

Direct Causticizing for Black Liquor Gasification in a Circulating Fluidized Bed

Final Project Report
DE-FG36-06GO16042

Project Period: September 30, 2006 - August 31, 2009

Scott Sinuefield, 404-894-5700, scott.sinuefield@ipst.gatech.edu

Xiaoyan Zeng

Alan W. Ball

Institute of Paper Science and Technology at GA Tech
500 Tenth St. NW
Atlanta, GA 30332-0620

DOCUMENT AVAILABILITY:

Reports are available free via the U.S. Department of Energy (DOE) Information Bridge:

Web Site <http://www.osti.gov/bridge>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and Informational Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Tel: (865) 576-8401
Fax: (865) 576-5728
E-mail: reports@osti.gov
Web Site: <http://www.osti.gov/contact.html>

Acknowledgment: This report is based upon work supported by the U. S. Department of Energy under Award # DE-FG36-06GO16042, which cost-sharing funds coming for Weyerhaeuser Co., Georgia Pacific Corp., and the State of Georgia.

Disclaimer: Any findings, opinions, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the Department of Energy.

Proprietary Data Notice: If there is any patentable material or protected data in the report, the recipient, consistent with the data protection provisions of the award, must mark the appropriate block in Section K of the DOE F 241.3, clearly specify it here, and identify them on appropriate pages of the report. Other than patentable material or protected data, reports must not contain any proprietary data (limited rights data), classified information, information subject to export control classification, or other information not subject to release. Protected data is specific technical data, first produced in the performance of the award, which is protected from public release for a period of time by the terms of the award agreement. Reports delivered without such notice may be deemed to have been furnished with unlimited rights, and the Government assumes no liability for the disclosure, reproduction or use of such reports.

Table of Contents

Executive Summary	5
Introduction	6
Background	7
Experimental	13
Results	
Experimental results	14
Material and Energy Balance	17
Economics	21
Conclusions- proposed process is viable	22
Recommendations- build pilot	22
References	23
Appendix A. Experimental Details	25
Appendix B. Experimental Data	30
Appendix C. Process Simulation Details	35
Appendix D. Economic Assessment	38

Lists of Figures, Tables and Appendices

Figure 1. Black liquor gasification process with titanate direct causticization	8
Figure 2. Experimental results of gasifying black liquor with titanate...	9
Figure 3. FactSage equilibrium prediction of CO ₂ concentrations...	10
Figure 4. Experimental results of gasifying black liquor with titanate...	11
Figure 5. Hydroxide recovered from char formed by BLG with titanate	15
Figure 6. Proposed process for pressurized BLG with titanate direct causticizing.	18
Table 1. High Yield Pulpig Processes	6
Table 2. Black liquor elemental composition used in this work	13
Table 3. Results of titration of char produced from BLG of Ti-doped black liquor	14
Table 4. Leaching of twice-used titanate	16
Table 5. Key flow rates for Figure 6	19
Table 6. Gas composition leaving gasifier (stream 6) in Figure 6	20
Table 7. Key process data from Figure 6	20
Table 8. NPV and IRR as a Function of Fuel Cost	21
Figure A1. IPST's Pressurized Entrained Flow Reactor	25
Figure A2. Another view of the PEFR.	26
Figure A3. Diagram of the PEFR showing pressure vessel	27
Figure A4. The leaching apparatus	29
Table B1. Experimental data	31
Table B2. Leaching data	33
Table C1. Model black liquor composition and properties	35
Table D1. Reference Mill Basis Data	38
Table D2. HTBLG Chemical Recovery Data	39

Table D3. Titanate ChemCad Balance Basis and Assumptions	40
Table D4. Capital Estimates Assumptions	41
Table D5. Summary of Total Installed Cost of [9]	42
Table D6. Summary of Total Installed Cost of Proposed Process	43
Table D7. Chemicals, Fuel Oil, and Electricity Costs (2009)	43
Table D8. Annual Chemicals, Fuel Oil, and Electricity Usages [9]	44
Table D9. Annualized O&M Costs	44
Table D10. Economic Assumptions	45
Table D11. Annual Costs for the Proposed Process	46
Table D12. NPV and IRR as a Function of Fuel Cost	45

Executive Summary

Gasification of black liquor (BLG) has distinct advantages over direct combustion in Tomlinson recovery boilers. In this project we seek to resolve causticizing issues in order to make pressurized BLG even more efficient and cost-effective. One advantage of BLG is that the inherent partial separation of sulfur and sodium during gasification lends itself to the use of proven high yield variants to conventional kraft pulping which require just such a separation. Processes such as polysulfide, split sulfidity, ASAQ, and MSSAQ can increase pulp yield from 1% to 10% over conventional kraft but require varying degrees of sulfur/sodium separation, which requires additional [and costly] processing in a conventional Tomlinson recovery process. However during gasification, the sulfur is partitioned between the gas and smelt phases, while the sodium all leaves in the smelt; thus creating the opportunity to produce sulfur-rich and sulfur-lean white liquors for specialty pulping processes.

A second major incentive of BLG is the production of a combustible product gas, rich in H_2 and CO. This product gas (a.k.a. “syngas”) can be used in gas turbines for combined cycle power generation (which is twice as efficient as the steam cycle alone), or it can be used as a precursor to form liquid fuels, such as dimethyl ether or Fischer Tropsch diesel.

There is drawback to BLG, which has the potential to become a third major incentive if this work is successful. The causticizing load is greater for gasification of black liquor than for combustion in a Tomlinson boiler. So implementing BLG in an existing mill would require costly increases to the causticizing capacity. In situ causticizing [within the gasifier] would handle the entire causticizing load and therefore eliminate the lime cycle entirely. Previous work by the author and others has shown that titanate direct causticizing (i.e. in situ) works quite well for high-temperature BLG (950°C), but was limited to pressures below about 5 bar. It is desirable however to operate BLG at 20-30 bar for efficiency reasons related to either firing the syngas in a turbine, or catalytically forming liquid fuels. This work focused on achieving high direct causticizing yields at 20 bars pressure.

The titanate direct causticizing reactions are inhibited by CO_2 . Previous work has shown that the partial pressure of CO_2 should be kept below about 0.5 bar in order for the process to work. This translates to a total reactor pressure limit of about 5 bar for air-blown BLG, and only 2 bar for O_2 -blown BLG. In this work a process was developed in which the CO_2 partial pressure could be manipulated to a level under 0.5 bar with the total system pressure at 10 bar during O_2 -blown BLG. This fell short of our 20 bar goal but still represents a substantial increase in the pressure limit. A material and energy balance was performed, as well as first-pass economics based on capital and utilities costs. Compared to a reference case of using BLG with a conventional lime cycle [Larson, 2003], the IRR and NPV were estimated for further replacing the lime kiln with direct causticizing. The economics are strongly dependent on the price of lime kiln fuel. At \$6/mmBTU the lime cycle is the clear choice. At \$8/mmBTU the NPV is \$10M with IRR of 17%. At \$12/mmBTU the NPV is \$45M with IRR of 36%.

To further increase the total allowable pressure, the CO_2 could be further decreased by further decreasing the temperature. Testing should be done at 750C. Also a small pilot should be built.

Introduction

Gasification of black liquor (BLG) has distinct advantages over direct combustion in Tomlinson recovery boilers [1, 8, 21]. In this project we address causticizing issues which, if resolved, will make BLG even more efficient and cost-effective. First we will discuss the major incentives of BLG over Tomlinson combustion. The inherent [partial] separation of sulfur and sodium during gasification lends itself to the use of proven high yield variants to conventional kraft pulping which require just such a separation. Processes such as polysulfide, split sulfidity, ASAQ, and MSSAQ can increase pulp yield from 1% to 10% over conventional kraft but require varying degrees of sulfur/sodium separation, which requires additional [and costly] processing in a conventional Tomlinson recovery process. However during gasification, the sulfur is partitioned between the gas and smelt phases, while the sodium all leaves in the smelt; thus creating the opportunity to produce sulfur-rich and sulfur-lean white liquors for specialty pulping processes. Some promising possibilities are shown in Table 1.

Table 1. Some High Yield Pulping processes		
Process	Yield increase	% of sulfur needed in gas phase (i.e. degree of sulfur/sodium separation)
Straight Kraft	-	0%
Kraft w/Split Sulfidity	0.5-1%	10%
Kraft w/Polysulfide & Anthroquinone	2-3%	40%
MSSAQ	2-6%	90%
ASAQ	1-10%	100%

The potential yield increase varies with the type of product (i.e. linerboard, tissue, etc.) so approximate ranges are given. High degrees of separation, such as 90-100% are limited to low temperature (600C) steam reforming of black liquor and are not likely to be achieved in this case. However, levels of sulfur separation to about 50% as a function of temperature to 1100C have been well documented.

A second major incentive of BLG is the production of a combustible product gas, rich in H_2 and CO. This product gas (a.k.a. “syngas”) can be used in gas turbines for combined cycle power generation (which is twice as efficient as the steam cycle alone), or it can be used as a precursor to form motor fuels, such as dimethyl ether or Fischer Tropsh diesel. However, there is a major drawback to BLG, which has the potential to become a third major incentive. That is that the causticizing load is greater for gasification of black liquor than for combustion in a Tomlinson boiler. This increase must at least be mitigated if black liquor gasifiers are to become a viable alternative to Tomlinson boilers in that the candidate mill’s existing lime cycle could be utilized as-is without costly capacity increase. Further, if complete causticization can be accomplished directly during gasification, then the costly lime cycle could be eliminated along with the recovery boiler.

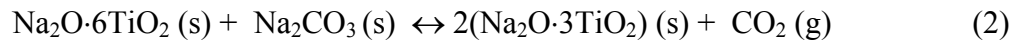
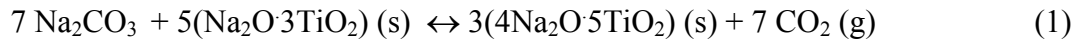
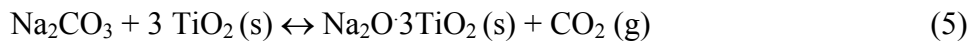
In the Tomlinson boiler the sulfur and sodium (and potassium) combine to form Na₂S (and K₂S), which leaves the boiler as molten smelt. The remaining sodium forms sodium carbonate (Na₂CO₃), which comprises the remainder of the smelt. After exiting the boiler the smelt enters the recausticizing plant, which converts most of the Na₂CO₃ to NaOH; the carbonate is converted to CO₂. The Na₂S remains unchanged in this step. The NaOH and Na₂S (along with some unconverted Na₂CO₃) leave the lime cycle as fresh white liquor for the pulping operation. However if black liquor is instead gasified, a portion of the sulfur leaves with the gas stream as H₂S and COS [9, 19]. While this is good for making specialty pulping liquors, it does leave excess sodium which leads to additional Na₂CO₃, which adds to the recausticizing load. So if an aging Tomlinson boiler were replaced with a gasifier of equal black liquor firing capacity, the recausticizing plant would have to process more Na₂CO₃, which would require costly upgrades, and thus reduce the overall incentive for firms to adopt BLG.

For an estimate for lime kiln fuel cost savings (assuming complete in situ causticization is possible thus eliminating the lime cycle), a single mill uses 400-600 lbs CaO per ton of pulp is required for causticization depending the grade of pulp produced [17]. Using 500 lb/ton as an average, a 1000 tpd pulp mill would require 90,000 bbls of #6 fuel oil per year to operate the lime kiln. At \$60/bbl, the savings is \$5.4M/yr. There is also the cost associated with operating the lime cycle (slakers, pumps, clarifier, lime mud handling equipment, etc.) but that is partially offset by operation of the leaching equipment required for caustic recovery (leaching tanks, pumps, etc).

Previous work has shown that [in situ] titanate direct causticizing integrates well with BLG, but only at pressures below 5 bar. Since BLG is best performed at 15-30 bar, there is a clear incentive to overcome the pressure limitation of melding BLG with direct causticizing. This project specifically addresses that pressure limitation.

Background

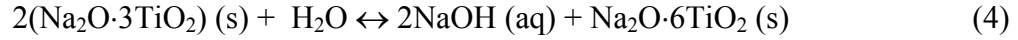
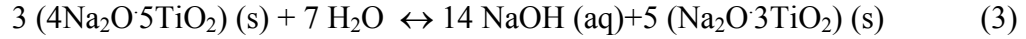
Titanate direct causticizing within the gasifier has the potential to perform the causticizing step in situ during BLG and thus eliminate the need for the lime cycle entirely. In this system, sodium trititanate and sodium hexatitanate are added to the liquor to bind up the sodium as pentatitanate during gasification and allow the carbon to be released as CO or CO₂. The main reactions involved are:



(Note that the Na-Ti compounds are typically abbreviated as NT3 for Na₂O·3TiO₂, N4T5 for 4Na₂O·5TiO₂, and NT6 for Na₂O·6TiO₂)

Reaction (5) is how make-up titanate is introduced to the system, and is not part of the cyclical chemistry. Reactions (1) and (2) are repeated cyclically however. In reaction (1) sodium is bound up with Ti to form the N4T5 (aka sodium pentatitanate). The solid phase (smelt) exiting the gasifier is sent to a leaching operation where the N4T5 is

leached back to NT3 via reaction (3), while forming a sodium hydroxide solution which can be used for pulping:



Recent research has shown that some of the NT3 can be leached even further, via reaction (4), to produce NT6, which is even more desirable for the cyclic stoichiometry in that more sodium is bound up titanium during gasification and is then released during leaching. Magnussen [4] found that reaction (4) occurs to about 65% conversion at a leaching temperature of 80C. The NT6 and NT3 solids are separated from the leachate and mixed with black liquor prior to entering the gasifier, where they react again according to reactions (1) and (2). The titanate compounds have very high melting points and are virtually insoluble; therefore the loss of titanate in this cyclic process is expected to be very small. Also, unlike the high quality TiO_2 commonly used in paint, there is a cost effective rutile form of TiO_2 that is acceptable for this application.

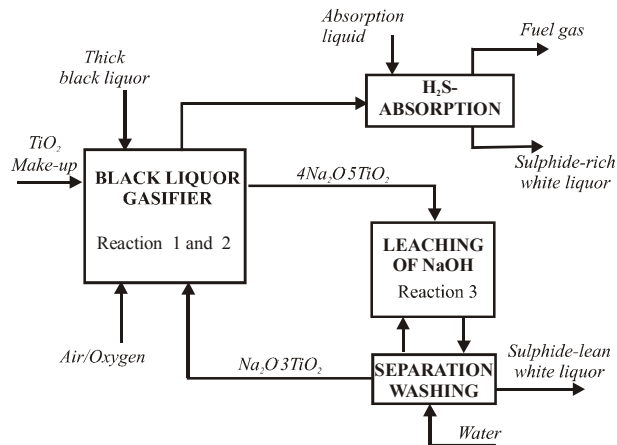


Figure 1. Black liquor gasification process with titanate direct causticization

The smelt would also contain a portion of the sulfur (as Na_2S), which would dissolve in water and remain in the leachate with the NaOH , effectively producing a white liquor that is hydroxide rich and sulfur lean. The remainder of the sulfur would leave the gasifier in the gas phase (mostly as H_2S and COS) and be recovered [most likely] in an absorption step. When recombined with a caustic scrubbing solution, the result would be a sulfur-rich white liquor. The overall process is shown in Figure 1 above. Furthermore, the gasification conditions (temperature, air ratio, etc.) can be manipulated to vary the sulfur split to some degree. Consequently, white liquors of varying sulfidity can be obtained for the high yield pulping process variants.

The stoichiometry is promising. But are these reactions thermodynamically favourable, and do they occur with the time frame of gasification of the organic carbon in the black liquor? Several studies have shown they are and do [2,3,6,7,11-15]. Previous work by

the authors [9] has evaluated the chemistry at high temperature entrained flow conditions (i.e. 5 seconds at 950C), and at low temperature steam reforming conditions (i.e. 50 hours at 600C in steam). Only the high temperature case is relevant here. Experimental results for the high temperature case are shown in Figure 2.

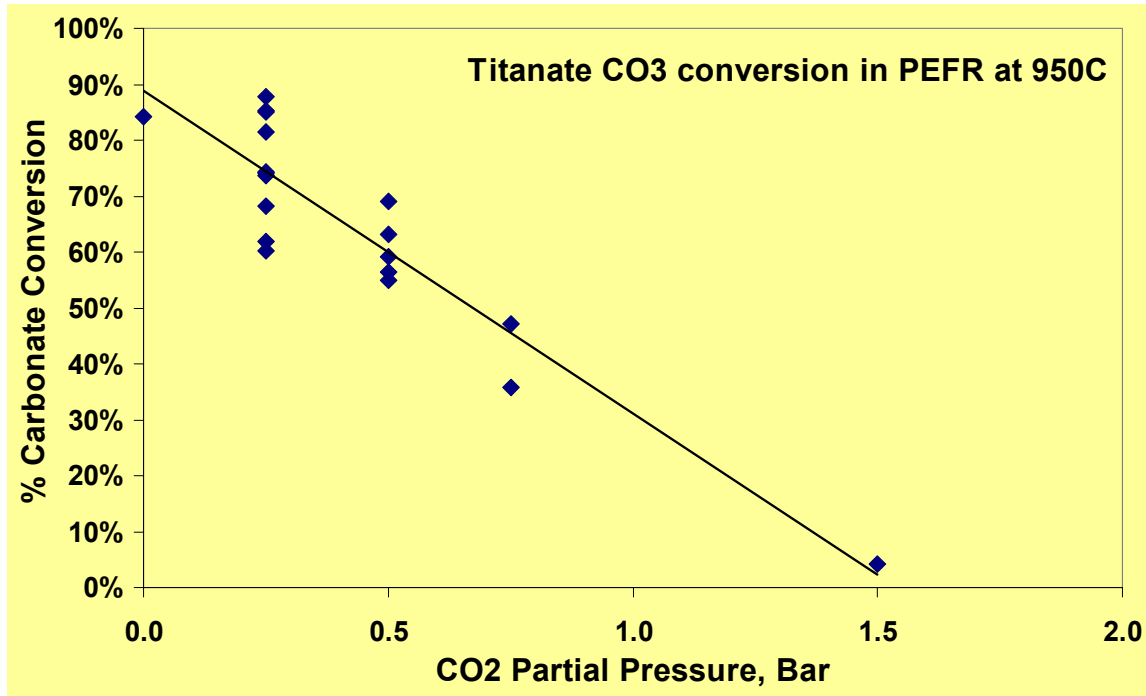


Figure 2. Experimental results of gasifying black liquor with titanate at 5 and 15 bars total pressure. The conversion of carbonate (i.e. formation of N4T5) decreases with increasing CO₂ partial pressure as expected from Reaction (1).

To evaluate the viability of using titanates for direct causticizing during BLG at conditions found in a high temperature gasifier, NT3 was mixed with black liquor at a ratio sufficient to causticize all of the carbonate remaining in the gasified char. The mixture was dried and pulverized, and screened-sieved to 63-90 microns. The BL/NT3 powder was then gasified in IPST's pressurized entrained flow reactor (PEFR) at 950C for approximately 5 seconds. CO₂ at varying concentration was used as the oxidizing gas: 5% and 10% CO₂ in N₂ at 5 and 15 bars total pressure. The conversion of the causticizing reaction (1) is shown in Figure 2 as a function of CO₂ partial pressure. 60% conversion is about the lowest acceptable level, which corresponds to 0.5 bar CO₂ in the syngas.

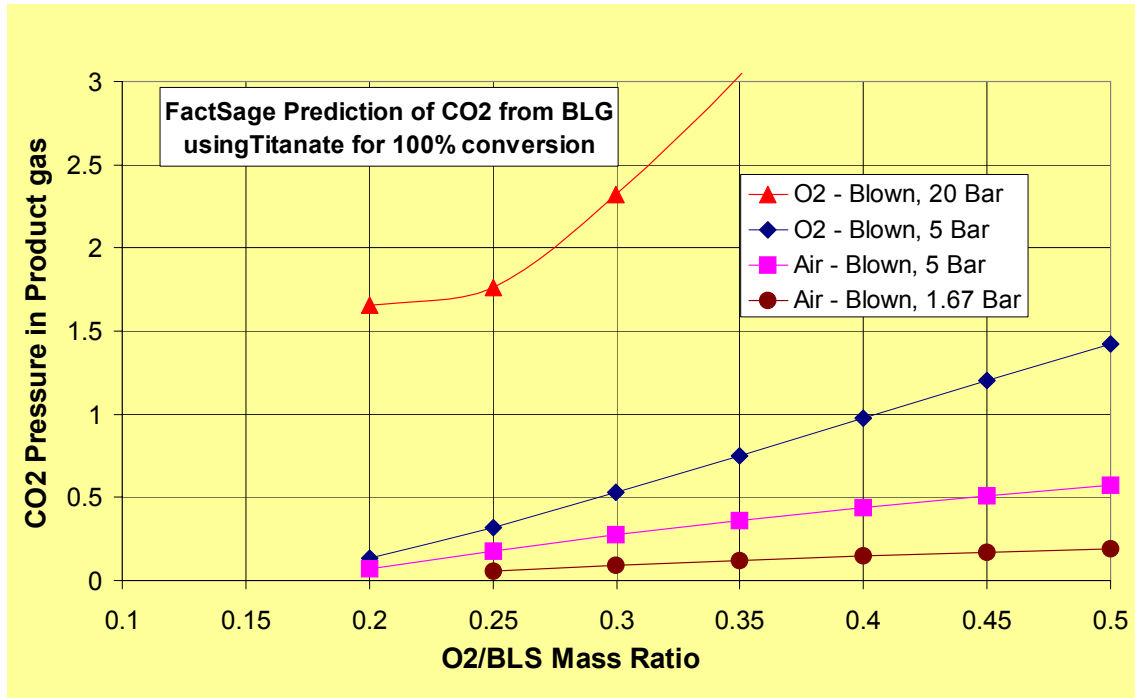


Figure 3. FactSage equilibrium prediction of CO₂ concentrations in the product gas for both air- and O₂-blown BLG as a function of stoichiometric O₂ to fuel ratio (i.e. 1.0 would be stoichiometric combustion)

Using this data it is possible to estimate if the direct causticizing reaction will proceed at industrial conditions by knowing the CO₂ level in the product gas. Figure 3 was generated by the FactSage 5.3 equilibrium modeling software. It shows the expected CO₂ levels in the syngas as a function of stoichiometric O₂ ratio. 0.35 would be a reasonable value for gasification of a biomass. From the experiments, we are looking for conditions where the CO₂ level is below about 0.5 bar. At O₂/BLS of 0.35, one can see that air-blown BLG up to 5 bars should give acceptable conversion. However the O₂-blown case at 5 bar would produce a CO₂ level around 0.75 bar, which would (using Figure 2) drive the causticizing conversion down to 40-50%. Decreasing the total pressure using pure O₂ would decrease the CO₂ and increase the conversion. Clearly though, using O₂ at 20 bars would result in a CO₂ concentration far too high for any causticizing to take place. Figure 4 shows the results of combining the data in Figure 2 with the modeling in Figure 3. It would be desirable to operate in the O₂-blown region to the right in Figure 4, however we need to find a way to limit the CO₂ partial pressure to get the higher conversions shown on the left of Figure 4. As stated previously, high pressures are required if BLG is to be used for efficient combined cycle power generation. In this study we seek to overcome the pressure/CO₂ restriction and achieve direct causticizing at 20 bar.

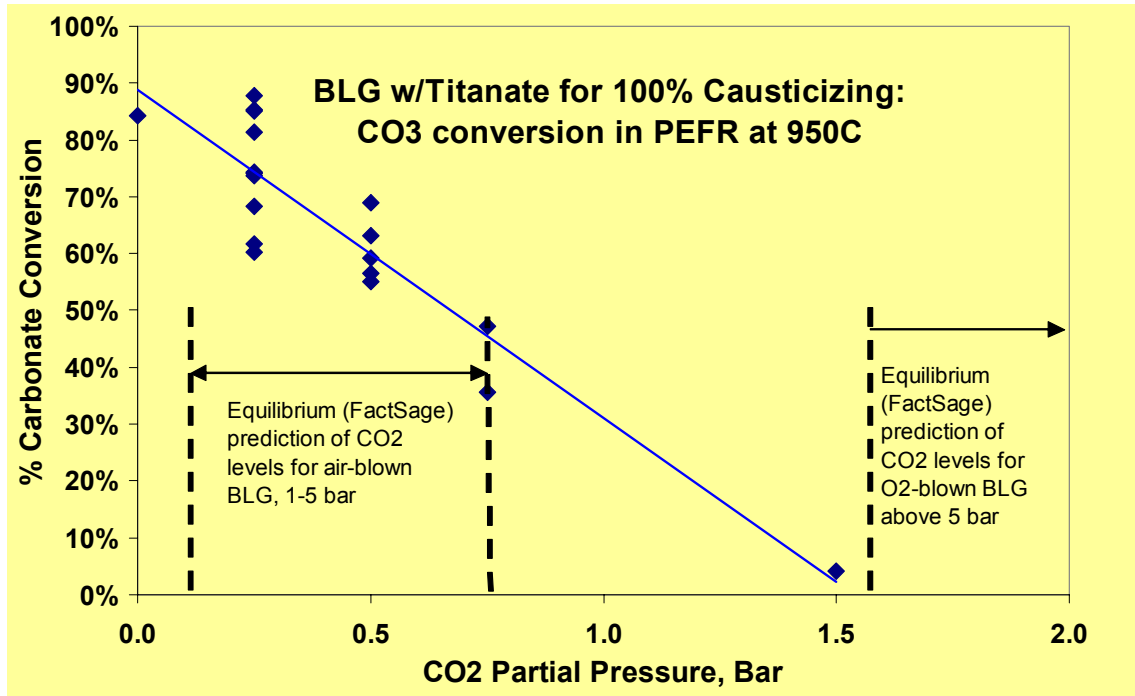


Figure 4. Experimental results of gasifying black liquor with titanate at 5 and 15 total pressure [9]. The conversion of carbonate (i.e. formation of N4T5) decreases with increasing CO₂ partial pressure as expected from Reaction (1).

Review of the Project Objectives

The overall objective is to develop a process that combines black liquor gasification with titanate direct causticizing in a pressurized circulating fluidized bed (CFB) reactor for the purpose of achieving fast gasification kinetics, and in situ causticization, along with the economy of scale benefits of pressurized operation. Note that a CFB (as opposed to entrained-flow) is needed for the added residence time required by lowering the temperature to 850°C. The original project objectives (*in italics*) were as follows with discussion included:

Task 1: Verify experimentally that gasification of fixed carbon in a black liquor-titanate mixture proceeds to at least 95% conversion at conditions suitable for a pressurized CFB configuration: within 8 seconds at 20 bar, and 850C. If 90% conversion cannot be achieved then a char carbon separation step will be added to the proposed process to recycle unburned carbon back to the gasifier. High carbon conversion was achieved, however it also found to be not as crucial as first thought. The fixed carbon remains with the leached solids and is therefore recycled back the gasifier. Thus the carbon is recycled to extinction.

Task 2: Verify experimentally that once the carbon has been gasified, that the solid phase causticizing reaction will proceed to at least 70% conversion after the CO₂-containing product gas has been removed from the system. This can also be carried out using the PEFR, customized apparatus in the thermochemical laboratory. If only 50 to 70% causticizing is obtained then we will have to allow for an extra processing step to

raise the conversion. This will add to the overall process cost. If at least 50% conversion cannot be obtained, then the process is probably not viable for combined causticizing and gasification. Sufficiently high conversions were obtained during gasification and leaching. This task was related to an early concept of having a two-stage reactor wherein the CO₂ was removed after the first stage and then the causticizing reactions would proceed further in a second stage.

Task 3: Determine the split of sulfur between the solid and gas phases and identify the consequent limitations on the resulting pulping liquors that can be produced (i.e. which, if any, high yield processes could be employed); also using the PEFR. Note: even if there is no sulfur split, it only means that a straight kraft process will be required. So this is not a critical juncture. The sulfur split was not measured due to limited resources. Early experiments did not produce any causticizing and thus the residence time was increased and the experiments repeated.

Task 4: Develop a viable procedure for leaching the solids to recover the caustic and produce a white liquor at the correct causticity and sulfidity for pulping. Various chemical separation processes such as acidification, complexing, and ion exchange will be considered. If none are found viable, then the fraction of leached NT3/NT6 that must be purged will be calculated based on allowable steady state NPE levels. This will be done in IPST's thermochemical laboratory. The leachate was found to have pH exceeding that required for white liquor. It can easily be diluted with mill water.

Task 5: Create a process flow sheet, including material and energy balances, of the CFB-based BLG recovery island. This task was completed.

Task 6: Perform an economic evaluation of the final process and compare with a Tomlinson-based reference case. If the process economics are deemed promising, then funding will be sought for a pilot phase. This task was completed.

Experimental

To experimentally evaluate the viability of using titanates for direct causticizing during BLG, NT3 was mixed with black liquor at a ratio sufficient to causticize all of the carbonate remaining in the gasified char (Rxns 1 and 2 above). Raw black liquor was graciously supplied by the Weyerhaeuser Co. Table 2 shows the elemental composition. Assuming complete gasification of hydrocarbons to H₂ and CO, and assuming 60% of the sulfur will partition to the char (40% to H₂S), then from the causticizing chemistry in Reactions 1-5, we may calculate the NT3 addition required to convert the char carbonate to hydroxide. It comes to 68 grams NT3 per 100 grams dry black liquor solids. Gasifying this doped liquor with CO₂ and H₂O vapor should lead to formation of a char with no carbonate. Leaching this char (see reactions 3 and 4) should yield a caustic leachate solution with about 0.004 mols of OH per gram of fixed-carbon-free char.

The NT3 is added to the liquid BL and thoroughly mixed. The mixture was then dried and pulverized, and screened-sieved to 63-90 microns. The BL/NT3 powder was then gasified in IPST's pressurized entrained flow reactor (PEFR) at 850C for approximately 5 seconds. CO₂ at varying concentration was used as the oxidizing gas: 5% and 10% CO₂ in N₂ at 5 and 15 bars total pressure. The key variable is the CO₂ partial pressure.

Table 2. Weyerhaeuser liquor elemental composition	
C	35.1%(by mass)
H	3.2%
O	34.22%
N	0.1%
Na	19.6%
K	1.14%
S	6.47%
Cl	0.17%

The pressurized entrained flow reactor (PEFR) is an electrically-heated, laminar flow, drop-tube reactor. Details, schematics, and pictures of the PEFR can be found in Appendix A. It allows for controlled conditions of temperature, residence time, gas composition, and pressure. As the reacted fuel exits the reactor, the solids (char) are collected in a cyclone for subsequent chemical analysis. The gases can be sampled on-line and/or sampled in gas bags for subsequent analysis. In this work gas analysis was not required. Such reactors have been employed for many years in combustion, gasification, and pyrolysis research. Monson and Germane [22] provide a review of several PEFR's, both in use and mothballed, around the world.

The collected solids (char) from each experiment were leached in water to carry out Reactions (3) and (4). The leachate is then titrated to measure the resulting hydroxide content. This is a measure of both the degree of causticizing and the efficiency of the leaching combined. These results are reported as a function of CO₂ partial pressure. Also of concern is the effect of repeated cycling of the titanate. To confirm that the titanates remain active, a batch of liquor/NT3 was gasified, the solids were leached, and the leached solids were mixed with fresh black liquor and gasified again and leached. The amount of hydroxide recovered from the first and second cycles was measured and compared to look for any sort of loss of effectiveness of the titanate.

A material and energy balance (MEB) for a titanate-based recovery process was performed using the Chemcad[®] process modeling software [22]. Details and assumptions are listed in Appendix C.

The economic analysis includes capital costs for major equipment, and operating costs, to obtain an estimate of the net present value (NPV), and internal rate of return (IRR) for the option of using direct titanate causticization given that a gasifier will be built. The reference case is the BLG cost-benefit analysis performed by Larson [21], which assumes to perform causticizing with an existing lime kiln. The NPV and IRR are then for the use of direct causticizing compared to the base case of BLG with a lime cycle. All assumptions of the analysis can be found in Appendix D

Results

The Experiments

Initially the gasification experiments yielded no hydroxide recovery, presumably because no causticizing took place. These results and conditions are shown in Table 3. In most cases no hydroxide was recovered from leaching of the char. In some cases, a small fraction of the amount expected was found.

Table 3. Results of titration of char produced from gasification of Ti-doped black liquor.				
Sample ID	Temp, C	Effective Length, mm	Gas Composition (balance N ₂)	mols NaOH per gram char
P070403A	850	1000	5%CO ₂ , 2%H ₂ O	0.00E+00
P070403B	850	1000	5%CO ₂ , 2%H ₂ O	0.00E+00
P070411A	850	500	5%CO ₂ , 2%H ₂ O	0.00E+00
P070411B	850	500	5%CO ₂ , 2%H ₂ O	0.00E+00
P070412A	850	500	10%CO ₂ , 2%H ₂ O	0.00E+00
P070412B	850	500	10%CO ₂ , 2%H ₂ O	0.00E+00
P070426A	850	2000	2%H ₂ O	3.45E-04
P070427A	850	2000	1% CO ₂ , 2%H ₂ O	0.00E+00
P070427B	850	2000	1% CO ₂ , 2%H ₂ O	0.00E+00
P070502A	850	2000	2% CO ₂ , 2%H ₂ O	2.82E-04
P070502C	850	2000	5% CO ₂ , 2%H ₂ O	0.00E+00
P070503A	850	2000	10%CO ₂ , 2%H ₂ O	0.00E+00
P070503B	850	2000	10%CO ₂ , 2%H ₂ O	0.00E+00
P070503C	850	2000	5% CO ₂ , 2%H ₂ O	0.00E+00
P070503D	850	2000	2% CO ₂ , 2%H ₂ O	2.96E-04
P070503E	850	2000	2%H ₂ O	3.30E-04

We know that under conditions similar to those of Table 3, but at 950°C, causticizing was achieved [9]. We can reasonably assume that at 850°C the causticizing kinetics are slower than at 950°C, and perhaps the short time in the PEFR (1.5 to 5 seconds in Table 3) was not enough for Reaction (1) to take place. Residence times were therefore increased to approximately 8 seconds. The CO₂ gas composition was varied from 1-5% with 5 bar total pressure, and fixed 2% H₂O.

The results at longer residence times are shown in Figure 5. Allowing more time for kinetics was successful. The shape of Figure 5 (850°C) is similar to the previous results shown in Figure 4 (950°C). In Figure 5 we have used mols of hydroxide recovered on the Y-axis as opposed to carbonate conversion. This reflects the combining of the causticizing reaction (Rxn 1) with the leaching reaction (Rxn 3). Note that the stoichiometric maximum in Figure 5 is 0.004 mols OH per gram char. Values below that level would indicate the sum of incomplete causticizing and incomplete leaching. Note also that Figure 5 represents first pass results only. That is there is no NT6 present. On subsequent cycling, Reactions (2) and (4) will also take place, thus increasing the hydroxide recovered at any given value of CO₂ partial pressure.

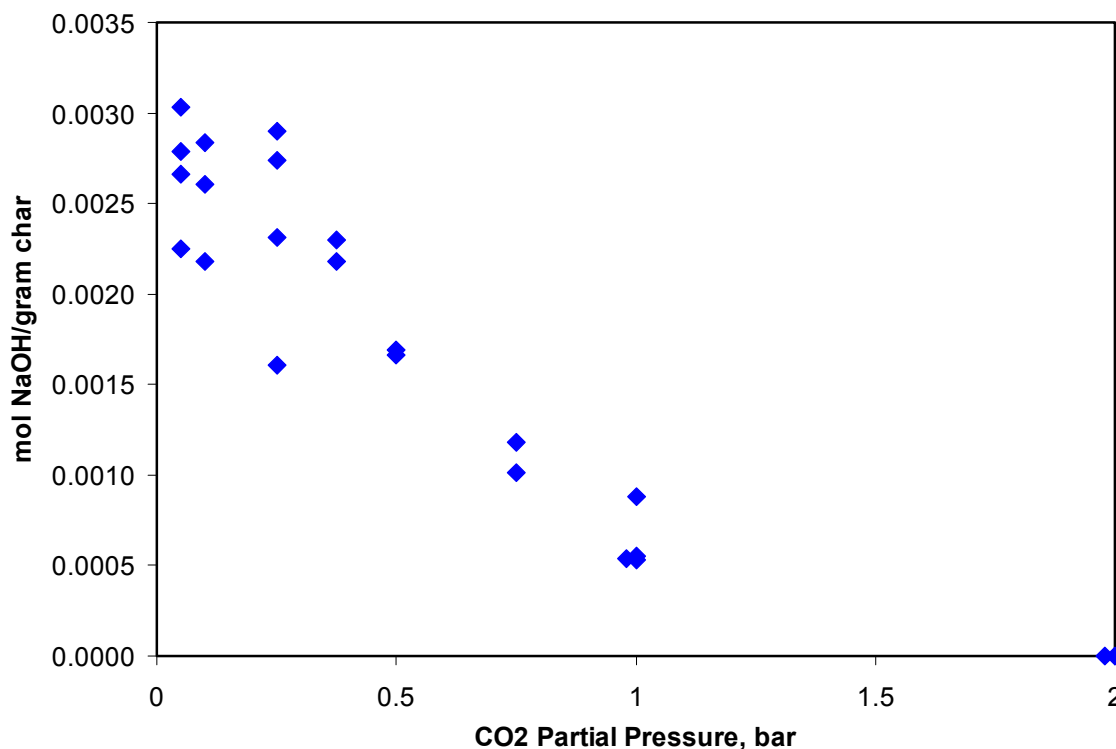


Figure 5. Hydroxide recovered from char formed by gasifying black liquor doped with 0.68g NT3/g dry BL solids at 850°C at varying CO₂ partial pressures. At this doping level the theoretical maximum hydroxide recovered would be 0.004 mols OH per gram char on carbon-free basis. Fixed carbon content was not measured. Data points shown are mols OH per gram char including fixed carbon.

As before, Figure 5 shows that the CO₂ partial pressure should be kept below about 0.5 bar to achieve reasonable conversion, and the lower the better. Thus if the gasifier pressure is 10 bar, then the desired CO₂ concentration should be below 5%. At 20 bar, it should be below 2.5%. Any solution to this limitation will require considerable manipulation of the gas composition. If enough oxygen is fed to gasify all of the fixed carbon, then we can expect much higher CO₂ levels in the syngas. One solution is to operate at very low O₂/fuel ratios, thus favoring the formation of H₂, CO, and light hydrocarbons, over CO₂ and H₂O. The problem with this approach is that little heat is released and the gasifier can only operate at lower temperatures. Another approach would be to separate the syngas from the solids leaving the gasifier and allow the solids to continue the causticizing reactions in a second reactor. However, since the causticizing reactions release pure CO₂, the partial pressure of CO₂ would be near the reactor pressure and the result would likely be reversal of the reactions. Still another approach might be to artificially manipulate the syngas composition within the gasifier. This subject will be discussed further in the next section.

Another important consideration is whether the leached solids are still reactive during subsequent recycling. Thus far in this project, we have used fresh NT3 to mix with black liquor and then gasify the mixture. It does not account for any sort of loss of reactivity of the titanates, nor does it allow for the formation of NT6 (i.e. Rxns 2 and 4). In a full scale system, the leached solids would be recycled and mixed with incoming black liquor and fed to the gasifier. To confirm reactivity of the solids, a sample of black liquor doped with 0.68g NT3/gDBLS was pyrolyzed in N₂ at 850C. The chart was then leached to recover hydroxide and convert the N4T5 back to NT3 and NT6. The NT3/NT6 was then mixed with fresh black liquor, dried, and ground in jar mill. This mix of fresh liquor and once-used titanate was then pyrolyzed again at 850C, and leached to measure the hydroxide recovered on the second “pass.” The results are shown above in Table 4.

In the first experiment on reactivity of leached solids, the hydroxide recovery increased somewhat from 0.00432 to 0.00494 mol NaOH per gram BLS. This is to be expected since NT3 would have been the only form of titanate in the first pass, whereas some NT6 would form during leaching and be present in the second pass. The second experiment yielded only 0.0038 mol NaOH per gram BLS. Obviously much more data would need to be taken to confirm the stability of recycling the NT3. However these experiments confirm significant activity remains after a first pass through the gasifier, indicating that the process remains viable. A separate study would be in order to confirm the effects of several repeated cycles.

Table 4. Leaching of Twice-Used Titanate		
Experiment	Mols NaOH formed/gram DBLS	Average
1 st pass black liquor with 0.68g NT3/gDBLS (reference).	0.00442	0.00432
Replicate leaching of 1 st pass.	0.00421	
Expt #080515, 2 nd pass, black liquor with 0.68g of leached solids/gDBLS.	0.00499	0.00494
Expt #080515, replicate leaching.	0.00488	
Expt #080721, 2 nd pass replicate conditions.	0.0038	0.0038

The Material and Energy Balance

The MEB was done using the Chemstations ChemCad[®] (version 6.1.4) process modeling software. We have shown experimentally that the causticizing chemistry works in situ during BLG at the temperature of interest (850°C). This result was expected given the previous results at 950°C. The crucial objective of this project was to devise a way to maintain the CO₂ partial pressure below 0.5 bar, while operating the gasifier at 20 bars (where the expected CO₂ partial pressure would be about 3-4 bar). We propose to manipulate the water-gas shift (WGS) reaction to convert as CO₂ to CO as possible.

The raw syngas in the gasifier, as in any gasification system, is rich in H₂, CO, and light hydrocarbons, as well as water vapor and CO₂. It is the CO₂ concentration in the gasifier that we wish to minimize. The water-gas shift (6) and Boudouard (7) reactions below govern the product gas distribution from a gasifier. By adding hydrogen to the syngas, reaction (6) is pushed to the left and thus the partial pressure of CO₂ is decreased. Reaction (7) becomes relevant at low O₂/fuel ratios where there is excess carbon. Operating at low O₂/fuel ratios will tend to form less CO₂ which is our goal.



Rather than purchasing H₂ to add to the gasifier, it can easily be separated from the syngas with a membrane and recycled. Since the recycled H₂ simply circulates, it is possible to use a large membrane and use a high H₂ recycle ratio, thus driving reaction (6) far to the left. All of this assumes that enough O₂ is used to generate enough to heat for the system to reach 850°C. In addition, reaction (7) can be used to inhibit CO₂ formation by maintaining a small amount of char carbon in the bed solids (if possible). We have already determined that char carbon does not impact leaching of the N4T5 solids and that the carbon remains bound with the NT3 leaving the leacher. However we will have to verify experimentally that char carbon entering with the NT3 does not interfere with the causticizing reactions during gasification. A process simulator such as ChemCad[™] is ideal (and expedient) to perform the iterative calculations to determine if all the necessary constraints can be met:

1. At 20 bar the CO₂ level remains below 0.5 bar (est) to allow in situ causticizing.
2. The heat released from partial oxidation must be sufficient to maintain 850°C.
3. Whether the required recycle ratios of H₂ and char carbon are within reason.

Figure 6 shows the proposed process for recycling H₂ back to the gasifier to shift the water-gas-shift reaction (Rxn 6) the left and thus minimize the CO₂ partial pressure. We use the ChemCad[™] simulator to estimate if there is enough H₂ to force the CO₂ partial pressure below 0.5 bar. The variables available to manipulate in Figure 6 in order to satisfy the three constraints are O₂ and water flow rates, the fraction of H₂ returned to the gasifier, and the fraction of the titanate solids that are diverted to the NPE washer.

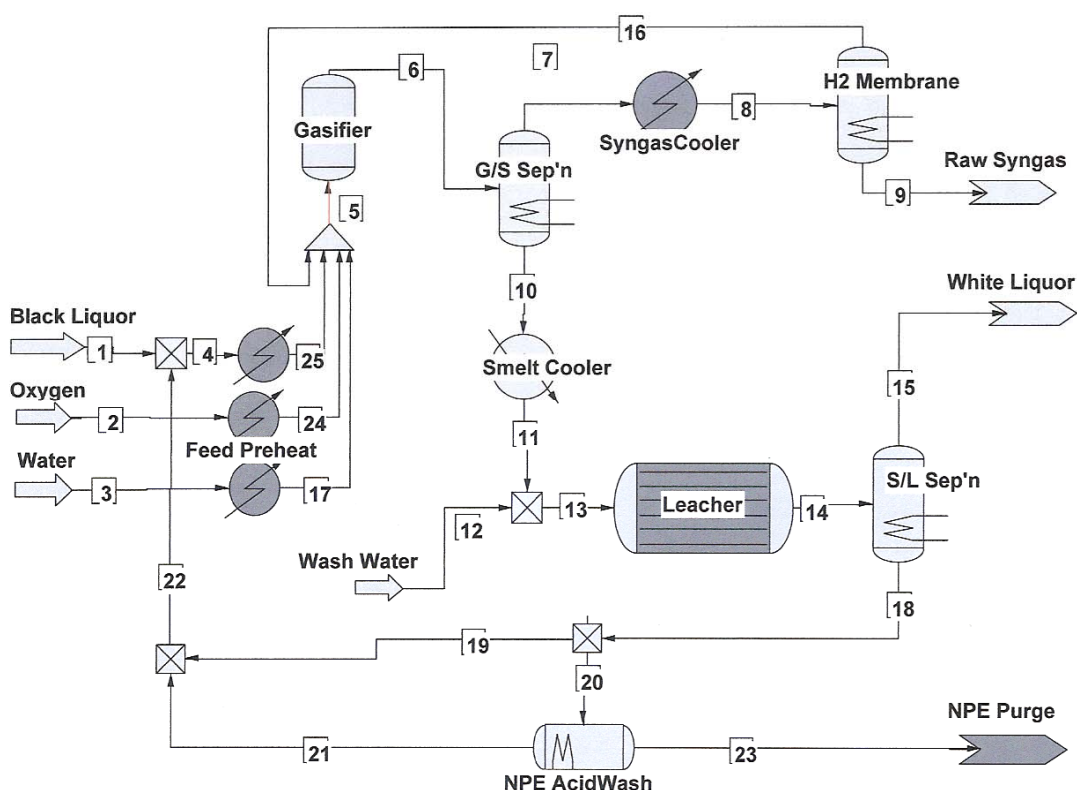


Figure 6. Proposed process for pressurized BLG with titanate direct causticizing. Hydrogen is recycled to affect the water-gas-shift reaction to reduce carbon dioxide.

In the proposed process shown in Figure 6, the inputs include the concentrated black liquor from the evaporators, as well as oxygen and water (to the steam generator). The leached titanate solids are mixed with the liquor and heated to 200°C prior to feeding into the gasifier. A membrane is used to separate a large fraction of the H₂ from the product gas and recycle it back the gasifier; the exact fraction being a control variable. In the gasifier the organic portion of the liquor is gasified into syngas, and the causticizing reactions take place. The syngas is cooled to 200°C prior to membrane separation. The raw syngas after removal of most of the H₂ would require further cleaning (i.e. H₂S removal, etc.) before use in a turbine, or Fischer-Tropsh plant. The solids (aka smelt) will require cooling which could be as simple as quenching in the leacher with some form of indirect cooling. Following the leaching reactions, the [now caustic] leachate (i.e. liquid phase) becomes the white liquor. It may require some small pH adjustment (not shown) but calculations show that the leaching reactions will take place at pH levels sufficient to produce a suitable white liquor. The leached solids (NT3) are then recycled back to be mixed with incoming black liquor. A fraction of the solids are diverted to an acid washer to dissolve and remove the non-process elements (NPE's). The flow rates of some of the key streams are shown in Table 5.

Table 5
Key Flow Rates for Figure 6
(in Kg/hr)

Steam #	1	2	3	5	6	8	9	10	12	15	16	17	18	21	23	24	25
Steam Name	Black Liquor	Oxygen	Water	Gasifier Feed	Gasifier Effluent	Cooled Syngas	Raw Syngas	Smelt	Wash Water	White Liquor	H2 Recycle	Steam 500C	Leached Solids	Washed Solids	NPE Purge	O2	Ti-Doped Liquor
Temp, C	90	25	50	182	857	200	200	857	30	200	200	500	200	200	200	500	200
Pressure, bar	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Total flow, Kg/hr	114232	68000	500	262566	262540	187145	153057	75395	25000	55515	34088	1500	45881	6597	135	68000	158978
Black Liquor Organics, Kg/hr	50418	0	0	50418	0	0	0	0	0	0	0	0	0	0	0	0	50418
Water, Kg/hr	20486	0	500	22997	38093	38093	38093	0	25000	19213	0	1500	2011	152	0	0	21497
Hydrogen	0	0	0	34088	35882	35882	1794	0	0	0	34088	0	0	0	0	0	0
Carbon Monoxide	0	0	0	0	58596	58596	58596	0	0	0	0	0	0	0	0	0	0
Carbon Dioxide	0	0	0	0	48546	48546	48546	0	0	0	0	0	0	0	0	0	0
Nitrogen	0	6028	0	6028	6028	6028	6028	0	0	0	0	0	0	0	0	6028	0
Oxygen	0	61972	0	61972	0	0	0	0	0	0	0	0	0	0	0	61972	0
Hydrogen Sulfide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sodium Carbonate	32484	0	0	32484	4384	0	0	4384	0	4384	0	0	0	0	0	0	32484
Sodium Sulfide	10386	0	0	10386	10386	0	0	10386	0	10386	0	0	0	0	0	0	10386
Sodium Chloride	323	0	0	323	323	0	0	323	0	323	0	0	0	0	0	0	323
(Na2O)(TiO2)3	0	0	0	15377	0	0	0	0	0	0	0	0	15377	2307	0	0	15377
(Na2O)(TiO2)6	0	0	0	27595	0	0	0	0	0	0	0	0	27595	4139	0	0	27595
(Na2O)4(TiO2)5	0	0	0	0	59404	0	0	59404	0	0	0	0	0	0	0	0	0
Sodium Hydroxide	0	0	0	0	0	0	0	0	0	0	0	0	0	21208	21208	0	0
NPE's	135	0	0	897	897	897	0	0	0	897	897	0	897	897	0	0	0

Table 5 shows many of the key flow rates and stream temperatures of the process shown in Figure 6. Detailed data for all streams are included in the appendices. From this we can already see that the temperature within the gasifier is 857°C which satisfies one of the criteria. The gas composition of stream 6 leaving the gasifier (and within the gasifier) is shown in Table 6. As we can see the ChemCad® simulation calculates the CO₂ volume content to be 4.7%. At 20 bar total pressure this translates to about 0.9 bar partial CO₂ pressure, which is greater than the desired value of 0.5 bar. Reading from Figure 5, the expected hydroxide recovery would only be about 0.001 mol NaOH/gram char which is a third of the maximum measured value of 0.003 mol/gram char. This would require that more titanate be circulated and would thus reduce the gasifier temperature. It is likely that a true optimization of the process model of Figure 6, would result in a lower CO₂ pressure in the gasifier. Another alternative is to lower the pressure to 10 bars total, which would give 0.47 bar CO₂ pressure, which would meet the criteria. One could also decrease the amount of water entering the system, or increase the recycle ratio; either of which would further push the WGS reaction further away from CO₂ formation. The variables in this model were manipulated manually (trial and error) to get close to a working solution. No mathematical optimization was performed. Additional work would likely yield a higher pressure solution.

Table 6
Gas Composition Leaving Gasifier (Stream 6) in Figure 6
(in mol %)

Hydrogen	76.3%
Carbon Monoxide	9.0%
Carbon Dioxide	4.7%
Nitrogen	0.9%
Oxygen	0.0%
Hydrogen Sulfide	0.0%
Water	9.1%
Ammonia	0.04%

Table 7.
Process Data from Figure 6.

H2 recycle ratio at membrane	0.95
Oxygen /Nitrogen composition	90%/10%
Leached solids diverted to wash	15%
Black liquor feed rate	114,232 Kg/hr
Black liquor preheat (to 200°C) load	20,000 MJ/hr
Oxygen preheating	32,000 MJ/hr
Steam preheating	4770 MJ/hr
Smelt cooling	-87,900 MJ/hr
Syngas cooling	-487,000 MJ/hr
Fixed carbon leaving gasifier	zero

Additional key process data and specifications for Figure 6 are shown in Table 7. The heat losses due to cooling are substantial. Much of heat could be recovered to provide both the required process feed heating, and steam generation for the mill. Again, no optimization was performed as this project was limited to the direct causticizing aspect. The complete set of process data for Figure 6 as well as the ChemCad[®] model assumptions can be found in Appendix C. Also noteworthy in Table 7 is the absence of H₂S in all of the streams. This is because the reactions to form H₂S from Na₂S in the gasifier were inadvertently omitted. We would have to assume that 60% of the sulfur would partition to the smelt phase but in the current model, all of it leaves with the smelt and leaches into the white liquor.

The Cost-Benefit Analysis

The economic analysis employs the same cost model used in Sinquefield and Cantrell [9]. In that project a titanate leaching system consisting of three leaching stages and an acid wash system for NPE removal was modeled to estimate the internal rate of return (IRR), and the net present value (NPV). The model utilized an extensive database of equipment prices to produce a +/-30% capital cost. For the process shown in Figure 6, we have one leaching stage, an acid wash system for NPE's, and a membrane separator for hydrogen recycle. The cost model in [9] can easily be adjusted (see appendix D for details):

- Add \$3MM to 'major equipment' for the membrane gas separator.
- Reduce the \$9.5MM cost of the leaching system agitators and pumps [9] by 60% to correct for one leaching stage versus three leaching stages in [9].
- Correct the TCC from 2006 to current price. The Chem Engr Plant cost index for Sept 2006 was 513, and for Sept. 2009 was 525.7
- Assume other construction direct and indirect costs are close enough to use for this study.

The details of the cost model can be found in Appendix D. Note that what we are modeling is the NPV and IRR of the titanate causticizing system instead of a lime cycle. The gasifier is already assumed to be being built and therefore not included. The lime is also assumed to already exist. The results are shown in Table 8. The savings of the titanate system is largely due to the saving in energy (fuel oil or natural gas) to fire the lime kiln. Therefore we have shown the results for a number of values of energy cost.

Table 8. NPV and IRR as a Function of Fuel Cost

\$/MMBtu displaced (i.e. oil or NG price)	NPV, \$MM	IRR, %
\$6/MMBtu	\$(6.6)	4.5%
\$8	\$10.6	16.8%
\$10	\$27.8	26.7%
\$12	\$45.0	36.3%
\$14	\$62.2	46.3%

The proposed system is therefore more favorable at higher energy prices. At \$10/MMBtu or higher, the system is economically attractive, and becomes very attractive as the price of fuel increases.

Conclusions

We have shown experimentally and through process modeling that the titanate direct causticizing chemistry for pressurized BLG is feasible up to at least 10 bars pressure at 850°C. 10 bars did not meet our goal of 20 bars. No optimization was done due to limited resources and scope. With process optimization the total pressure could likely be increased somewhat. There is also the possibility of adding additional hydrogen to further affect the WGS reaction and further inhibit CO₂ formation and thus allow the total pressure to be raised above 10 bar.

As expected the CO₂ partial pressure is the factor limiting the pressure. If the reactor temperature were further lowered to 750°C, the oxygen demand would correspondingly decrease as would the CO₂. It is possible some fixed carbon would circulate with the solids and further decrease the CO₂ level via the Boudouard reaction (which did not play a role at 850°C). Any reduction in CO₂ pressure would allow the causticizing chemistry to work at higher total system pressures. The lower temperature would also slow the kinetics and thus require a longer residence time. A large circulating fluid bed reactor would be the preferred type to achieve the required residence times.

Additionally we have shown that the concept of separating hydrogen and recycling it back the gasifier can drastically shift the WGS reaction and significantly reduce the CO₂ concentration in the syngas. This has application beyond the titanate causticizing process. It can be used to manipulate the H₂/CO ratio in Fischer-Tropsch and other syngas to chemicals processes.

The process economics are favorable for the BLG with titanate causticizing as long as fuel (for heat) costs are above about \$8 to \$10/MMBtu. While energy prices fluctuate, the long-term trend is to increase. Therefore novel processes with increased efficiencies must be considered for the industry to remain competitive.

Future Work

Additional work in this area would include optimizing the process to further reduce CO₂ partial pressure. This would allow higher total system pressures. Lowering the temperature to 750°C should definitely be investigated given the improvements found by going from 950°C to 850°C. While it is not mandatory to gasify black liquor at 20 bar or higher, the higher pressures results in smaller pressure vessels and better process economics. Also when the syngas is already pressurized it can be cleaned hot (or at least warm) and fed directly to a gas turbine without cooling to typical scrubbing temperatures and then recompressing it. F-T processes are typically carried out at 50-100 bar so 10 bar versus 20 in this system will not appreciably affect the viability. [Continued over]

We will also research further applications of recycling hydrogen for manipulation of the WGS reaction. Lastly, a pilot black liquor gasifier with titanate recovery system and hydrogen recycle could be built to verify the process model.

Acknowledgements

This work was performed under a grant from the U.S. Dept. of Energy, with matching funds from the Weyerhaeuser Co., Georgia Pacific, and the State of Georgia. We gratefully acknowledge their support.

References

- [1] Tucker, P., et.al., "Closing in on a Step Change in Power Generation from Self-Generated Fuels — The Pathway Parts 1 and 2", TAPPI Solutions, Jan & Feb, 2002
- [2] Nohlgren, I., PhD Thesis, Lulea University, Sweden, 2002
- [3] Nohlgren, I., Sricharoenchaikul, V., Sinquefield, S., Frederick, W., Theliander, H., "Black Liquor Gasification with Direct Causticization Using Titanates in a Pressurized Entrained-Flow Reactor Part 1: Kinetics of the Causticization Reaction", *J. Pulp Pap. Sci.*, 2003, 29(4), 107-113
- [4] Magnusson, K., "The Recycling Effects on the Solid Sodium Titanate process", M.S. Thesis, Chalmers University, Sweden, 2003
- [5] Dahlquist, E., Jones, A., "Presentation of a Dry Black Liquor Gasification Process with Direct Causticization", *TAPPI J.*, 4(5), 2005
- [6] Nohlgren, I., Sricharoenchaikul, V., Sinquefield, S., Frederick, W., Theliander, H., "Black Liquor Gasification with Direct Causticization Using Titanates in a Pressurized Entrained-Flow Reactor Part 2: Carbon and Carbon Species Transitions", *J. Pulp Pap. Sci.*, 2003, 29(10).
- [7] Nohlgren, I., Sricharoenchaikul, V., Sinquefield, S., Frederick, W., Theliander, H., "Black Liquor Gasification with Direct Causticization using Titanates in a Pressurized Entrained-Flow Reactor, Part 3: Sulfur and Sulfur Species Transitions", *J. Pulp Pap. Sci.*, 2004.
- [8] Minutes of IEA Annex XV Meeting on Black Liquor and Biomass Gasification in Turku, Finland, August 30 – September 1, 2004
- [9] Sinquefield, S.A, Cantrell, J., Zeng, X., Ball, A., Empie, H.J. "Causticizing for Black Liquor Gasifiers", U.S. DOE project DE-FC26-02NT41492, Oct. 2007.
- [11] Zou, X., "Recovery of Kraft Black Liquor Including Direct Causticization", Ph. D. Thesis, McGill University, Montreal, QC, Canada (1991).
- [12] Nohlgren, I., Theliander, H., Zhuang, Q. and Van Heiningen, A.R.P, "Model Study of the Direct Causticization Reaction Between Sodium Triticitanate and Sodium Carbonate", *CJChE* 78(3): 529-539 (2000).
- [13] Palm, M. and Theliander, H., "Kinetic Study on the Direct Causticization reaction Including Titanates and Titanium Dioxide", *Chem. Eng. Journ.* 68: 87-94 (1997).
- [14] Zhuang, Q., Gai, H., van Heiningen, A.R.P., Nohlgren, I. and Theliander, H., "Direct Causticization of Kraft Black Liquor with Recycled Sodium Titanate", *1998 Int. Chem. Recov. Conf*, Tampa, Florida, USA, June 1-4, 831-839 (1998).

- [15] Zeng, L., "Kraft Black Liquor Gasification and Direct Causticization in a Fluidized Bed", Ph.D. Thesis, University of New Brunswick, Fredericton, N.B., Canada (1997).
- [16] Richards, T., "Recovery of Kraft Black Liquor- Alternative Processes and Systems Analysis", PhD Thesis, Chalmers University, Sweden 2001
- [17] Green, R.P., Hough, G., "Chemical Recovery in the Alkaline Pulping Process", 3rd Ed, TAPPI Press, 1992
- [19] Sinquefield, S., Sricharoenchaikul, V., Frederick, W.J., Dayton, D., Ratcliff, M., French, R., Carpenter, D., and Lewnard, J., "Black Liquor Gasification I: The Impact of Pressure on C-H-O-S gas Speciation and Tar Components During Pyrolysis", International Chemical Recovery Conference, Whistler BC, June 11-14, 2001
- [20] Levenspiel, O., *The Chemical Reactor Omnibook*, OSU Press
- [21] Larson, E., Consoni, S., Katofsky, R., "A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry", U.S. DOE report, October, 2003.
- [22] ChemCad 6.2 process simulation software. www.Chemstations.com
- [23] Monson, C.R, Germane, G.J., "A High-Pressure Drop-Tube Facility for Coal Combustion", Energy and Fuels, 1993, 7, pp928-936.

APPENDIX A

Experimental Details

Pressurized Entrained Flow Reactor (PEFR)

The experimental portion of the work was performed in a specialized reactor that can mimic the conditions of temperature, pressure, residence time, and gas composition found in full scale gasifiers. A PEFR is a special case of a Laminar Entrained-Flow Reactor. LEFR's have been used extensively to investigate coal, biomass, and black liquor combustion and gasification. The advantages of using a laminar entrained-flow reactor for gasification studies are the rapid heating and cooling rates which allow for experiments at nearly isothermal conditions for controlled amounts of time, and the possibility to make experiments in controlled and well-defined gas atmospheres. In these reactors, solid particles of the material to be gasified are entrained in the primary gas stream and fed into the reactor via a water-cooled injection tube. A secondary gas stream, which constitutes the main part of the reaction gas is preheated to the desired reaction temperature and then enters the reactor concentric to the particles and primary gas stream. The solid particles and the primary gas are rapidly heated (particle heating rates of 10^4 - 10^5 °C/s) by radiation from the hot reactor walls and convection from the hot secondary gas. The flow pattern through the reactor is laminar to prevent deposition of particles on the reactor walls. The gas and particles exit via a water-cooled probe. They are rapidly cooled by a quench gas that is introduced at the upper tip of the collector. The particles are separated from the sample gas and collected, and the gas is sent to gas analyzers. Placing such a reactor inside a pressure vessel allows for variable pressure. Photos and drawings of the PEFR are shown in Figures A1 - A3.



Figure A1. IPST's Pressurized Entrained Flow Reactor



Figure A2. Another view of the PEFR. Ceiling clearance is 39 feet.

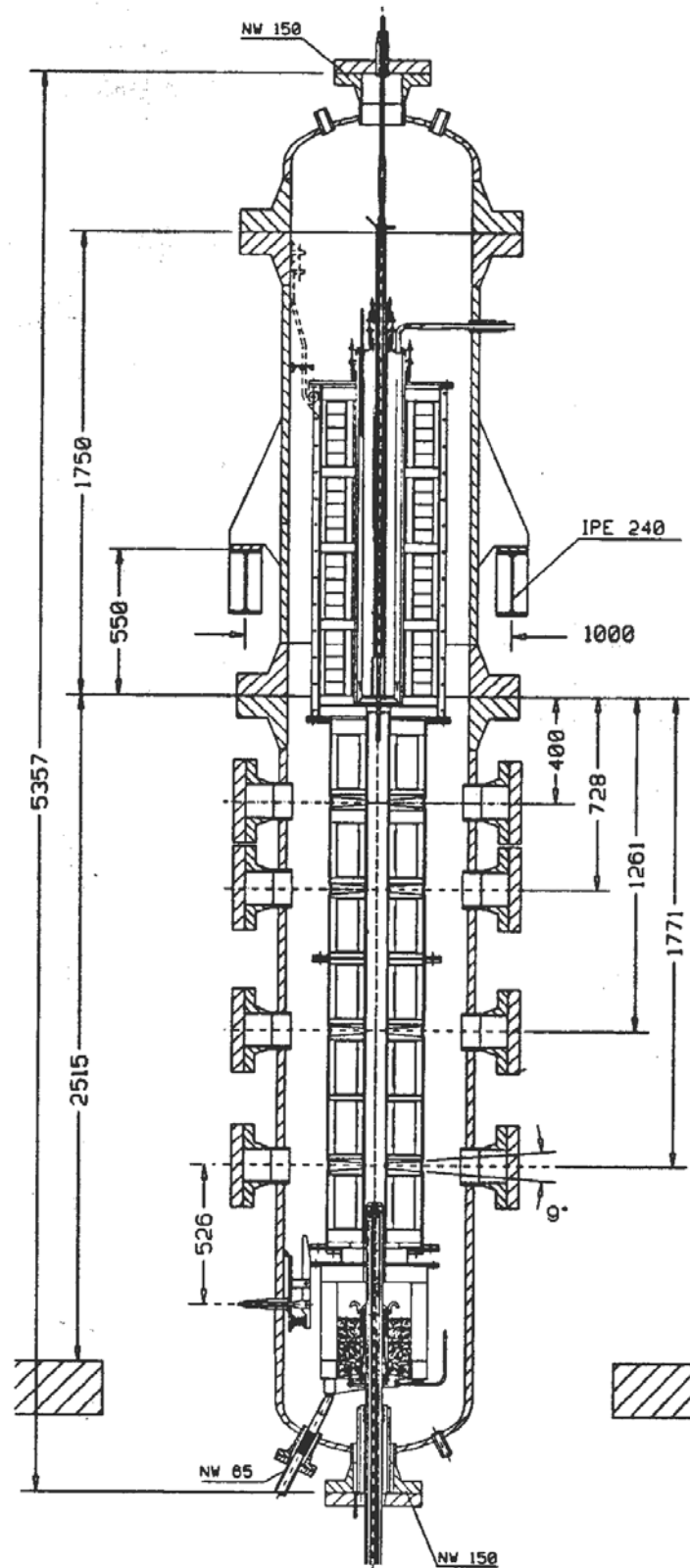


Figure A3. Diagram of the PEFR showing pressure vessel. Dimensions are millimeters.

Experimental Procedures.

The mixture ratio (doping levels) reflect the amount calculated from the stoichiometry above to achieve complete causticizing: 68 grams NT3 per 100 grams DBLS. The mixture is prepared wet and then dried in an Anhydro Lab 1 spray drier. The spray-dried solids were then sieved to 63-90 microns for use in the entrained flow reactors.

After reacting the doped liquors in the respective reactors, the residual solid material (char) was collected, and leached (see below). The leachate was then titrated (below) to determine the amount of hydroxide present. This gives the degree of causticizing obtained by reactions 3 and 4.

Char Leaching and Titration Procedure

For the titanate and manganate cases, the char must be leached in accordance with reactions (3) and (9) to obtain aqueous hydroxide and the insoluble starting agent (which would be recycled to the gasifier with fresh black liquor in the real world process). The leachate (solution) can then be titrated for determination of carbonate and hydroxide concentrations.

The analytical leaching of the char samples was carried out in a 500 ml 3-necked flask (Figure 4) equipped with a water-cooled condenser, a thermometer and a Pasteur pipette through which N₂ gas was bubbling through in order to eliminate air (O₂ and CO₂). While provided constant stirring with magnetic stirrers, the flask was heated via an oil bath in order to bring the water to boil. Evaporated water was condensed on the condenser and fell back down into the flask. When the distilled and deionized water reached its boiling point, 1.000 g of the recycled sample was added to the boiling water. The leaching time was 90 minutes in order to ensure complete reaction. Some of the samples were leached multiple times as explained in later sections.

After the leaching time had elapsed, the flask with the contents was removed from the oil bath and allowed to cool to room temperature. When cooled, the solution was quantitatively transferred to a previously weighed 60 ml 4-5.5 μ m fine glass filter Büchner funnel set up on a 1-liter Erlenmeyer flask and suction filtered by using an aspirator. The filtrate was thereafter transferred to a 250 ml volumetric flask and diluted with distilled and deionized water and put aside for further analysis. The filter cake was dried in an oven overnight (105 °C), and then weighed and stored for further analysis. Finally, the filtrate's caustic concentration was determined by acidimetric titration in a 751 GPD Titrino from Metrohm.

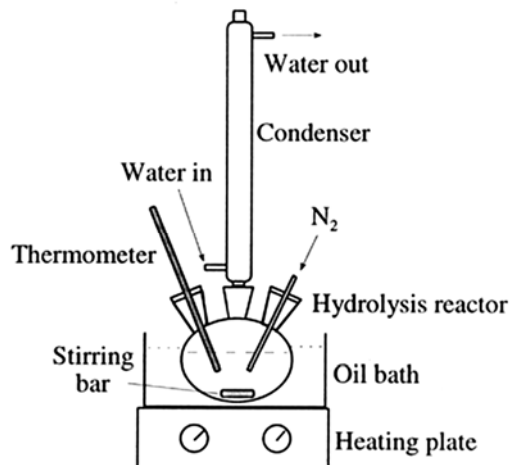
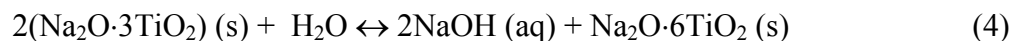
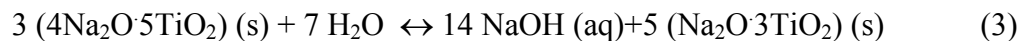


Figure A4. The leaching apparatus.

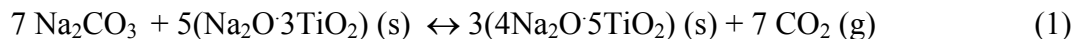
A 25 ml sample volume of the Na-Ti leachate was pipetted into a beaker. Barium chloride, 10 wt%, was added to the sample to bind any anions, such as carbonate, that would interfere with the titration of OH^- . After adding phenolphthalein (PP) indicator, the mixture was titrated to the PP end point 8.67 with a 0.1 M HCl solution. The volume of added HCl was noted and the NaOH concentration was calculated (see Appendix B).

To account for sulfide a formaldehyde solution (HCHO , 40% in water) was added to convert Na_2S to NaOH. If there were any sulfide ions present, the pink color should return. If the pink color of PP returned, the mixture was titrated again to the PP end point.

The leaching allows reactions (3) and (4) to release the hydroxide into solution. Previous work [9] has shown that reaction (3) is effectively complete and that reaction (4) proceeds about 65%.



Since all of the N4T5 is leached back to either NT3 or NT6, the remaining variable is the degree of conversion in reaction (1). Thus the hydroxide recovered is a measure of the carbonate converted in reaction (1). This saves us the extra step of measuring the carbonate content in the char and then leaching the char to measure the hydroxide recovered.



APPENDIX B

Experimental Data

The experimental conditions are shown in Table B1 along with resulting char weights. Table B2 shows the data for titration of the char to measure the hydroxide recovered from the leaching.

Table B1
Experimental Data

Sample/Date	Reactor Temperature (°C)	Reactor Pressure (Bar)	Collector Height (mm)	Bulk Velocity (cm/s)	Initial Weight (g)	Final Weight (g)	Fuel Fed (g)	Reynold's #	Gas Composition	Water Pump Setting	Water Added (mL/min)	Primary Ratio	Quench Ratio	Sample Time (min.)	Feed Rate (g/Min)	Weight of Char (g)
P070329A	850	5	1000	20	699	695	4	851	5%CO2, 2%H2O	30	1.76	3.9:1	.25:1	6.5	0.6	1.5
B	850	5	1000	20	695	692	3	851	5%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.3	2.36
P070403A	850	5	1000	20	795	787	8	851	5%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.8	5.93
B	850	5	1000	20	787	782	5	851	5%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.5	3.94
P070411A	850	5	500	20	733	728	5	851	5%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.5	3.03
B	850	5	500	20	728	726	2	851	5%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.2	1.78
P070412A	850	5	500	20	720	718	2	875	10%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.2	1.33
B	850	5	500	20	718	716	2	875	10%CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	0.2	1.58
P070426A	850	5	1998	20	722	718	4	828	2%H2O	30	1.76	3.9:1	.25:1	10	0.4	0.94
B	850	5	1998	20	718	715	3	828	2%H2O	30	1.76	3.9:1	.25:1	10	0.3	0.35
P070427A	850	5	1996	20	729	723	6	832	1% CO2, 2%H2O	30	1.76	3.9:1	.25:1	15	0.4	0.74
B	850	5	1996	20	723	714	9	832	1% CO2, 2%H2O	30	1.76	3.9:1	.25:1	18	0.5	1.07
P070502A	850	5	1998	20	708	703	5	837	2% CO2, 2%H2O	30	1.76	3.9:1	.25:1	15	0.333333	0.65
B	850	5	1998	20	703	698	5	837	2% CO2, 2%H2O	30	1.76	3.9:1	.25:1	20	0.25	0.11
C	850	5	1998	20	698	695	3	851	5% CO2, 2%H2O	30	1.76	3.9:1	.25:1	20	0.15	1.45
D	850	5	1998	20	695	695	0	851	5% CO2, 2%H2O	30	1.76	3.9:1	.25:1	8	0	0
P070503A	850	5	1998	20	590	560	30	875	10%CO2, 2%H2O	30	1.76	3.9:1	.25:1	2	15	2.4
B	850	5	1998	20	528	585	-57	875	10%CO2, 2%H2O	30	1.76	3.9:1	.25:1	4.5	-12.6667	1.77
C	850	5	1998	20	546	580	-34	851	5% CO2, 2%H2O	30	1.76	3.9:1	.25:1	6	-5.66667	0.68
D	850	5	1998	20	660	643	17	837	2% CO2, 2%H2O	30	1.76	3.9:1	.25:1	2.75	6.181818	5.43
E	850	5	1998	20	628	644	-16	828	2%H2O	30	1.76	3.9:1	.25:1	5	-3.2	4.91
P070507A	950	5	1998	20	706	696	10	832	1% CO2, 2%H2O	30	1.76	3.9:1	.25:1	4	2.5	no char
B	950	5	1998	20	695	687	8	837	2% CO2, 2%H2O	30	1.76	3.9:1	.25:1	4	2	no char
C	950	5	1998	20	687	676	11	851	5% CO2, 2%H2O	30	1.76	3.9:1	.25:1	10	1.1	no char
P070509A	950	5	1998	20	667	661	6	480	1% CO2, 2%H2O	30	1.76	3.9:1	.25:1	4	1.5	0.15
B	950	5	1998	20	661	655	6	483	2% CO2, 2%H2O	30	1.76	3.9:1	.25:1	4	1.5	0.7
P070510A	950	5	1998	20	654	650	4	480	1% CO2, 2%H2O	30	1.76	3.9:1	.25:1	7	0.571429	
P070605A	950	5	1999	20	755	751	4	477	2% H2O	14.1	1.04	3.9:1	.25:1	10	0.4	0
B	950	5	1999	20	751	748	3	480	1% CO2, 2%H2O	14.1	1.04	3.9:1	.25:1	10	0.3	0
P070801A	950	5	1999	10	724	717	7	241	2% CO2, 2%H2O	3	0.52	3.9:1	.25:1	10	0.7	not enough char to collect
B	950	5	1999	10	717	712	5	241	2% CO2, 2%H2O	3	0.52	3.9:1	.25:1	10	0.5	not enough char to collect
P070803A	950	5	1999	10	739	731	8	241	2% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	10	0.8	not enough char to collect
B	950	5	1999	10	731	725	6	241	2% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	10	0.6	not enough char to collect
P070821A	950	5	1999	10	733	727	6	241	2% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	10	0.6	plug – not enough char to collect
B	950	5	1999	10	727	722	5	241	2% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	10	0.5	plug – not enough char to collect
P070823A	950	5	1999	10	732	725	7	241	2% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	10	0.7	1.14

Table B1 (continued)

Sample/Date	Reactor Temperature (°C)	Reactor Pressure (Bar)	Collector Height (mm)	Bulk Velocity (cm/s)	Initial Weight (g)	Final Weight (g)	Fuel Fed (g)	Reynold's #	Gas Composition	Water Pump Setting	Water Added (mL/min)	Primary Ratio	Quench Ratio	Sample Time (min.)	Feed Rate (g/Min)	Weight of Char (g)
B	950	5	1999	10	725	718	7	241	2% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	12	0.58	0.55
C	950	5	1999	10	718	710	8	245	5% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	20	0.4	1.45
D	950	5	1999	10	710	702	8	245	5% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	22	0.363636	1.44
P070831A	850	5	1999	10	730	xxx		279	2% CO2, 2%H2O	4.3	0.60	1.5:1	1.:1	20		3.93
B	850	5	1999	10	xxx	xxx		279	2% CO2, 2%H2O	4.3	0.60	1.5:1	1.:1	20		2.86
C	850	5	1999	10	xxx	xxx		284	5% CO2, 2%H2O	4.3	0.60	1.5:1	1.:1	25		1.76
D	850	5	1999	10	xxx	xxx		284	5% CO2, 2%H2O	4.3	0.60	1.5:1	1.:1	25		1.52
P070905A	850	5	1999	10	726	716	10	277	1% CO2, 2%H2O	4.3	0.60	1.5:1	1.:1	20	0.5	1.19
B	850	5	1999	10	716	708	8	277	1% CO2, 2%H2O	4.3	0.60	1.5:1	1.:1	20	0.4	1.56
C	950	5	1999	10	708	697	11	240	1% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	25	0.44	1.19
D	950	5	1999	10	697	690	7	240	1% CO2, 2%H2O	3.5	0.55	1.5:1	1.:1	25	0.28	0.84
P080318A	850	5	1900	10	713	710	3	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	10	0.3	1.2919
P080318B	850	5	1900	10	710	707	3	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	10	0.3	0.9533
P080318C	850	5	1900	10	707	702	5	308	20% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	20	0.25	1.6968
P080318D	850	5	1900	10	702	698	4	308	20% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	20	0.2	1.4705
P080320A	850	5	1900	10	689	683	6	316	40% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	25	0.24	
P080320B	850	5	1900	10	683	679	4	316	40% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	25	0.16	
P080424A	850	5	1990	10	698	694	4	288	7.5% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	15	0.27	1.21
P080424B	850	5	1900	10	694	690	4	288	7.5% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	15	0.27	1.21
P080424C	850	5	1900	10	690	685	5	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	20	0.25	1.41
P080424D	850	5	1900	10	685	680	5	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	20	0.25	1.23
P080508A	850	5	1900	10	684	682	2	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	18	0.11	----
P050830A	850	5	1900	10	684	681	3	300	15%CO2, 2%H2O	4.1	0.59	1.25:1	1.:33	20	0.15	1.04
P050830B	850	5	1900	10	681	678	3	300	15%CO2, 2%H2O	4.1	0.59	1.25:1	1.:33	20	0.15	1.05
P080530C	850	5	1900	10	678	674	4	308	20%CO2, 2%H2O	4.5	0.61	1.25:1	1.:33	20	0.20	
P080530D	850	5	1900	10	674	671	3	308	20%CO2, 2%H2O	4.5	0.61	1.25:1	1.:33	20	0.15	
P080626A	850	5	1900	10	714	710	4	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	20	0.20	1.31
P080626B	850	5	1900	10	710	704	6	292	10% CO2, 2% H2O	4.5	0.61	1.25:1	1.:33	20	0.30	1.27

Table B2
Leaching Data

Sample ID	Temp C	Pressure bar	%CO2	P CO2, bar	Leaching Time (min)	Sample Wt. (g)	Empty Funnel (g)	Funnel+Residue (g)	Residue (g)	Leachate vol. (mL)	aliquot (mL)	[HCl] titrant conc	Vol. HCl (mL)	[NaOH] (mol/L)	[NaOH] (mol/g char)
P070403A	850	5	5.00%	0.25	90	1.0001	61.1536	61.5930	0.4394	250	25	0.1	0	0.00E+00	0.00E+00
P070403B	850	5	5.00%	0.25	90	0.9999	61.5247	61.9543	0.4296	250	25	0.1	0	0.00E+00	0.00E+00
P070411A	850	5	5.00%	0.25	90	0.9994	60.9279	61.3975	0.4696	250	25	0.1	0	0.00E+00	0.00E+00
P070411B	850	5	5.00%	0.25	90	0.9996	61.1155	61.5222	0.4067	250	25	0.1	0	0.00E+00	0.00E+00
P070412A	850	5	10.00%	0.5	90	0.9988	70.6045	70.9971	0.3926	250	25	0.1	0	0.00E+00	0.00E+00
P070412B	850	5	10.00%	0.5	90	0.9985	61.4982	61.7307	0.2325	250	25	0.1	0	0.00E+00	0.00E+00
P070426A	850	5	0.00%	0	90	0.6196	60.9201	61.1725	0.2524	250	25	0.1	0.214	8.56E-04	3.45E-04
P070427A	850	5	1.00%	0.05	90	0.5337	61.4713	61.6506	0.1793	250	25	0.1	0	0.00E+00	0.00E+00
P070427B	850	5	1.00%	0.05	90	0.8187	61.0935	61.4232	0.3297	250	25	0.1	0	0.00E+00	0.00E+00
P070502A	850	5	2.00%	0.1	90	0.4830	61.0511	61.2008	0.1497	250	25	0.1	0.136	5.44E-04	2.82E-04
P070502C	850	5	2.00%	0.1	90	0.9990	60.9202	61.3140	0.3938	250	25	0.1	0	0.00E+00	0.00E+00
P070503A	850	5	5.00%	0.25	90	0.9997	61.4636	61.8523	0.3887	250	25	0.1	0	0.00E+00	0.00E+00
P070503B	850	5	5.00%	0.25	90	0.9996	70.6021	71.0118	0.4097	250	25	0.1	0	0.00E+00	0.00E+00
P070503C	850	5	5.00%	0.25	90	0.4956	61.0622	61.2453	0.1831	250	25	0.1	0	0.00E+00	0.00E+00
P070503D	850	5	2.00%	0.1	90	0.9994	60.5069	61.0163	0.5094	250	25	0.1	0.296	1.18E-03	2.96E-04
P070503D	850	5	2.00%	0.1	90	0.9994	60.5069	61.0163	0.5094	250	25	0.1	0.276	1.10E-03	2.76E-04
P070503E	850	5	2.00%	0.1	90	1.0002	69.4719	69.9576	0.4857	250	25	0.1	0.330	1.32E-03	3.30E-04
P070503E	850	5	2.00%	0.1	90	1.0002	69.4719	69.9576	0.4857	250	25	0.1	0.342	1.37E-03	3.42E-04
SB070607	850	5	0.00%	0	90	1.002	70.6033	71.3805	0.7772	250	25	0.1	3.942	1.58E-02	3.93E-03
SB070607	850	5	0.00%	0	90	1.002	70.6033	71.3805	0.7772	250	25	0.1	3.954	1.58E-02	3.95E-03
P070828A	850	5	2.00%	0.1	90	0.7668	60.5076	61.0199	0.5123	250	25	0.1	1.672	6.69E-03	2.18E-03
P070828C	850	5	5.00%	0.25	90	0.9761	61.0582	61.7246	0.6664	250	25	0.1	2.258	9.03E-03	2.31E-03
P070828D	850	5	5.00%	0.25	90	0.9407	76.1224	76.6906	0.5682	250	25	0.1	1.512	6.05E-03	1.61E-03
P070831A	850	5	2.00%	0.1	90	0.9974	61.4544	62.1815	0.7271	250	25	0.1	2.826	1.13E-02	2.83E-03
P070831B	850	5	2.00%	0.1	90	0.9907	61.0377	61.7522	0.7145	250	25	0.1	2.584	1.03E-02	2.61E-03
P070831C	850	5	5.00%	0.25	90	0.9993	60.5133	61.2406	0.7273	250	25	0.1	2.894	1.16E-02	2.90E-03
P070831D	850	5	5.00%	0.25	90	0.9859	61.0568	61.7739	0.7171	250	25	0.1	2.700	1.08E-02	2.74E-03
P070905A	850	5	1.00%	0.05	90	0.9633	76.1255	76.8231	0.6976	250	25	0.1	2.566	1.03E-02	2.66E-03
P070905B	850	5	1.00%	0.05	90	0.9979	61.4583	62.2140	0.7557	250	25	0.1	3.024	1.21E-02	3.03E-03
P070905C	850	5	1.00%	0.05	90	0.7949	61.0321	61.5965	0.5644	250	25	0.1	2.214	8.86E-03	2.79E-03

Table B2 (continued)

Sample	Temp	Pressure	%CO2	P	Leaching Time	Sample Wt.	Empty Funnel	Funnel+Residue	Residue	Leachate	aliquot	[HCl] titrant	Vol. HCl	[NaOH]	[NaOH]
ID	C	bar		CO2, bar	(min)	(g)	(g)	(g)	(g)	vol. (mL)	(mL)	conc	(mL)	(mol/L)	(mol/g char)
P070905D	850	5	1.00%	0.05	90	0.5529	61.0593	61.4379	0.3786	250	25	0.1	1.244	4.98E-03	2.25E-03
P080318A	850	5	10.00%	0.48	90	0.9975	60.5046	61.0228	0.5182	250	25	0.1	0		
P080318A	850	5	10.00%	0.50	90	0.9975	60.5046	61.0228	0.5182	250	25	0.1	0		
P080318B	850	5	10.00%	0.52	90	0.8134	61.4545	61.9276	0.4731	250	25	0.1	0		
P080318C	850	5	20.00%	0.98	90	1.0013	61.4598	62.1254	0.6656	250	25	0.1	0.542	2.17E-03	5.41E-04
	850	5													
P080318D	850	5	20.00%	1.00	90	0.9961	76.1221	76.7712	0.6491	250	25	0.1	0.526	2.10E-03	5.28E-04
P080320A	850	5	40.00%	1.98	90	0.6767	61.0547	61.4658	0.4111	250	25	0.1	0		0.00E+00
	850	5													
P080320B	850	5	40.00%	2.00	90	0.7677	61.6313	61.6313	0.0000	250	25	0.1			0.00E+00
SB080320	850	1	5.00%		90	1.0008	70.6022	71.4048	0.8026	250	25	0.1	3.254	1.30E-02	3.25E-03
SB080424	850	1	5.00%	0.05	1st 90	92.36				250					
SB080424					2nd 90				64.88	250					
SB080424					90	1.0005	61.0483	61.7588	0.7105	250	25	0.1	4.426	1.77E-02	4.42E-03
SB080424(Titrate again)					90	1.0005	61.0483	61.7588	0.7105	250	25	0.1	4.214	1.69E-02	4.21E-03
P080424A	850	5	7.50%	0.375	90	0.9994	61.6370	62.3531	0.7161	250	25	0.1	2.298	9.19E-03	2.30E-03
P080424B	850	5	7.50%	0.375	90	1.0011	61.0088	61.7409	0.7321	250	25	0.1	2.180	8.72E-03	2.18E-03
P080424C	850	5	10.00%	0.5	90	1.0010	S4			250	25	0.1	1.692	6.77E-03	1.69E-03
P080424D	850	5	10.00%	0.5	90	1.0003	S5			250	25	0.1	1.660	6.64E-03	1.66E-03
SB080515	850	1	5.00%		90	1.0085	61.6334	62.3257	0.6923	250	25	0.1	5.028	2.01E-02	4.99E-03
SB080515(titrate again)					90	1.0085	61.6334	62.3257	0.6923	250	25	0.1	4.918	1.97E-02	4.88E-03
P080530A	850	5	15.00%	0.75	90	1.0008	61.0429	61.7404	0.6975	250	25	0.1	1.184	4.74E-03	1.18E-03
P080530B	850	5	15.00%	0.75	90	0.9994	60.9970	61.6935	0.6965	250	25	0.1	1.014	4.06E-03	1.01E-03
P080530C	850	5	20.00%	1	90	0.9706	61.4357	62.0991	0.6634	250	25	0.1	0.854	3.42E-03	8.80E-04
P080530D	850	5	20.00%	1	90	0.9711	61.6373	62.2853	0.6480	250	25	0.1	0.534	2.14E-03	5.50E-04
P080626A	850	5	10.00%		90	1.0025	61.6385(S1)			250	25	0.1	1.100	4.40E-03	1.10E-03
P080626B	850	5	10.00%		90	1.0022	70.6074(N1)			250	25	0.1	1.372	5.49E-03	1.37E-03
SB080721	850	1	5.00%		90	1.0011	70.9806(N2)			250	25	0.1	3.806	1.52E-02	3.80E-03

APPENDIX C

ChemCad Process Simulation Details

Chemstations ChemCad™ is a commercially available chemical process simulation program. Details can be found at www.chemstations.com. It has an extensive thermodynamic database and numerous thermodynamic models for determining phase equilibrium. It can also model electrolytes in aqueous solution, which is required for this project. Such simulators are especially useful when there are recycle streams present, which require iterative calculations.

For the process flow sheet shown in Figure 6, the input data and unit specifications are detailed here. Although Chemcad contains an extensive database, black liquor is not among the species. The black liquor was modeled as the sum of the inorganic compounds (which are found in the database), plus a model molecule which represents the organic fraction of the liquor, plus water. For the liquor used in this study the molar ratios of C/H/O led to a compound with formula $C_{16}H_{19}O_4$. The properties of this model molecule ("Organic Black Liquor") were copied from a species with the same formula. The resulting black liquor feed stream (1) composition in Figure 6 is thus shown in Table C-1. The oxygen stream was assumed to come from a low grade on-site air separation unit. Such units produce an oxygen stream with roughly 10% nitrogen. Total flow rates for all streams are shown in Table 5 in the main body of the report.

Table C1. Model Black Liquor Properties

Stream		1 Black Liquor properties:			
Property	Units	Overall	Vapor	Liquid	Solid
Temperature deg	C	90			
Pressure	bar	20			
Vapor fraction		0.00E+00			
Critical T deg	C	436.44			
Critical P	bar	318.22			
Std sp. gr. * air	1	2.388			
Deg API		-32.59			
Enthalpy	kJ/h	-9.24E+08	0.00E+00	-3.94E+08	-5.30E+08
Molar flow	kmol/h	1777.141	0	1332.013	445.128
Mass flow	kg/h	122915	0	71199.856	51715.147
Avg. mol. wt.		69.164	0	53.453	116.18
Actual dens	kg/m3	2347.64	0	2204.888	2577.378
Actual vol	m3/h	52.357	0	32.292	20.065
Std liq vol	m3/h	85.917	0	65.853	20.064
Std vapor	m3/h	39832.211	0	29855.265	9976.945
Cp	kJ/kg-K		0	1.664	1.067
Z factor			0	2.51E-02	
Viscosity	cP		0	0.4711	
Thermal cond.	W/m-K		0	0.4913	
Surface tension	dyne/cm			52.9944	

Flowrates in kg/h

Hydrogen	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Carbon Monoxide	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Carbon Dioxide	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Nitrogen	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Oxygen	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Hydrogen Sulfide	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Water	kg/h	2.05E+04	0.00E+00	2.05E+04	0.00E+00
Carbon	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sodium Carbonate	kg/h	3.25E+04	0.00E+00	0.00E+00	3.25E+04
Sodium Sulfate	kg/h	1.89E+04	0.00E+00	0.00E+00	1.89E+04
Sodium Sulfide	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sodium Chloride	kg/h	3.23E+02	0.00E+00	0.00E+00	3.23E+02
(Na2O)(TiO2)3	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
(Na2O)(TiO2)6	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
(Na2O)4(TiO2)5	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Ammonia	kg/h	1.62E+02	0.00E+00	1.62E+02	0.00E+00
Org Black Liquor	kg/h	5.04E+04	0.00E+00	5.04E+04	0.00E+00
Sodium Hydroxide	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Methane	kg/h	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Silicon Dioxide	kg/h	1.35E+02	0.00E+00	1.35E+02	0.00E+00

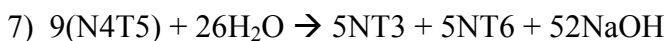
The gasifier includes the following six reactions:

- 1) $\text{C}_{16}\text{H}_{11}\text{O}_4 + 6\text{O}_2 \rightarrow 16\text{CO} + 9.5\text{H}_2$ Conv = 1, $\Delta\text{H} = -1110$ kJ/mol $\text{C}_{16}\text{H}_{11}\text{O}_4$
- 2) $(\text{NT6}) + \text{Na}_2\text{CO}_3 \rightarrow 2(\text{NT3}) + \text{CO}_2$ Conv = 1, $\Delta\text{H} = 15$ kJ/mol NT6
- 3) $5(\text{NT3}) + 9\text{Na}_2\text{CO}_3 \rightarrow 3(\text{N4T5}) + 7\text{CO}_2$ Conv = 0.85, $\Delta\text{H} = 62$ kJ/mol Na_2CO_3
- 4) $2\text{CH}_4 + \text{O}_2 \rightarrow 4\text{H}_2 + 2\text{CO}$ Conv = 1, $\Delta\text{H} = -71.4$ kJ/mol
- 5) $\text{H}_2 + \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ Conv = 1, $\Delta\text{H} = -524.8$ kJ/mol
- 6) $\text{H}_2 + \text{CO}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$ Water-gas-shift equilibrium

The methane reaction was included in case we needed to add some methane to the gasifier to increase the temperature. There should be reactions to reduce the sodium sulfate in the liquor to sodium sulfide, and then form some hydrogen sulfide, however these reactions were inadvertently overlooked. It is of little consequence as the sulfur reactions were not the focus of the work. But it would have been interesting to track the fate of sulfur.

The gas-solid separator leaving the gasifier, and the solid-liquid separator are simple phase separators. For the latter we assume 5% of the water leaves with the solids, which is low without the use of a centrifuge. For the hydrogen membrane, it is assumed that 95% of the hydrogen is recycled back the gasifier.

The leacher is where the N4T5 is hydrolyzed and reforms NT3, NT6, and white liquor. The reaction is:



For the divider leading to the NPE acid wash, 15% of the solids are diverted for NPE removal. In the acid wash, the NPE's are assumed to be 100% dissolved and removed by acid.

The above information as well as the results in Table 5, should be sufficient for someone skilled with ChemCad to reproduce the simulation.

APPENDIX D

Economic Assessment

We intend to compare the proposed process developed in this work (which we will refer to as CFBBLG for Circulating Fluid Bed Black Liquor Gasification) to Larson's [21] cost-benefit study on the use of pressurized HTBLG in conjunction with a conventional lime cycle for caustic recovery.

The reference mill used for this study is an integrated pulp and paper mill producing uncoated freesheet paper from a 65/35 mix of hardwood and softwood. The mill produces about 5.4 MM lbs/day of black liquor solids (BLS). The HTBLG case data from the Larson Study is used for the base case in this study. Table D1 shows the basic data used for the study, and Table D2 shows the chemical recovery data. We will estimate the NPV and IRR for the proposed titanate process assuming the process in the Larson study is already being built. The tables that follow provide the method used in estimating the cost of a titanate recycle system [9] consisting of three leaching stages, and acid wash system, and associated pumps and piping. We will then adjust these results to provide a rough estimate of the total installed cost for the current system consisting of a single leaching stage, acid wash, associate dipping, and a membrane gas separator.

Table D1
Reference Mill Basis Data

Product Flow	md mtpd	1725
Unbleached Pulp Rate	bd stpd	1580
Mill Hardwood/Softwood Mix	% HW, % SW	65% HW, 35% SW
Digester Yield	% for softwood	48.75
	% for hardwood	49.75
Wood To Process (91% of total)	bd stpd	3,208
Hog Fuel (9% of total)	bd stpd	317
Total Wood Used	bd stpd	3,525
Black Liquor Solids Concentration	% solids	80
BL Solids Flow Rate	lb BLS per day	5,419,646
	kg BLS per day	2,458,311
	BLS mtpd	2,458
BL Specific Gravity		1.428
BL Flow	lpm	1,495
BL Energy Content	kJ per kg of BLS (HHV)	13,874
	Btu per lb of BLS (HHV)	5,966
MW, HHV 394.7		
BL Solids Composition, mass%	C	32.97
	H	3.70
	O	36.88
	S	4.27
	Na	20.03
	K	1.93
	Ash/Cl	0.22

Table D2
HTBLG Chemical Recovery Data

Wood charge, mt/d	3,198	
Causticization efficiency, %	81%	
Active Alkali (as Na ₂ O), mtpd	584	
Active Alkali (as Na ₂ O)/Wood	0.183	
Lime availability, %	90%	
White Liquor in lime mud, mtpd	749	
Water for slaking, mtpd	137.5	
Green Liquor TTA, g/l as Na ₂ O	130	
Water in White Liquor, mtpd	5,240	
White Liquor TTA, g/l as Na ₂ O	133	
TTA in Weak Wash, mtpd	87.9	
Black Liquor	mtpd	mtph
BLS	2,458	102
S	105	4.38
Na	492.4	20.52
K	47.5	1.98
Cl	2.7	0.11
Ash	2.7	0.11
*Smelt	mtpd	mtph
Na ₂ S	120.0	5.0
NaOH	20.0	0.8
Na ₂ CO ₃	1005.6	41.9
NaCl	4.5	0.2
Ash	2.7	0.1
TTA	1152.8	48.0

*Note - the Larson Study assumes that potassium and sodium are equivalent and both elements are included in the smelt sodium compounds.

Abbreviations	
Black Liquor Solids	BLS
Bone dry	bd
Hard Wood	HW
Soft Wood	SW
High Temp BLG	HTBLG
Machine Dry	md
Metric Tons	mt
Metric Tons per Day	mtpd
Total Titratable Alkali	TTA
Higher Heating Value	HHV
Short Tons per Day	stpd
Liters per Minute	lpm

The CFBBLG case developed here leads to full direct causticizing (i.e. no lime), hence the conventional caustic plant is shut down. As discussed previously for the economical use of titanate, it must be recovered and recycled back to the black liquor prior to gasification as shown in Figure 6. Following smelt dissolving, titanate remains in the green liquor as a suspended solid. By assuming physical properties of the titanate being similar to lime mud, we can extrapolate to a mill-scale process utilizing a large leaching

tank for 60 minutes reaction residence time, followed by disc filtration. The aqueous phase is white liquor for pulping, and the solids are remixed with black liquor and fed to the gasifier. A portion of the titanate solids stream (10%) is transferred to an acid slurry mix tank. The purpose of the acid slurry tank is to mix hydrochloric acid with the titanate solids. The acid dissolves the NPEs from the titanate. The acid slurry is transferred to a disc filter. Filtrate from the NPE purge filter flows by gravity to an NPE purge filtrate tank. Caustic is added to neutralize the acid. The neutralized filtrate then flows to the sewer. Solids from the NPE purge filter are conveyed to a new black liquor mix tank. Titanium dioxide makeup is added to the black liquor mix tank as well via a screw conveyor. It is assumed that the mill already has available hydrochloric acid and caustic make-down and delivery systems. Potassium remains in the system either as potassium titanate or potassium hydroxide and carbonate. Potassium lowers the melting point of recovery boiler ash and is a primary cause of boiler tube pluggage in Tomlison recovery boilers. In a CFBBLG system, the potassium poses no problem. A new agitated heavy (50%) black liquor mix tank is required to recycle the titanate prior to the black liquor concentrator. This allows the 85% solids titanate recycle stream to be uniformly mixed prior to concentrating the black liquor to 80% solids for gasification. The titanate suspended solids flow is substantial, adding about 40% to the overall mass flow of the [dry basis] black liquor. The black liquor volume flow increases about 20%. Although no increase to the evaporation capacity of the black liquor concentrator is required, modifications are required to increase the hydraulic capacity. Primarily pump and motor upgrades are required. An allowance will be included in the capital estimate to cover concentrator upgrades for the increased liquor flow. The additional suspended solids should enhance the crystallization process and reduce fouling for 80% solids liquor production by providing sites for crystallization to take place rather than on heat transfer surface areas.

Total Installed Cost

The Sinquefeld/Cantrell study [9] utilized Jacob's extensive database of equipment pricing. The estimates were (and will be) +/- 30% accuracy factored total installed cost (TIC). The estimates will be based on preliminary process flow diagrams, priced equipment lists, and project scope descriptions. The key flow rates are shown in Table D3 below.

Titanate ChemCad Balance Basis and Assumptions	
Smelt	(w/o potassium)
Na ₂ CO ₃ , mt/hr	4.76
NaOH, mt/hr	0.79
Na ₂ S, mt/hr	4.73
HCl, mt/hr	0.67
NPEs (Dissolved), mt/hr	3.15
Inerts (Suspended), mt/hr	1.46
Black Liquor Sodium Carbonate Converted, %	88.0
Leaching Caustic Recovery, %	86.1
Titanate Split to NPE Purge, %	10
HCl ratio to Treated Solids, kg/kg	0.1

Equipment pricing in [9] was obtained from Andritz for disc filters and leaching tank agitators. Pump pricing was obtained from ITT Goulds. All other equipment pricing was obtained from Jacobs' historical database. Piping, structural, electrical, and controls material and equipment were factored based on the process equipment direct cost. The estimates assumed an engineering, procurement, and construction management (EPC) type contract to execute the project. The estimates assumed a site in the southeastern United States, non-union, and no escalation was included. Other estimating assumptions are listed in Table D4 below.

Table D4
Capital Estimates Assumptions

General Information	
Basis of Premium Time	100% of the hours worked on 50-hour weeks
Per Diem Requirements	Per Diem at \$5.00 per hour on 100% of hours
Constructability	Unknown – depending on site
Construction Support Labor	20% of direct labor
Non Payroll Insurance, Taxes, Permits	
Sales Tax	5% of TIC
Building Permits	Allowance provided for building permits
Environmental Permits	Unknown – depending on site
Construction Management	4% of TIC
Engineering	10% of TIC for titanate
Outside Consultants	DCS configuration, soils testing, and outside survey
Owner's Cost	4% of TIC
Spare Parts	5% of equipment cost
Check-Out & Commissioning	5% of engineering and allowances for vendors
Allowance for Unforeseen	10% on all costs which equates to 8.33% of TIC
Escalation	0%, Estimated in today's costs (2009)

The net result of the above cost model yielded the prices shown in Table D5 below. Details can be found in [9].

Table D5
Summary of Total Installed Cost of [9]

CONSTRUCTION DIRECT COSTS		Totals
MAJOR EQUIPMENT		\$13,285,767
DEMOLITION		\$0
SITE EARTHMOVING		\$0
SITE IMPROVEMENTS		\$0
PILING, CAISSONS		\$0
BUILDINGS		\$630,000
CONCRETE		\$398,573
MASONRY, REFRACTORY		\$0
STRUCTURAL STEEL		\$262,660
ROOFING AND SIDING		\$0
FIRE PROOFING		\$0
PROCESS DUCTWORK (NON-BUILDING)		\$0
PIPING		\$2,759,363
INSULATION – PIPE, EQUIPMENT & DUCTWORK		\$0
INSTRUMENTATION		\$2,125,723
ELECTRICAL		\$611,357
PAINTING, PROTECTIVE COATINGS		\$0
FURNITURE, LAB & SHOP EQUIPMENT		\$0
Total Direct Costs		\$20,073,442
CONSTRUCTION INDIRECT		
CONSTRUCTION SUPPORT LABOR		\$292,456
TEMPORARY CONSTRUCTION FACILITIES (IN WAGE RATES)		\$0
PREMIUM TIME		\$192,365
CRAFT FRINGE BENEFITS (IN WAGE RATES)		\$0
CRAFT PER DIEM (\$5 PER HOUR ON 100 % OF THE HOURS)		\$382,367
PAYROLL TAXES & INSURANCE (IN WAGE RATES)		\$0
SMALL TOOLS (IN WAGE RATES)		\$0
CONSUMABLE SUPPLIES (IN WAGE RATES)		\$0
CONSTRUCTION EQUIPMENT (IN WAGE RATES)		\$0
FIELD STAFF (IN WAGE RATES)		\$0
NON-PAYROLL TAX, INSURANCE & PERMITS		\$156,897
CONSTRUCTION HOME OFFICE COST (IN WAGE RATES)		\$0
CRAFT START-UP ASSISTANCE		\$20,304
CONTRACTOR'S CONSTRUCTION OVERHEAD & FEE		\$835,157
Total Indirect		\$1,879,546
Total Construction Costs (TCC)		\$21,952,988
PROJECT INDIRECT		
CONSTRUCTION MANAGEMENT	4.00% of TIC	\$1,262,297
ENGINEERING PROFESSIONAL SERVICES	10.00% of TIC	\$3,156,840
STUDY COST	0.00% of TIC	\$0
OUTSIDE CONSULTANT SERVICES	0.22% of TIC	\$70,000
OWNER'S COST	4.00% of TIC	\$1,262,297
SPARE PARTS	2.16% of TIC	\$680,189
NON-CRAFT START-UP ASSISTANCE	0.98% of TIC	\$307,842
ALLOWANCE FOR UNFORESEEN	9.09% of TIC	\$2,869,245
ESCALATION (EXCLUDED - DATES UNKNOWN)	0.00% of TIC	\$0
ROUND OFF		(\$697)
Total Installed Cost (TIC)		\$31,561,000

To use the extensive work done in [9] for an estimate of the titanate system proposed here we will make the following corrections to the model in Table D5:

- Add \$3MM to ‘major equipment’ for the membrane gas separator.
- Reduce the \$9.5MM cost of the leaching system agitators and pumps [9] by 60% to correct for one leaching stage versus three leaching stages in [9].
- Correct the TCC from 2006 to current price. The Chem Engr Plant cost index for Sept 2006 was 513, and for Sept. 2009 was 525.7
- Assume other construction direct and indirect costs are close enough to use for this study.

Adding the above corrections to Table D5 produces the results in Table D6 below. The TIC of \$27,477,000 will be used to compute the IRR and NPV of the current proposed design.

Table D6
Summary of Total Installed Cost of Proposed Process

Total Construction Costs, TCC		\$19,111,877
Construction Management	4.00% of TIC	\$764,388
Engineering Professional Services	10.00% of TIC	\$1,911,636
Study Cost	0.00% of TIC	\$0
Outside Consultant Services	0.22% of TIC	\$42,389
Owner’s Cost	4.00% of TIC	\$764,388
Spare Parts	2.16% of TIC	\$411,891
Non-Craft Start-Up Assistance	0.98% of TIC	\$186,415
Allowance for Unforeseen	9.09% of TIC	\$1,737,482
Escalation (excluded – dates unknown)	0.00% of TIC	\$0
Round Off		(\$312)
Total Installed Cost (TIC)		\$27,477,000

Operating Costs

Next we estimate the operating costs for the 25 year project life, and from that, calculate the IRR and NPV. Table D7 shows the chemicals, fuel oil, and electricity costs based on 2009 prices.

Table D7
Chemicals, Fuel Oil, and Electricity Costs (2009)

#6 Fuel Oil , \$/MMBtu	\$14.00
Electricity , \$/MWh	\$70.00
Titanium Dioxide, \$/mt	\$480.00
Hydrochloric Acid, \$/mt	\$135.00
Sodium Hydroxide, \$/mt	\$370.00

Table D8 shows chemicals, fuel oil, and electricity usage or savings as compared to the base case (i.e. the costs over and above the base case of a BLG-based recovery island using a lime cycle).

Table D8
Annual Chemicals, Fuel Oil, and Electricity Usages [9]

Fuel Oil Savings	217,386	1,086,928 MMBtu/yr
Electricity Savings	4,310	7,038 MWh/yr
Titanium Dioxide Usage		3,951 mt/yr
Hydrochloric Acid Usage		5,559 mt/yr
Sodium Hydroxide Usage		3,912 mt/yr

Table D9 shows the costs or savings items. Avoided cost savings are treated as positive cash flow. The annual maintenance cost for the base case is based on 5% of the capital cost of a new lime kiln and caustic plant of similar capacity. This capital cost is approximately \$35,000,000.

Table D9
Annualized O&M Costs

	Annual \$	
	Base	Titanate
Avoided Cost Savings		
Avoided Lime Kiln Fuel Oil (@\$10/MMBtu)		10,869,280
Avoided Electricity Purchases		422,282
Total		11,291,562
Direct Operating Costs		
Titanate		1,896,391
Hydrochloric Acid		750,454
Sodium Hydroxide		1,447,375
Incremental Waste Treatment Costs (.10 KW/lpm)		30,521
Operations & Maintenance	1,750,000	1,373,850
Total	1,750,000	5,498,591

Both the internal rate of return (IRR) and net present value (NPV) analyses will be performed relative to the base case. The key inputs to the analyses are the TIC for the titanate system, and the net difference in operating costs between the titanate system and the lime cycle. Table D10 shows the economic assumptions used for the analyses.

Table D10
Economic Assumptions

Financial Parameters	
Annual Inflation Rate	4.0%
Debt Fraction of Capital	50%
Equity Fraction of Capital	50%
Interest Rate on Debt	8.0%
Return on Equity	15%
Resulting Discount Rate used for NPV calculations	9.9% (after tax)
Income Tax Rate (combined Federal & State)	40%
Economic Life (years)	25
Depreciation Method	20-year MACRS ¹
Construction Time	1 yr
Mill Assumptions	
Annual Operating Hours	8,330
Annual O&M Costs, % of Capital Cost	5%
Start-up Assumptions	
Year 1 of Operation	100%
(1 – Modified Accelerated Cost Recovery System (MACRS) per IRS Tax Code)	

Table D11 on the following page shows the annualized costs at \$10/MMBtu for fuel. The numbers change for each value of fuel cost. The IRR is the discount rate at which the net present value (NPV) is zero. This is done using goal seek with the spreadsheet and comes out to 26.7% for an NPV of \$27.8M. Both the NPV and IRR are strongly dependent on the price of the fuel oil displaced. Lime kilns use considerable fuel in the form of bunker oil or natural gas. Table D12 shows the NPV and IRR for our proposed process as a function of the cost of displaced kiln fuel.

Table D12
NPV and IRR as a Function of Fuel Cost

\$/MMBtu displaced (i.e. oil or NG price)	NPV, \$MM	IRR, %
\$6/MMBtu	\$(6.6)	4.5%
\$8	\$10.6	16.8%
\$10	\$27.8	26.7%
\$12	\$45.0	36.3%
\$14	\$62.2	46.3%

Table D11
Annual Costs for the Proposed Process

Titanate Case

Year -->	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Avoided Cost Savings																
Avoided Lime Kiln Fuel Oil		11,304,051	11,756,213	12,226,462	12,715,520	13,224,141	13,753,107	14,303,231	14,875,360	15,470,375	16,089,190	16,732,757	17,402,067	18,098,150	18,822,076	19,574,959
Avoided Electricity Purchases		439,173	456,740	475,009	494,010	513,770	534,321	555,694	577,921	601,038	625,080	650,083	676,086	703,130	731,255	760,505
Subtotal - Avoided Cost Savings		11,743,224	12,212,953	12,701,471	13,209,530	13,737,911	14,287,428	14,858,925	15,453,282	16,071,413	16,714,269	17,382,840	18,078,154	18,801,280	19,553,331	20,335,464
Direct Operating Costs																
Titanium Dioxide		1,972,247	2,051,136	2,133,182	2,218,509	2,307,250	2,399,540	2,495,521	2,595,342	2,699,156	2,807,122	2,919,407	3,036,183	3,157,630	3,283,936	3,415,293
Hydrochloric Acid		780,472	811,691	844,159	877,925	913,042	949,564	987,546	1,027,048	1,068,130	1,110,855	1,155,290	1,201,501	1,249,561	1,299,544	1,351,526
Sodium Hydroxide		1,505,270	1,565,481	1,628,100	1,693,224	1,760,953	1,831,391	1,904,647	1,980,833	2,060,066	2,142,468	2,228,167	2,317,294	2,409,986	2,506,385	2,606,640
Incremental Waste Treatment Costs		31,742	33,012	34,332	35,706	37,134	38,619	40,164	41,771	43,441	45,179	46,986	48,866	50,820	52,853	54,967
Operations & Maintenance		1,428,804	1,485,956	1,545,394	1,607,210	1,671,499	1,738,359	1,807,893	1,880,209	1,955,417	2,033,634	2,114,979	2,199,578	2,287,561	2,379,064	2,474,226
Subtotal - Operating Costs		5,718,535	5,947,276	6,185,168	6,432,574	6,689,877	6,957,472	7,235,771	7,525,202	7,826,210	8,139,259	8,464,829	8,803,422	9,155,559	9,521,781	9,902,652
Financing																
Interest	1,055,117	1,011,154	967,190	923,227	879,264	835,301	791,338	747,374	703,411	659,448	615,485	571,522	527,558	483,595	439,632	395,669
Principal	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540
Cumulative Principal	549,540	1,099,080	1,648,620	2,198,160	2,747,700	3,297,240	3,846,780	4,396,320	4,945,860	5,495,400	6,044,940	6,594,480	7,144,020	7,693,560	8,243,100	8,792,640
Subtotal - Financing	1,604,657	1,560,694	1,516,730	1,472,767	1,428,804	1,384,841	1,340,878	1,296,914	1,252,951	1,208,988	1,165,025	1,121,062	1,077,098	1,033,135	989,172	945,209
Total Expenses Before Taxes	1,604,657	7,279,229	7,464,007	7,657,935	7,861,378	8,074,718	8,298,350	8,532,686	8,778,153	9,035,198	9,304,283	9,585,890	9,880,520	10,188,694	10,510,953	10,847,861
Income Taxes	(1,143,373)	1,236,058	1,406,971	1,578,222	1,749,527	1,921,265	2,093,824	2,260,232	2,399,788	2,544,222	2,693,731	2,848,406	3,008,790	3,174,661	3,346,687	3,524,668
Total Expenses After Taxes	461,284	8,515,287	8,870,978	9,236,157	9,610,905	9,995,983	10,392,174	10,792,917	11,177,941	11,579,420	11,998,014	12,434,297	12,889,310	13,363,355	13,857,641	14,372,529
Net Cash Flow from Operations	(461,284)	3,227,937	3,341,975	3,465,314	3,598,625	3,741,928	3,895,254	4,066,007	4,275,341	4,491,993	4,716,255	4,948,544	5,188,844	5,437,925	5,695,691	5,962,936
Equity Capital Invested	(13,738,500)															
Total Net Cash Flow	(14,199,784)	3,227,937	3,341,975	3,465,314	3,598,625	3,741,928	3,895,254	4,066,007	4,275,341	4,491,993	4,716,255	4,948,544	5,188,844	5,437,925	5,695,691	5,962,936
Discount Factor	1.0	1.1	1.2	1.3	1.5	1.6	1.8	1.9	2.1	2.3	2.6	2.8	3.1	3.4	3.7	4.1
NPV (\$ million)	\$27.8	(14,199,784)	2,937,158	2,766,992	2,610,655	2,466,867	2,334,033	2,210,801	2,099,831	2,009,043	1,920,701	1,834,934	1,751,874	1,671,469	1,593,908	1,447,087
IRR	26.7%															
Total Capital Invested	27,477,000															
Discount Rate	1.099															

Table D11 (continued)

Titanate Case

	16	17	18	19	20	21	22	23	24	25
Avoided Cost Savings										
Avoided Lime Kiln Fuel Oil	20,357,958	21,172,276	22,019,167	22,899,934	23,815,931	24,768,568	25,759,311	26,789,683	27,861,271	28,975,722
Avoided Electricity Purchases	790,925	822,562	855,465	889,683	925,271	962,282	1,000,773	1,040,804	1,082,436	1,125,733
Subtotal - Avoided Cost Savings	21,148,883	21,994,838	22,874,632	23,789,617	24,741,202	25,730,850	26,760,084	27,830,487	28,943,707	30,101,455
Direct Operating Costs										
Titanium Dioxide	3,551,905	3,693,981	3,841,740	3,995,410	4,155,226	4,321,435	4,494,293	4,674,064	4,861,027	5,055,468
Hydrochloric Acid	1,405,587	1,461,810	1,520,282	1,581,094	1,644,337	1,710,111	1,778,515	1,849,656	1,923,642	2,000,588
Sodium Hydroxide	2,710,906	2,819,342	2,932,116	3,049,401	3,171,377	3,298,232	3,430,161	3,567,367	3,710,062	3,858,465
Incremental Waste Treatment Costs	57,166	59,453	61,831	64,304	66,876	69,551	72,333	75,227	78,236	81,365
Operations & Maintenance	2,573,195	2,676,123	2,783,168	2,894,495	3,010,275	3,130,686	3,255,913	3,386,149	3,521,595	3,662,459
Subtotal - Operating Costs	10,298,759	10,710,709	11,139,137	11,584,703	12,048,091	12,530,015	13,031,215	13,552,464	14,094,562	14,658,345
Financing										
Interest	351,706	307,742	263,779	219,816	175,853	131,890	87,926	43,963	0	
Principal	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	549,540	
Cumulative Principal	9,342,180	9,891,720	10,441,260	10,990,800	11,540,340	12,089,880	12,639,420	13,188,960	13,738,500	
Subtotal - Financing	901,246	857,282	813,319	769,356	725,393	681,430	637,466	593,503	549,540	
Total Expenses Before Taxes	11,200,004	11,567,991	11,952,456	12,354,059	12,773,484	13,211,444	13,668,682	14,145,967	14,644,102	14,658,345
Income Taxes	3,709,288	3,900,365	4,098,606	4,303,850	4,945,684	5,227,578	5,456,377	5,693,624	5,939,658	6,177,244
Total Expenses After Taxes	14,909,292	15,468,356	16,051,063	16,657,908	17,719,168	18,439,022	19,125,058	19,839,591	20,583,760	20,835,589
Net Cash Flow from Operations	6,239,591	6,526,482	6,823,569	7,131,709	7,022,034	7,291,827	7,635,025	7,990,896	8,359,947	9,265,866
Equity Capital Invested										
Total Net Cash Flow	6,239,591	6,526,482	6,823,569	7,131,709	7,022,034	7,291,827	7,635,025	7,990,896	8,359,947	9,265,866
Discount Factor	4.5	5.0	5.5	6.0	6.6	7.3	8.0	8.8	9.6	10.6
NPV (\$ million)	1,377,822	1,311,349	1,247,536	1,186,417	1,062,941	1,004,349	956,888	911,273	867,479	874,870
IRR										
Total Capital Invested										
Discount Rate										

Direct Causticizing for Black Liquor Gasification in a
Circulating Fluidized Bed

Final Project Report
DE-FG36-06GO16042

LAST PAGE