(without costs for steam)*

Δ = 0.19 €ct/Nm³ COG
≈ 31 %
### Sale Scenario Impact on TCO

<table>
<thead>
<tr>
<th>Sale Scenario</th>
<th>Process Route</th>
<th>Cleaning Costs € ct / Nm³ COG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scenario</strong></td>
<td><strong>(NH₄)₂SO₄ €/t</strong></td>
<td><strong>S° €/t</strong></td>
</tr>
<tr>
<td>Medium level</td>
<td>180</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>250</td>
</tr>
<tr>
<td>High level</td>
<td>180</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>320</td>
</tr>
<tr>
<td>Low level</td>
<td>120</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>250</td>
</tr>
</tbody>
</table>
Conclusions

Wet Oxidation Route

Advantages:
- High cleaning efficiency (<2 mg H₂S / Nm³ COG, 30 mg NH₃ / Nm³ COG)
- No HP-scrubbing required

Disadvantages:
- Higher operating costs
- NH₃ and HCN pre-scrubbing required
- Catalyst as consumable required
- Quality of Sulphur S° often deteriorated yielding lower revenues
- Contaminated wastewater streams need special treatment
- Susceptible for contamination
- Dependence on suppliers for catalyst and ADA (consumables)

Absorption / Stripping Route

Advantages:
- Lower operating costs
- No consumable catalyst required
- NH₃-scrubbing included
- High quality Sulphur S° with high revenues
- No contaminated wastewater; wastewater directly delivered to the BET

Disadvantages:
- Lower cleaning efficiency (300 mg H₂S / Nm³ COG, 30 mg NH₃ / Nm³ COG)
- HP-scrubbing necessary to achieve a H₂S concentration of below 2 mg/Nm³ in the clean gas (if demanded)
Thank you for your attention!