Conversion of Black Liquor in a Fluidized Bed Steam Reformer

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Outline

- Intro – BL steam reforming
  - Fluidized bed steam reforming
  - Commercial installations
  - Steam reforming research

- This study – Experimental system

- Liquor conversion in a steam reformer
  - Fate of organic carbon
  - Factors impacting carbon conversion
  - Development-scale versus full-scale

- Conclusions
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Black Liquor Steam Reforming

- Alternative to combustion in recovery boiler
  - Improved energy efficiency
  - Better environmental performance
  - Can improve pulp yield and quality
  - Safer technology

- Fluidized bed reforming
  - Steam for fluidizing and reactant
  - Operating temp. ~1120°F (605°C)
  - Endothermic process – indirect heating
  - Bed solids made of "ash" product from reforming

- Developers
  - MTCI – Process development
  - TRI – Commercial installations
Norampac Steam Reformer

- Trenton, ON, Canada
- Startup June 2003
- 1x100 tds/day reformer
- Carbonate liquor
- No product gas conditioning – Sent directly to boiler
- Bed heaters fired on natural gas

Photos courtesy of Norampac
G-P Big Island Steam Reformer

- Big Island, Virginia
- Startup Spring 2004
- 2x100 tds/day reformer
- Carbonate liquor
- Product gas handling
  - Superheater
  - Venturi scrubber
  - Gas cooler
  - H2S scrubber
- Bed heaters fired with clean product gas

Photos courtesy of Georgia-Pacific Corp.
Steam Gasification Research

- Atmospheric studies
  - 1980s – 1990s
  - Van Heiningen

- Pressurized studies
  - 1990s
  - Whitty, Frederick, Hupa (Åbo Akademi)
  - VTT Finland

- In-house development at MTGI
  - 1980s – 1990s
  - Proprietary
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U. Utah Steam Reforming System

- Black Liquor Tank (heated)
- Circ. pump
- Feed pump
- Pressure control valve
- Internal cyclone
- Freeboard
- Bed heaters
- After-burner
- Natural Gas
- Air
- Gas to slipstream reactors
- Dry gas to analyzers
- H₂O in
- H₂O out
- H₂O in
- H₂O out
- CW in
- CW out
- Exhaust
- Cooler/condenser
- Condensate
- Water
- Soften
- R.O.
- Boiler
- Super heater
- Steam
- Lock hopper
- Bed solids
- N₂
- Pressure release
- Steam
- Air
- Natural gas
- Air
- Nitrogen
Gasification Research Facility
Steam Reformer Bed Section

- Sample Port
- Thermocouple
- Thermocouple Leads
- Heater Bundles
- Power Leads
- Sample Port
- Liquor Injector
Steam Reformer Bed Section
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Black Liquor Conversion

- **Drying**
- **Pyrolysis**
- **Char gasification**

Chemical reactions:

\[ \text{H}_2\text{O(g)} + \text{C(s)} \rightarrow \text{H}_2\text{(g)} + \text{CO(g)} \]

\[ \text{H}_2\text{O(g)} + \text{CO(g)} \rightarrow \text{H}_2\text{(g)} + \text{CO}_2\text{(g)} \]
Fate of Organic Carbon

Gas (CO, CH₄, CO₂)

Organic carbon

Tars

Bed Solids
# Carbon Conversion

Approximate fate of organic carbon

<table>
<thead>
<tr>
<th>Location</th>
<th>Gases</th>
<th>Tars</th>
<th>Bed Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utah</td>
<td>65-85%</td>
<td>10-30%</td>
<td>2-8%</td>
</tr>
<tr>
<td>Big Island</td>
<td>58-80%</td>
<td>4-20%</td>
<td>10-25%</td>
</tr>
<tr>
<td>PDU</td>
<td>95-99%</td>
<td>0%</td>
<td>0.5-2%</td>
</tr>
</tbody>
</table>
Tars – Variation in Results

- **Residence time**
  - Utah: 2 + 8 seconds in bed + freeboard
  - Big Island: 10 + 7 seconds in bed + freeboard

- **Temperature**
  - Utah freeboard exit temperature: 420°C (790°F)
  - Big Island freeboard exit temp: 590°C (1095°F)

- **Measurement technique**
  - Utah: Cold trap to –20°C with dichloromethane
  - Big Island: Difference from system balance plus cold trap measurements
  - MTCI PDU: No specific effort to trap tars
Char Conversion Studies

- Determine factors that impact char carbon conversion (residual bed carbon)
  - Temperature
  - Presence of product species (H₂ and CO)

- Consider difference between small scale PDU studies and full-scale systems
  - Small-scale systems achieve >95% conversion to gases (+ tars)
  - Full scale system achieving only 70-85% carbon conversion
Bed Carbon versus Time

Pure steam. No liquor feed.

Organic Carbon Content (wt%)

Time (hours)

Reaction order = 0.0

Reaction order = 0.5

Reaction order = 1.0
Lab-Scale Char Conversion Studies

Influence of hydrogen on gasification rate

![Graph showing the influence of hydrogen on gasification rate. The x-axis represents \( H_2 \) partial pressure in bar, ranging from 0.0 to 1.4. The y-axis represents the maximum rate in \( \times 10^4 \) s\(^{-1}\), ranging from 0 to 20. Two curves are shown: one for 2% \( H_2 \) and another for 4% \( H_2 \). The curves indicate a decrease in the maximum rate with increasing \( H_2 \) partial pressure.](image-url)
Lab-Scale Char Conversion Studies

Influence of carbon monoxide on gasification rate

![Graph showing the influence of carbon monoxide on gasification rate. The graph plots the maximum rate (in x10^4, s^-1) against the CO partial pressure (in bar). Two curves are shown: one for 2% CO and another for 4% CO. The maximum rate decreases as the CO partial pressure increases.]
Bed Carbon versus Time

Pure steam. No liquor feed.
Bed Carbon versus Time

Addition of 25% H₂

- Pure Steam
- Steam with 25% H₂

Ave. 0.16%C/hr
Ave. 0.75%C/hr

Carbon Content (wt%)

Time (hours)
Bed Carbon versus Time

Addition of CO

Carbon Content (wt%) vs. Time (hours)

- Pure Steam
- With CO addition

Ave. 0.48 %C/hr for 6.4% CO
Ave. 0.75 %C/hr for 2.6% CO
Ave. 0.52 %C/hr for 6.4% CO
Ave. 0.56 %C/hr for 2.6% CO
## Reactor Comparison

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PDU</th>
<th>Utah</th>
<th>Full-scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed height, ft</td>
<td>4</td>
<td>5</td>
<td>33</td>
</tr>
<tr>
<td>Bed area, ft²</td>
<td>2.3</td>
<td>0.54</td>
<td>104</td>
</tr>
<tr>
<td>Bed mass, lb</td>
<td>725</td>
<td>200</td>
<td>233,000</td>
</tr>
<tr>
<td>Steam feed, lb/hr</td>
<td>223</td>
<td>42</td>
<td>12,250</td>
</tr>
<tr>
<td>BLS feed, lb/hr</td>
<td>14</td>
<td>12</td>
<td>6,400</td>
</tr>
<tr>
<td>Steam/fuel ratio</td>
<td>16</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Feed/bed area</td>
<td>6</td>
<td>22</td>
<td>61</td>
</tr>
</tbody>
</table>

- **17 psia**
- **44 psia**
Steam and H₂

- Steam only with no liquor injection
- Assumes 0.5 wt% of bed (as C) converted per hour
- Uses bed mass, steam flows from real systems
- Assumes water-gas shift always at equilibrium
- Assumes bed solids are well-mixed
Full versus PDU Scale

Rates and associated conversions

**Full/PDU ratios at top of bed:**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$P_{H_2}$:</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>$P_{CO}$:</td>
<td>53.0</td>
<td></td>
</tr>
<tr>
<td>Rate (van Heiningen):</td>
<td>0.706</td>
<td></td>
</tr>
<tr>
<td>Rate (Whitty 1):</td>
<td>0.600</td>
<td></td>
</tr>
<tr>
<td>Rate (Whitty 2):</td>
<td>0.021</td>
<td></td>
</tr>
</tbody>
</table>

- Decrease from 97% to 75% carbon conversion requires that the rate becomes 20% as fast (for reaction order = 0.5)

**Van Heiningen**

\[
Rate = \frac{3 \times 10^8 [CO] [H_2O]}{[H_2O]^{1.42} [H_2]} e^{-25.200 / T}
\]

**Whitty 1**

\[
Rate = 10^{-4} e^{28,000 \left( \frac{1}{923} \right) \left( \frac{1}{T} \right) - \frac{9.01}{1 + \frac{p_{H_2}}{0.449 p_{H_2O}} + 7.09 p_{CO}}}
\]

**Whitty 2**

\[
Rate \left( \times 10^4 \right) = 3.312 + 1.157 p_{H_2O} + 0.07119 p_{CO}^2 - 2.943 p_{H_2} - 3.869 p_{CO} + \frac{0.6595}{p_{CO}}
\]
BL Char vs. Bed Solids

Black liquor char
BET Surface area: 5-100 m²/g

Reformer bed solids
BET Surface area: < 0.5 m²/g
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- Higher concentrations of product gases in large fluidized bed reformer contributes to decreased conversion relative to small system
  - Higher concentrations of H2 and CO
  - Higher pressure of large system
- Surface area of particles in large reformer may also contribute to lower conversion
  - Pressure at black liquor injection point roughly 3 times higher
  - May impact coating of black liquor
- Fundamental rate information for bed solids would be useful
Acknowledgements

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