In Situ Causticizing for Black Liquor Gasification

Phase 2 Topical Report
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BACKGROUND

Black liquor gasification offers a number of attractive incentives to replace Tomlinson boilers but it also leads to an increase in the causticizing load. Reasons for this have been described in previous reports (FY04 ERC, et.al.). The chemistries have also been covered but will be reviewed here briefly.

Direct causticization using titanates → In this system sodium trititanate is added to the liquor to bind up the sodium as pentatitanate and allow the carbon to be released as CO or CO₂. The main reactions involved are considered to be:

[Abbreviated NT3, NT4T5, NT6]

Reaction (1) is how make-up titanate is introduced to the system. Reactions (2) and (3) are repeated cyclically in the gasifier. The sodium pentatitanate formed in the gasifier is leached with water, forming solid sodium trititanate and sodium hydroxide (white liquor) via reaction (4):

Recent work at IPST has shown that NT3 can be further leached to NT6 via reaction (5), which has additional causticizing potential than NT3 via reaction (3). The leached NT3 and NT6 solids are separated from the caustic (white liquor) and recycled to the gasifier/reactor where reactions (2) and (3) repeat. For HTBLG the remaining solution is sulfur-lean white liquor since some Na₂S is present. For LTBLG the remaining solution is non-sulfur white liquor since virtually no Na₂S is present in the solid phase. The H₂S is separated from the gasification gas and can be used to produce an aqueous sulfur-rich stream. Consequently, white liquors of varying sulfidity can be obtained as shown in Figure 1 below.

Figure 1. Black liquor gasification process with titanate direct causticization

Direct causticization using manganates → In this system Mn_3O_4 is added to bind up the sodium and allow carbon to be released as CO or CO_2 . For gasification, the process schematic would be analogous to that shown in Figure 1. Eames and Empie (2001) have determined the causticization reaction to be:

Over 98% conversion was obtained in under 24 hours for both the solid (650-850°C), and liquid (850-950°C) phase regimes chosen for this work. Mn_3O_4 is recovered and hydroxide is formed upon hydrolysis:

Autocausticization using borates → In this process the sodium would be bound up by borate in the gasifier as follows:

The caustic is recovered upon hydrolysis:

Note here that autocausticization differs from direct causticization in that there is no precipitation of the agent upon hydrolysis; it circulates through the pulping cycle. The dregs would be the only precipitates, resulting in a convenient removal mechanism. The drawback is that the circulating borates are essentially dead load with respect to the pulping operation, somewhat limiting the throughput capacity. The use of borates for partial autocausticizing (as incremental capacity) in kraft mills is well documented, and mill trials have been successful.

RESULTS

Experimental results of the causticizing reactions with black liquor are presented here. Results of the modeling work were presented in detail in the Phase 1 report. They are included in Table 2 for comparison but will not be discussed in detail.

The causticizing agents were added to black liquor in the ratios shown in Table 1, mixed, and then spray-dried. The mixture ratios (doping levels) reflect amount calculated from the stoichiometry above to achieve specified conversions shown in the table. The solids were sieved to 63-90 microns for use in the entrained flow reactors. The firing conditions are shown in Table 2. Pictures and descriptions of the reactors can be found in the Phase 1 annual report.

Following gasification, the solids (char) was collected and analyzed by coulometric titration (for carbonate and total carbon), and by inductively coupled plasma emission spectroscopy (ICP) for a wide array of metals.

Table 1 Causticizing Agent Additions to Black Liquor			
	Compound	g/Kg DBLS	Metal/Na mass ratio
Titanate (100% conv)	$\text{Na}_2\text{O} \cdot 3\text{TiO}_2$	960	1.34
Borate (100% conversion)	$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$	264	0.11
Borate (20% conversion)	$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$	59	0.03
Manganate (100% conv)	Mn_3O_4	970	3.62
Manganate (40% conv)	Mn_3O_4	388	1.45

Table 2 Gasification Conditions		
	Steam Reforming	High Temp Entrained Flow
Reactor	LEFR (as semi-batch)	PEFR
Temp, C	600	950
Pressure, Bar	1	5 and 15
Feed Gas	50% H_2O in N_2 , with and w/o 5% and 10% CO_2	5% and 10% CO_2 in N_2 , with and w/o 3% H_2O
Residence time	50 hours	5 seconds

A number of reference runs were made with undoped liquor for comparison. The causticizing conversion level was calculated by comparing the carbonate in the doped char to the carbonate in undoped char under similar gasification conditions and allowing for the dilution factor of the agent and the possibility that the agent affects the sulfur split between the gas and char.

The results for the titanates at high temperature are shown in Figure 2. As expected from the stoichiometry and L'Chatlier's principal, CO_2 inhibits all of the desired reactions. In order to utilize the results, we estimate the CO_2 concentration in the syn gas leaving a full scale gasifier over a range of conditions (Figure 3). These results are then superimposed on the experimentally derived conversion levels to estimate if the process in question would work in the real gasifier. The ranges of CO_2 concentration are shown in Figure 2 to estimate the conditions for which titanates would be effective at high temperature. We estimate that from 1 to 5 bars total reactor pressure, the CO_2 levels during BLG would be low enough to allow titanate direct causticizing (Task 1.1.2) to work to high conversion levels. This would correspond to a low pressure air or O_2 -blown booster gasifier such as the one at Weyerhaeuser, New Bern. However, at 20 bars the conversion drops to zero. In order to be effective at 20 bars the process would have to be modified to lower the CO_2 partial pressure in the product gas.

Figure 2. Titanate direct causticizing conversion at high temperature entrained flow as a function of CO₂ partial pressure.

Figure 3. Equilibrium calculations of CO₂ levels from black liquor gasification over a range of oxygen to fuel ratios. Realistic values are around 0.3

The results for titanate direct causticizing during steam reforming (task 1.1.3) are shown in Figure 4. With no CO₂ present, high conversions were achieved. However when 10% CO₂ was added, the conversion dropped to zero. Thus the titanate chemistry will not work for steam reforming in its current configuration. FactSage modeling suggests however that at 650C the reaction would reach high conversion. Given that titanates would also raise the smelting temperature of the char, the steam reformer temperature might well be raised to 650C without problems with bed sintering. For the present, no further work will be done with titanates for steam reforming.

Figure 4. Titanate direct causticizing during steam reforming at 1 bar.

The experimental results for the borates (task 1.3.1) are shown in Figures 5 and 6 for partial (20%) conversion. This would be appropriate for either a booster or full scale gasifier when the existing lime kiln will be used to handle the bulk of the causticizing load. At high temperature and low pressures, the chemistry reaches high conversion due to low CO₂ partial pressure. The borates will be tested for complete causticization at 950C and low pressure as well. However, as before, at 20 bars total pressure, the CO₂ would be sufficiently high to inhibit the conversion of this reaction as well.

The steam reforming case for the borates at 20% conversion is shown in Figure 6. Again, the CO₂ levels would be too high in the real gasifier to achieve any conversion. FactSage modeling suggests that the temperature would have to reach 925C before the causticizing reactions move forward in this case. Borates for steam reforming will not be considered further.

Figure 5. Borate autocausticization at high temperature

Figure 6. Borate autocausticization during steam reforming

The experimental results for gasification of manganate-doped black liquor are shown in Tables 3 and 4. For the high temperature case, zero conversion was achieved. Manganates for high temperature gasification will not be considered further.

Table 3. Manganate conversion during high temperature gasification

Gas Conditions	Stoichiometric maximum conversion based on Mn added	Fixed (i.e. char) carbon in smelt	Experimental causticizing conversion
5%CO ₂	100%	0.6%	0%
10%CO ₂	100%	0.5%	0%
5%CO ₂	40%	0.1%	0%
10%CO ₂	40%	1.7%	0%

For the steam reforming case (task 1.2.2), manganates gave complete conversion in almost all cases, with and without CO₂ present. Experiments with manganates will continue into the non-process element removal stage of the project.

Table 4. Manganate conversion during steam reforming

Gas Conditions	Fixed (i.e. char) carbon in smelt	Experimental causticizing conversion
50%H ₂ O	0.00%	100%
50%H ₂ O	0.05%	100%
50%H ₂ O	0.01%	100%
50%H ₂ O+10%CO ₂	0.03%	95%
50%H ₂ O+10%CO ₂	0.02%	100%

The results for all of the cases are summarized in Table 5 below. Three of the six combinations will be retained for non-process element removal, and caustic recovery experiments.

Table 5 Summary of Conclusions for In Situ Causticizing			
	LTBLG 600C, steam	HTBLG, air 950C, 1.67 bar	HTBLG, O2 950C, 5-15 bar
Titanate, complete causticizing, experimental results	No	Yes	No
Ti: FactSage Equil model	Yes if >650C	Yes	Yes
Manganate, complete causticizing, experimental results	Yes	No	No
Mn: FactSage Equil model	N/A	N/A	N/A
Borate, 20% causticizing, experimental results	No	Yes	No
B: FactSage Equil model	No	Yes	Yes
Borate, complete causticizing, experimental results	pending	pending	pending
B: FactSage Equil model	No	Yes	Yes

Task 2. Once the causticization conversion has been confirmed, the chars must be hydrolyzed (leached) to recover the hydroxide for pulping and return the agent back to a form where it can be returned to the gasifier and again causticize more carbonate. The overall process is shown in Figure 7 below. The amount of hydroxide formed during leaching must be compared to the carbonate consumed to verify material balance closure. Also the leached solids and leachate must be characterized to determine the fate of the non-process elements.

Figure 7. Hydroxide recovery and non-process element removal schematic

Chars from the successful causticizing processes above were hydrolyzed (leached) and titrated to measure the hydroxide recovered for comparison to the carbonate causticized. Details of the procedures and all raw data will be presented in the final report. The results are summarized here for brevity:

- For the HT titanate char hydroxide recovery varied over a wide range. There were concerns that some of the pores may have been closed due to sintering, thus isolating the N4T5 from the water. Ultimately, a 3-stage leaching has proven successful thus far; although more work will be done to confirm.
- For the HT borate char at 20% doping level, hydroxide recovery was high. Since borates are soluble in white liquor and circulate through the pulping cycle, the only precipitates are the NPE's
- Hydroxide recovery from leaching magnate chars was consistently 40% of what was expected. Recall that complete causticizing was obtained. We are characterizing the manganate leached solids to try and resolve the discrepancy.

The leachate and leached solids from both the manganate and titanate processes were analyzed by ICP emission spectroscopy for an array of metal species. For most species the material balance closure was good. Some species were quite dilute; near the detection level. Key findings were:

- Most of the B, Cr, Si, and V split to the leachate phase
- The remaining non-process elements favor the solid phase. SEM-EDS analysis is being used to determine if the NPE's are distributed uniformly in the solid particles, or if the NPE are concentrated within a small fraction of the solids.

The results of the SEM-EDS analysis will determine which removal processes can be employed. The chemical processes will be tested in our labs. For the physical processes (if appropriate), the vendors of such processing equipment will given the solids characterization and removal criteria, and asked to provide estimates of suitability. Processes identified to date include:

- Ion exchange
- $\text{Mg}(\text{OH})_2$ complexing
- Acid titration
- Laminar air classification (size/density difference)
- Density-based separation for slurries
  - APIC jig → air pulses produce bed with density gradient
  - Knelson/Falcon concentrators → centrifugal

FUTURE WORK

Plans for year 3 include:

- Further characterize the leached solids to determine how non-process elements are distributed with respect to phases. This will narrow the removal options to test
- Resolve the hydroxide material balance for the manganate case. If hydroxide cannot be balanced with carbonate, then must abandon this option.
- Test the chemical processes for non-process element removal in the lab.
- Test borates at 100% conversion for HTBLG.
- Conduct the mill integration study.
- Conduct the economic evaluation.

REFERENCES

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