PULPING OPTIONS WITH BLACK LIQUOR GASIFICATION

Hasan Jameel
Jean Renard

Gasification of Black Liquor
Separation of Inorganic Chemicals

- Tomlinson Furnace
  - smelt S/Na ratio = black liquor S/Na ratio

- Gasification Process: Inorganic pulping chemicals are effectively separated.
  - high sodium/low sulfur fumes
  - low sodium/high sulfur gas

Therefore, ability to generate liquors of various compositions by judicious treatment of these two streams.
Black Liquor Gasification

Effective separation of inorganic pulping chemicals
- high sodium/low sulfur stream
- low sodium/high sulfur stream

Two technologies
- High Temperature
  - Operate at about 1000°C
  - Inorganics leave as smelt
- Low Temperature
  - Operate at less than 700°C
  - Inorganics leave as solids

BLG Pulping Technologies

- Split Sulfdity Pulping
- Polysulfide Pulping
- Alkaline Sulfite Pulping
  - Alkaline Sulfite AQ
  - Mini-Sulfide Sulfite AQ
Split Sulfidity Pulping

- Use of separate sulfur rich and sulfur lean streams to optimize kraft process
- Lowest capital cost technology alternative

Benefits from Split Sulfidity Pulping

- Increase yield at same kappa number
- Lower kappa number at same yield
  - reduced bleaching cost
  - lower environmental impact
**Split Sulfidity Pulping – Process Diagram**

**Split Sulfidity Economics**

<table>
<thead>
<tr>
<th></th>
<th>Kraft Base Case</th>
<th>BLG (5:1)</th>
<th>BLG (10:1)</th>
<th>BLG (20:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Make-up Lime</td>
<td>0.61</td>
<td>0.96</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td>Kiln Fuel</td>
<td>8.35</td>
<td>10.73</td>
<td>10.47</td>
<td>10.34</td>
</tr>
<tr>
<td>Total</td>
<td>191.51</td>
<td>194.98</td>
<td>194.59</td>
<td>194.39</td>
</tr>
<tr>
<td>Energy Credit</td>
<td>-51.28</td>
<td>-51.28</td>
<td>-51.28</td>
<td>-51.28</td>
</tr>
<tr>
<td>Net Operating Cost</td>
<td>140.23</td>
<td>143.70</td>
<td>143.31</td>
<td>143.11</td>
</tr>
</tbody>
</table>

- Investigated $H_2S/CO_2$ Co-absorption ratios of 5:1, 10:1, 20:1
- Cost analysis for listed operating variables for pulping and chemical recovery only
- The analysis does not incorporate Power generation, Capital or other process related cost items
**Capital Cost**

- **Digester already has capability for extended delignification**
  - MCC/EMCC/ITC: $100,000
  - RDH: $100,000
- **Digester does not have extended delignification**
  - Continuous: $1-1.5 million
  - Batch: $5-20 million
- **Modifications to Recaust**
  - Slaker: $0.5-1 million

**Green Liquor Pretreatment**

- Avoid recaust penalties by reducing load on recovery through Green Liquor recycle
- Utilize S/Na split from BLG to increase yield through green liquor pretreatment
- Operate process at lower % EA while maintaining same % TTA
- Impact on pulping and recovery?
Green Liquor Pretreatment – Process Diagram

Green Liquor Pretreatment Benefits

- 1-2 % Yield increase at same Kappa
- Decrease Kappa number at same yield
- When pulping to 30 Kappa – possible to lower EA from 16% in reference to 13.5%

Andrews, E.K., Ph.D. Dissertation, North Carolina State University, 1982
Decreasing %EA to pulp at same %TTA

Charged [TTA] vs. System EA % on wood

Simulated cases balancing Na₂CO₃, NaOH and H₂S to decrease %EA charged to pulping operation

Green Liquor Pretreatment – Results

Comparison of Variable Operating Costs ($/ODtP)

<table>
<thead>
<tr>
<th></th>
<th>Kraft Base Case</th>
<th>% EA (19)</th>
<th>% EA (17)</th>
<th>% EA (15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Lime</td>
<td>0.61</td>
<td>0.89</td>
<td>0.80</td>
<td>0.71</td>
</tr>
<tr>
<td>Kiln Fuel</td>
<td>8.35</td>
<td>10.01</td>
<td>8.96</td>
<td>7.91</td>
</tr>
<tr>
<td>Total</td>
<td>191.51</td>
<td>188.60</td>
<td>186.38</td>
<td>184.08</td>
</tr>
<tr>
<td>Energy Credit</td>
<td>-51.28</td>
<td>-47.44</td>
<td>-47.77</td>
<td>-47.99</td>
</tr>
<tr>
<td>Net Operating Cost</td>
<td>140.23</td>
<td>141.15</td>
<td>138.61</td>
<td>136.09</td>
</tr>
</tbody>
</table>

- Cost analysis for listed operating variables for pulping and chemical recovery only
- The analysis does not incorporate Power generation, Capital or other process related cost items
Polysulfide Pulping

**OPPORTUNITIES:**
- Increased pulp yield at a given Kappa Number
  - Decreased wood cost
  - Potential incremental pulp capacity

**CHALLENGE:**
- Maximizing polysulfide application, hence yield increase, without upsetting the Na/S balance of the mill
- Some impact on delignification rate

---

Polysulfide Pulping

*Advantage of Gasification*

**Polysulfide Generation through White Liquor Oxidation**
- Difficulty of maintaining selectivity of oxidation to polysulfide.
- Maximum polysulfide charge limited to 1.5% PS on wood
- Yield increase limited to 1.5-2% on wood

**Black Liquor Gasification Produces Gas Stream containing H₂S:**
- Oxidation of H₂S to elemental sulfur
- Dissolution of sulfur in low sulfidity white liquor: high polysulfide charge without upsetting Na/S balance
**Polysulfide Pulping**

![Yield vs Polysulfide Charge](Image)

**Preparation of Polysulfide**

- **Dissolve elemental sulfur in the white liquor**
  \[ \text{Na}_2\text{S} + \text{S}_0 = \text{Na}_2\text{S}_x \]

- **Oxidation of white liquor**
  \[ \text{Na}_2\text{S} + \text{O}_2 + \text{H}_2\text{O} = 2\text{S}_0 + 4 \text{NaOH} \]
  \[ \text{Na}_2\text{S} + \text{S}_0 = \text{Na}_2\text{S}_x \]
**Oxidation of H₂S**

- **Claus Process**
  - catalytic reduction of H₂S to elemental sulfur
  - used in oil refining
  - use of one to four catalytic converters

---

**Production of Polysulfide Liquor**
Impact on Pulp Production Cost

<table>
<thead>
<tr>
<th>% $S_0$ on wood</th>
<th>Wood cost, $/BDT</th>
<th>Bleached Pulp Cost, $/BDT</th>
<th>Cost Saving @$860 BDT/D</th>
<th>Capital Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>143</td>
<td>228</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>131</td>
<td>214</td>
<td>$4.2$MM/yr</td>
<td>$5$ MM</td>
</tr>
<tr>
<td>7.0</td>
<td>123</td>
<td>206</td>
<td>$7.0$MM/yr</td>
<td>$8.5$ MM</td>
</tr>
</tbody>
</table>

Two Stage Polysulfide Pulping

- Polysulfide decomposes at temperatures >$160°$C
- Initial stage done with polysulfide liquor
- Final stage done with normal kraft or soda liquor
- Ability to produce liquors with different compositions well suited for two stage polysulfide process
Alkaline Sulfite Pulping

**Alkaline Sulfite- AQ (ASAQ)**
- total alkali charge of 22% as Na₂O
- sodium sulfite (80% of alkali)
- sodium carbonate (10% of alkali)
- sodium hydroxide (10% of alkali)
- AQ (0.1-0.2% on OD wood)

**Mini-Sulfide Sulfite AQ (MSSAQ)**
- total alkali charge of 22% as Na₂O
- sodium sulfide (15% of total alkali)
- sodium sulfite (85% of total alkali)
- AQ (0.1-0.2% on OD wood)

ASAQ and MSSAQ Benefits

**Unique features**
- pulp yield for liner board is 10% pt higher than kraft
- brightness of MSS-AQ pulp much higher
  - MSS-AQ pulps easier to bleach with ECF and TCF sequences
  - advantage for high quality printing on linerboard
- need for caustic room, lime kiln and associated energy usage eliminated
- yield advantage decreases for bleached pulps
  - pulp to 50 kappa follow with oxygen bleaching
- Lower TRS emissions
### ASAQ/MSSAQ Process

- Wood to Digester
- AS/MSS Liquor to Absorber
- AQ to H2S Burner
- Dissolving Tank to Gasifier
- Refiners Screens BSW to Evaporators
- Pulp

### Linerboard Variable Production Cost

<table>
<thead>
<tr>
<th>Cost Element</th>
<th>Kraft-Tomlinson</th>
<th>MSSAQ-BLGCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>$113</td>
<td>$95</td>
</tr>
<tr>
<td>AQ</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td>$151</td>
<td>$134</td>
</tr>
<tr>
<td>Saving</td>
<td>$17</td>
<td></td>
</tr>
</tbody>
</table>
Production Cost - MSS-AQ

<table>
<thead>
<tr>
<th>Cost Element</th>
<th>Kraft-O2 ECF</th>
<th>MSSAQ-O2 ECF</th>
<th>MSSAQ-O2 TCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>$141</td>
<td>119</td>
<td>119</td>
</tr>
<tr>
<td>AQ</td>
<td>0</td>
<td>9.92</td>
<td>9.92</td>
</tr>
<tr>
<td>Pulping Make-up Utilities</td>
<td>$13.8</td>
<td>$8.2</td>
<td>$1.3</td>
</tr>
<tr>
<td>Utilities</td>
<td>$15.4</td>
<td>$15.0</td>
<td>$15.1</td>
</tr>
<tr>
<td>Bleaching-chemicals &amp; utilities</td>
<td>$46.5</td>
<td>$44.1</td>
<td>$52.3</td>
</tr>
<tr>
<td>Total</td>
<td>$216</td>
<td>$196.5</td>
<td>$198.5</td>
</tr>
<tr>
<td>Savings</td>
<td>0</td>
<td>$19.5</td>
<td>$17.5</td>
</tr>
</tbody>
</table>

MSS-AQ Environmental Advantages

- **Air Pollution Abatement:**
  - little or no TRS emission
  - No fugitive TRS emission from washers, contaminated condensates: low odor mill

- **Water Pollution Abatement:**
  - Pulp bleaches easily
  - low ClO₂ usage/AOX discharge for ECF bleaching
  - TCF bleaching with minimal pulp strength loss: virtually closed cycle bleached pulp mill

- **Elimination or significant decrease for caustic room/lime kiln:**
  - Elimination of fossil fuel/decreased CO₂ emission
Alkaline Sulfite Oxygen Pulping

- The yield advantage of ASAQ/MSSAQ decreases rapidly with kappa number
- These pulps respond very well to oxygen bleaching
- Stop pulping at 50 kappa, followed by oxygen to 20 kappa

Pulping Options Summary

- **Split Sulfidity White Liquors**
  - take advantage of the ability to generate white liquors of different sulfidity
  - take full advantage of extended delignification to reduce bleaching costs and environmental impact
  - savings of up to $2/ODT
### Pulping Options Summary

#### Polysulfide Pulping
- Convert part of $H_2S$ stream to elemental sulfur. Sulfur later dissolved in white liquor to produce polysulfide
- Increased pulp yield (wood cost saving or incremental production)
- Production cost saving: $12-16/ODTP for 3%PS and $18-24/ODTP for 7%PS
- Incremental pulp cost saving $8-10 million for 3%PS and $15-19 million for 7%PS

#### Alkaline Sulfite Process or Mini-Sulfide Sulfite AQ Process
- Convert most of the $H_2S$ stream to $SO_2$
- Dissolve $SO_2$ in quenching liquor containing $Na_2S$, $NaOH$, and $Na_2CO_3$ to generate AS/MSS liquor
- Drastically reduced TRS
- Elimination or decrease of causticization requirements
Pulping Options Summary

- Alkaline Sulfite Process or Mini-Sulfide Sulfite AQ Process
  - increased pulp yield (lower wood cost, incremental production)
  - savings of up to $20/ODT
  - profit from incremental production: $18-22 million/year