In situ Causticizing for Black Liquor Gasifiers
DOE project #DE-FC26-02NT41492
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Black Liquor Colloqium
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Both the high and low temperature BLG technologies produce higher causticizing load than a recovery boiler.

**Entrained-flow gasifier**
- 950°C, O₂- or air-blown,
- ~5 sec residence time

**Fluidized bed gasifier**
- ~600°C, steam driven,
- ~50 hrs residence time
Background/Incentives

- BLG offers significant incentives for adoption but the causticizing load increase must be addressed.
- Titanates, borates and manganates (et.al.) have been shown to preferentially bind with sodium and potassium during gasification to form a salt, and allow carbonate to be released as CO/CO₂.
- Release hydroxide upon hydrolysis and return to original form.
- Chemistries have been thoroughly proven for Na₂CO₃. Need to test with black liquor.
- Partial causticization would mitigate the increase, while 80+% causticizing would eliminate the lime cycle.
- A 1000 dtpd pulp mill uses 90,000 bbls/yr #6 fuel oil. (= $4.5 Million/yr at current prices)
- Total US kraft pulp production is 156,700 ton/day. 100% adoption = 14 Million bbls/yr fuel oil saved (= $700 Million/yr in fuel saved)
**Project Objectives/Deliverables**

(IPST and Jacobs Engineering)

- Phase 1: Gasify mixtures of black liquor and causticizing agents at realistic BLG conditions and determine which chemistries hold promise (previous studies have focused on sodium carbonate only). Utilize equilibrium modeling and experimentation. (IPST) Phase 1 report.

- Phase 2: For the successful methods verify caustic recovery, characterize NPE's, and identify feasible NPE purge. (IPST) Phase 2 report >> Dec, ‘05

- Phase 3: For methods passing Phase 2 (if any), determine the best ways of integrating them into the mill, and perform economic evaluations and compare with conventional technology. (Jacobs + IPST) Final report.
Chemistry of Direct Causticizing using Titanates

- Sodium is bound up by titanates within the gasifier:

\[
\begin{align*}
Na_2CO_3 + 3 \text{TiO}_2 (s) & \leftrightarrow Na_2O \cdot 3\text{TiO}_2 (s) + \text{CO}_2 (g) \\
7Na_2CO_3 + 5(\text{Na}_2O \cdot 3\text{TiO}_2)(s) & \leftrightarrow 3(4\text{Na}_2O \cdot 5\text{TiO}_2)(s) + 7\text{CO}_2(g) \\
\text{Na}_2O \cdot 6\text{TiO}_2(s) + \text{Na}_2CO_3(s) & \leftrightarrow 2(\text{Na}_2O \cdot 3\text{TiO}_2)(s) + \text{CO}_2(g) \\
\text{[Abbreviated NT3, N4T5, NT6]} \\
\end{align*}
\]

- The caustic is later recovered by hydrolysis:

\[
\begin{align*}
3(4\text{Na}_2O \cdot 5\text{TiO}_2)(s) + 7\text{H}_2\text{O} & \leftrightarrow 14\text{NaOH}(aq) + 5(\text{Na}_2O \cdot 3\text{TiO}_2)(s) \\
2(\text{Na}_2O \cdot 3\text{TiO}_2) (s) + \text{H}_2\text{O} & \leftrightarrow 2\text{NaOH} (aq) + \text{Na}_2O \cdot 6\text{TiO}_2 (s) \\
\approx 0.65 \\
\end{align*}
\]
Chemistry of Direct Causticizing using Manganates

- Sodium is bound up by manganate within the gasifier:
  \[ \text{Na}_2\text{CO}_3 + \text{Mn}_3\text{O}_4 \rightleftharpoons 2\text{NaMnO}_2 + \text{MnO} + \text{CO}_2 \]

- The caustic is later recovered by hydrolysis:
  \[ 2\text{NaMnO}_2 + \text{MnO} + \text{H}_2\text{O} \rightleftharpoons 2\text{NaOH(aq)} + \text{Mn}_3\text{O}_4 \text{(s)} \]

- Sulfur must be in gas phase (i.e. LTBLG only) since manganate will oxidize sulfide in the solid phase
  \[ \text{Na}_2\text{S} + 4\text{Mn}_3\text{O}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + 12\text{MnO} \]
Chemistry of Borate Autocausticization

- Sodium is bound up by borate within the gasifier:
  \[2\text{NaBO}_2 + \text{Na}_2\text{CO}_3 \leftrightarrow \text{Na}_4\text{B}_2\text{O}_7 + \text{CO}_2\ [\text{Jansen}]
  \[\text{NaBO}_2 + \text{Na}_2\text{CO}_3 \leftrightarrow \text{Na}_3\text{BO}_3 + \text{CO}_2\ [\text{Tran, et.al.}]

- The caustic is later recovered by hydrolysis:
  \[\text{Na}_3\text{BO}_3 + \text{H}_2\text{O} \leftrightarrow 2\text{NaOH(aq)} + \text{NaBO}_2 \text{ (aq)}\]

- Borate is soluble and circulates with the pulping liquor
Direct Causticizing Process Overview

Air, O2, steam → Gasifier → Raw Syn Gas

Black liquor → Mixing

Leaching

Char

Leached solids → Dregs Purge(?)

Dregs Purge(?)

White liquor for pulping

Raw White Liquor
Tasks 1.x.1, Equilibrium Modeling.

Example of Equilibrium Speciation Predictions Using FactSage5.1. For Steam BLG with borate, the autocausticization reactions should take place above 925°C.

Smelt Composition from Steam BLG w/Borate
(100g H2O vapor + 100g DBLS, Na/B=2.4)

- Na2S
- Na4B2O5
- NaBO2
- KBO2
- Na2CO3
- KCl
- Total

Typical steam reforming BLG temp = 600

Celcius

600 650 700 750 800 850 900 950 1000
**Tasks 1.x.1, Equilibrium Modeling.**

**Summary of Results (predictions)**

*FactSage 5.1*

<table>
<thead>
<tr>
<th></th>
<th>Steam reforming at 600°C</th>
<th>O2-blown at 950°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanates</td>
<td>No (but predicted to work above 650°C)</td>
<td>Works at all pressures</td>
</tr>
<tr>
<td>Borates</td>
<td>No (need 925°C minimum)</td>
<td>Works below 2.5 bar and above 910°C</td>
</tr>
<tr>
<td>Manganates</td>
<td>No thermodynamic data for NaMnO2</td>
<td>No thermodynamic data for NaMnO2</td>
</tr>
</tbody>
</table>
Causticizing agents were then mixed with black liquor and gasified at realistic conditions.

<table>
<thead>
<tr>
<th></th>
<th>Low Temp</th>
<th>High Temp Pressurized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>LEFR (SB)</td>
<td>PEFR</td>
</tr>
<tr>
<td></td>
<td>(semi-batch)</td>
<td></td>
</tr>
<tr>
<td>Temp, C</td>
<td>600</td>
<td>950</td>
</tr>
<tr>
<td>Pressure, bar</td>
<td>1</td>
<td>5 and 15</td>
</tr>
<tr>
<td>Feed gas</td>
<td>50% H₂O in N₂ with and w/o CO₂</td>
<td>CO₂ in N₂ with and w/o 5% H₂O</td>
</tr>
<tr>
<td>Residence time</td>
<td>50 hours</td>
<td>5 seconds</td>
</tr>
</tbody>
</table>
Experimental Results

Gasifying doped black liquor for causticizing at realistic conditions
Task 1.1.2 Titanate Results from PEFR at 950C, 5 seconds, in CO2, 100% causticizing

BLG w/Titanate for 100% Causticizing:
CO3 conversion in PEFR at 950C

Equilibrium (FactSage) prediction of CO2 levels for O2-blown BLG above 5 bar
Equilibrium (FactSage) prediction of CO2 levels for air-blown BLG, 1-5 bar
**Task 1.1.3 Titanate Results from LEFR(SB) at 600°C, 50 hours, 50% H2O, 100% causticizing**

**Equilibrium (FactSage) prediction of CO2 levels for steam BLG (reforming) at 1.0 bar and above.**

BLG w/Titanate for 100% Causticizing:
CO3 conversion at 600°C in steam + CO2
Task 1.3.1 Borate Results from PEFR at 950C, 5 seconds, in CO2, 20% causticizing

BLG w/Borate for 20% Causticizing: CO3 conversion in PEFR at 950C

Equilibrium (FactSage) prediction of CO2 levels in product gas over range of reasonable O2/Fuel ratios for air-blown BLG at 1.67 bar.
**Task 1.3.1 Borate Results from LEFR(SB) at 600°C, 50 hours, 50% H2O, 20% causticizing**

BLG w/Borate for 20% Causticizing:
CO3 conversion at 600°C in steam + CO2

Equilibrium (FactSage) prediction of CO2 levels for steam BLG (reforming) at 1.0 bar and above.
Manganate Results from both cases

<table>
<thead>
<tr>
<th>Gas Conditions</th>
<th>Stoichiometric maximum conversion based on Mn added</th>
<th># of runs</th>
<th>Average Experimental causticizing conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Temp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% &amp; 10% CO2 in N2</td>
<td>100%</td>
<td>4</td>
<td>0%</td>
</tr>
<tr>
<td>at 950C, 5 bar, 5 sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Temp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% H2O + 10%CO2 in N2</td>
<td>100%</td>
<td>5</td>
<td>100%</td>
</tr>
<tr>
<td>at 600C, 50 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Task 2. Leaching and Hydroxide Recovery

Typical values for hydroxide recovered in a single titration of char as % of stoichiometric carbonate causticized (i.e. OH closure).

Ti at 950°C, doped for 100% conv:

- 54% average recovery for 10 runs (range 32% - 88%)

B at 950°C, doped for 20% conv:

- 18% average recovery for 5 runs (range 16% - 20%)

Mn at 600°C, doped for 100% conv:

- 39% average recovery for 5 runs (range 31% - 44%)
Task 2. Leaching and Hydroxide Recovery

Manganate leached solids are not suitable for recycle after two 90-minute leachings at 80°C. It does not return to the starting material. Accounts for missing OH⁻ from leaching

<table>
<thead>
<tr>
<th>Element</th>
<th>% of element in char found in 2nd leached solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>98%</td>
</tr>
<tr>
<td>Na</td>
<td>29%</td>
</tr>
<tr>
<td>K</td>
<td>94%</td>
</tr>
</tbody>
</table>
Task 2. Leaching and Hydroxide Recovery

Staged countercurrent leaching may be required for Ti

<table>
<thead>
<tr>
<th>Experiment</th>
<th>D02/24/04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Causticizing CO3 conversion</td>
<td>88%</td>
</tr>
<tr>
<td>OH recovered on 1st leaching</td>
<td>86.1%</td>
</tr>
<tr>
<td>OH recovered on 2nd leaching</td>
<td>8.9%</td>
</tr>
<tr>
<td>OH recovered on 3rd leaching</td>
<td>3.6%</td>
</tr>
<tr>
<td>Total of 3 stages</td>
<td>98.6% (of the OH expected)</td>
</tr>
</tbody>
</table>
Fate of NPE’s after Leaching (example Ti exp’t)

Predominantly split to solid phase
Ca, Cu, Fe, *Mg, Mn, Ti

Predominantly split to leachate (liquid) phase
*B, Cr, S, V

Substantially divided
Al (25% to solid)
K (15% to solid as K₂O·3TiO₂)
*Si (20% to solid)
(*achieved very poor mass balance closure)

- Characterize solid phase mixture
- Look for viable ways to remove
SEM-EDS of Leached Ti solids (expt P040224A)

First pass at major species. Will do additional runs for NPE’s
Are some particles enriched with NPE’s??
2nd SEM-EDS of Leached Ti solids (expt P040224A)

- 0.7% of char sulfur
- K as K₂O·3TiO₂
2\textsuperscript{nd} SEM-EDS of Leached Ti solids (expt D071904)
Implications for Dregs Removal from Ti solids

- Al and Si could be forming discrete particles
- Other NPE’s (Fe, Zn, Sn) appear to be finely dispersed among leached solids.
- Chemical separation will be most viable
- FactSage model of NPE leaching indicates HCl is the only viable choice. BaSO4 is not dissolved by other acids.
- Model predicts that 0.15 kg HCl/kg leached solids will dissolve all species but BaSO4. Need 0.4 kg/kg for BaSO4
- NPE leaching experiments now under way.
## Summary of Experimental Results for Causticizing and Leaching for BLG

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Causticizing Conditions</th>
<th>Leaching Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Titanates for 100% conv</strong></td>
<td><strong>600C, 50hrs Steam reforming</strong></td>
<td>No; CO2 is too high in product gas</td>
</tr>
<tr>
<td><strong>Borates for 20% conv</strong></td>
<td><strong>600C, 50hrs Steam reforming</strong></td>
<td>No; CO2 is too high in product gas</td>
</tr>
<tr>
<td><strong>Manganates for 100% conv</strong></td>
<td><strong>950C, 5sec using CO2 and H2O</strong></td>
<td>No; achieved 100% caust’n but fails during leaching.</td>
</tr>
</tbody>
</table>
Goals for 2006

- Perform HCl titrations on Ti leached solids to gauge NPE removal efficiency.
- Publish results to date in open literature
- Phase 3. Mill integration study, including: design basis, material & energy balances, process scope descriptions, flow diagrams, major equipment, +/-25% capital estimate.
- Phase 3. Economic evaluation of in situ caust’n and comparison with BLG w/conventional lime cycle.
- Test borates at higher conversion for HTBLG (if time allows)
Questions?