Causticizing Aspects and Sulfur Recovery in Black Liquor Gasification

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Low Temperature Gasification

MTCI GASIFIER

Sulfur-free Black liquor

Atmospheric Fluidized bed reactor (600°C)

Gas cleanup

TO GAS TURBINE

Steam

Solids (Na₂CO₃)
Consequence of Sulfur Release during KBL Gasification

- Sulfur must be removed from gasification gas for liquor preparation and turbine protection
- Formation of sulfur-rich and sulfur-lean white liquor streams
- Possibility to produce elemental sulfur, and thus polysulfide liquor
Continuous System-Hi/Lo Sulfidity

Preparation of Polysulfide

- **Dissolve elemental sulfur in white liquor (WL)**
  \[ \text{NaHS} + \text{NaOH} + n \text{S}_2 \rightarrow \text{Na}_2\text{S}_n\text{S} + \text{H}_2\text{O} \quad (n=2-3) \]
- **Oxidation of white liquor**
  \[ 3 \text{NaHS} + \text{O}_2 \rightarrow \text{Na}_2\text{S}_2\text{S} + \text{NaOH} + \text{H}_2\text{O} \]
  \[ 2 \text{Na}_2\text{S}_3 + 6 \text{NaOH} \rightarrow 4 \text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \]

1. Elemental sulfur decreases alkali content of WL
2. WL oxidation does not significantly change alkali content of cooking liquor
Various H₂S scrubbing processes are possible:

1. Absorption in weak wash.

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{S} \rightarrow \text{NaHS} + \text{NaHCO}_3 \quad (1) \]

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2 \text{NaHCO}_3 \quad (2) \]

This increases lime requirements as can be inferred from:

\[ 2\text{NaHCO}_3 + 2\text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 + 2\text{NaOH} + \text{H}_2\text{O} \quad (3) \]

\[ \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + 2 \text{NaOH} \quad (4) \]

2. Physical/chemical H₂S absorption-stripping systems.

Adds complexity of Claus plant for H₂S to S conversion. Also recovered H₂S still contains CO₂ (about equimolar)

<table>
<thead>
<tr>
<th>Gasification Temperature (°C)</th>
<th>Increase in Causticization (%)</th>
<th>Increase in lime kiln fuel (% of gasifier output)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>60 - 70</td>
<td>7.0 – 8.1</td>
</tr>
<tr>
<td>1000</td>
<td>25</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Direct Causticization with TiO₂

Direct causticization reactions in gasifier:

\[ 3 \text{TiO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O.3TiO}_2 + \text{CO}_2 \]  \hspace{1cm} (1)

\[ 5 (\text{Na}_2\text{O.3TiO}_2) + 7 \text{Na}_2\text{CO}_3 \rightarrow 3 (4\text{Na}_2\text{O.5TiO}_2) + 7 \text{CO}_2 \]  \hspace{1cm} (2)

Hydrolysis reaction in leacher:

\[ 3 (4\text{Na}_2\text{O.5TiO}_2) + 7 \text{H}_2\text{O} \rightarrow 5 (\text{Na}_2\text{O.3TiO}_2) + 14 \text{NaOH} \]  \hspace{1cm} (5)

Direct Causticization in the MTCI Steam Reformer
Fluid Bed Operating Conditions with Direct Causticization

- Complete direct causticization in 50 hours at 675 °C in steam reformer
- At 700 °C or higher the reformer must be pressurized to convert all Na$_2$S in H$_2$S
  \[ \text{Na}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S} \]
- At 800 °C complete direct causticization in 0.3 hrs and pressure of 3.5 bar in reformer
- KBR oxygen blown recirculating FB at 827 °C and 25.6 bar appears consistent complete H$_2$S release

Minimum Charge of TiO$_2$ or Na$_2$O.3TiO$_2$

- For kraft black liquor with a sodium content of 19 weight % based on dry solids:
  - TiO$_2$ charge of 41 w/w % (kbl dry solids basis)
  - Na$_2$O.3TiO$_2$ charge of 89 % (on kbl dry solids)
- In practice a minimum Na$_2$O.3TiO$_2$ charge equal to the dry black liquor solids weight is needed, because of incomplete conversion to 4Na$_2$O.5TiO$_2$
Sulfate Reduction Kinetics

$$\text{Na}_2\text{SO}_4 + 3\text{C} \rightarrow \text{Na}_2\text{S} + \text{CO} + \text{CO}_2$$

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sulfate Conversion in 1 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>°F</td>
</tr>
<tr>
<td>550</td>
<td>1022</td>
</tr>
<tr>
<td>600</td>
<td>1112</td>
</tr>
<tr>
<td>650</td>
<td>1202</td>
</tr>
<tr>
<td>700</td>
<td>1292</td>
</tr>
</tbody>
</table>

Heats of Reaction and Temperatures of Titanate and Lime Causticizing

<table>
<thead>
<tr>
<th>Process/Reaction</th>
<th>Temperature (°C)</th>
<th>Heat of Reaction (kJ/mol NaOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Causticizing</td>
<td>675</td>
<td>30.5</td>
</tr>
<tr>
<td>Leaching</td>
<td>100</td>
<td>7.6</td>
</tr>
<tr>
<td>Lime</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcination</td>
<td>850</td>
<td>85</td>
</tr>
<tr>
<td>Slaking/Causticizing</td>
<td>100</td>
<td>-34.6</td>
</tr>
</tbody>
</table>
Advantages of Direct Causticization with TiO₂ for Low T Gasification

• 4.5% increase in overall energy efficiency compared to conventional recovery.
• Elimination of lime cycle (Annual saving of 100,000 barrels of oil for 1000 TPD mill.
• Increased carbon conversion
• Increased tar conversion
• Conversion of sulfate to H₂S

Potential Problems or Risks

• Large Amount of titanate solids handling
• Disintegration of titanate particles during leaching
• Agglomeration of bed particles
• Too large TiO₂ losses in solids handling and NPE removal
**Sulfur Capture By A Regenerative Calcium Based Process**

**Sulfur Capture:**

\[
\begin{align*}
H_2S + CaO & \rightarrow CaS + H_2O \quad (1a) \\
H_2S + CaCO_3 & \rightarrow CaS + CO_2 + H_2O \quad (1b)
\end{align*}
\]

**CaS Conversion:**

\[
\begin{align*}
CaS + NaOH & \rightarrow NaHS + Ca(OH)_2 \quad (2a) \\
CaS + Na_2CO_3 + H_2O & \rightarrow CaCO_3 + NaHS + NaOH \quad (2b)
\end{align*}
\]

**Calcination:**

\[
\begin{align*}
Ca(OH)_2 & \rightarrow CaO + H_2O \quad (3a) \\
CaCO_3 & \rightarrow CaO + CO_2 \quad (3b)
\end{align*}
\]

Note that: \( Na_2S + H_2O \rightarrow NaHS + NaOH \)

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**Combining Calcium Based Sulfur Recovery with Gasification**

- Calcination in gasification gas of 1 or 20 atm.
  requires temperature above resp. 775 and 975 °C
- Calcination of CaCO₃ and avoiding H₂S recapture
  by Na₂CO₃ are incompatible
- Desulphurization with CaO in separate reactor at
  100 °C above steam reformer with TiO₂ as bed;
  however no temperature restrictions with dolomite
- Desulphurization with CaCO₃ or CaO may be
  combined with high T gasification
**Integrated Low T Gasification**

**Process Integration Advantages for Low T Process Version**

- Production of NaOH and sulfur rich liquors
- Conversion of sulfate into H₂S
- Increased carbon conversion
- Increased tar conversion (also in CaS reactor!)
- Elimination of lime cycle
Conclusions

**Black Liquor Gasification Technology**

- may make the P and P Industry independent of fossil fuel, a net exporter of electricity, and dramatically reduce greenhouse gas emissions

- needs further development in areas of causticizing requirement and sulfur recovery