PULPING OPTIONS WITH BLACK LIQUOR GASIFICATION

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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 Sulfidity 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 Sulfdity Pulping – Process Diagram

- Black Liquor
- Oxygen
- Gasifier
- Fume Collection
- H2S Scrubber
- H2S Stripper
- H2S Scrubber
- Slaker 1
- Slaker 2
- Impregnation
- Digester
- Chips
- Gas Turbine
- Raw Fuel Gas
- Weak Wash
- Sulfide Lean Green Liquor
- Sulfide Rich White Liquor
- Sulfide Lean White Liquor
- Pulp
### Split Sulfdidity Economics

#### Comparison of Variable Operating Costs ($/ODtP)

<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>
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<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>
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<tr>
<td>Energy Credit</td>
<td>-51.28</td>
<td>-51.28</td>
<td>-51.28</td>
<td>-51.28</td>
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<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 $\text{H}_2\text{S}/\text{CO}_2$ 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

Simulated cases balancing Na$_2$CO$_3$, NaOH and H$_2$S 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>
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<tr>
<td>Kiln Fuel</td>
<td>8.35</td>
<td>10.01</td>
<td>8.96</td>
<td>7.91</td>
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<tr>
<td>Total</td>
<td>191.51</td>
<td>188.60</td>
<td>186.38</td>
<td>184.08</td>
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<tr>
<td>Energy Credit</td>
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<td>-47.44</td>
<td>-47.77</td>
<td>-47.99</td>
</tr>
<tr>
<td><strong>Net Operating Cost</strong></td>
<td><strong>140.23</strong></td>
<td><strong>141.15</strong></td>
<td><strong>138.61</strong></td>
<td><strong>136.09</strong></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 $H_2S$:**
  - Oxidation of $H_2S$ 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

Yield, % OD Wood

Polysulfide Sulfur, % on Wood
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 $H_2S$

- **Claus Process**
  - catalytic reduction of $H_2S$ to elemental sulfur
  - used in oil refining
  - use of one to four catalytic converters
Production of Polysulfide Liquor

- Sulfur Dissolution
- Pulp Mill
- Evaporators
- Gasifier
- H₂S Oxidizer
- H₂S Absorber
- Caustic Plant
- Dissolving Tank
- Bleached Pulp
## 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>
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<tr>
<td>3.0</td>
<td>131</td>
<td>214</td>
<td>$4.2$MM/yr</td>
<td>$5$ MM</td>
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<td>7.0</td>
<td>123</td>
<td>206</td>
<td>$7.0$MM/yr</td>
<td>$8.5$ MM</td>
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</tbody>
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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 Na$_2$O
  - 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 Na$_2$O
  - 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
## Linerboard Variable Production Cost

<table>
<thead>
<tr>
<th>Cost Element</th>
<th>Kraft-Tomlinson</th>
<th>MSSAQ-BLGCC</th>
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<tr>
<td>Wood</td>
<td>$113</td>
<td>$95</td>
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<tr>
<td>AQ</td>
<td>0</td>
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<td><strong>Total</strong></td>
<td><strong>$151</strong></td>
<td><strong>$134</strong></td>
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<td><strong>Saving</strong></td>
<td><strong>$17</strong></td>
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<tr>
<td>Cost Element</td>
<td>Kraft-O2 ECF</td>
<td>MSSAQ-O2 ECF</td>
</tr>
<tr>
<td>------------------------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Wood</td>
<td>$141</td>
<td>119</td>
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<tr>
<td>AQ</td>
<td>0</td>
<td>9.92</td>
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<td>Pulping</td>
<td>$13.8</td>
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<tr>
<td>Make-up</td>
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<td>Utilities</td>
<td>$15.4</td>
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<tr>
<td>Bleaching-chemicals &amp; utilities</td>
<td>$46.5</td>
<td>$44.1</td>
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<tr>
<td>Total</td>
<td>$216</td>
<td>$196.5</td>
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<tr>
<td>Savings</td>
<td>0</td>
<td>$19.5</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
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
Pulping Options Summary

- **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