

**Project Title: Integration of the Mini-Sulfide Sulfite Anthraquinone (MSS-AQ) Pulping Process and Black Liquor Gasification in a Pulp Mill**

DOE Award No: DE-FG3606GO16041

Project Period: 9/2006-12/2008

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Acknowledgment: “This report is based upon work supported by the U. S. Department of Energy under Award No. DE-FG3606GO16041.

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## Executive Summary

### **Integration of the Mini-Sulfide Sulfite Anthraquinone (MSS-AQ) Pulping Process and Black Liquor Gasification in a Pulp Mill**

As many of the recovery boilers and other pieces of large capital equipment of U.S. pulp mills are nearing the end of their useful life, the pulp and paper industry will soon need to make long-term investments in new technologies. The ability to install integrated, complete systems that are highly efficient will impact the industry's energy use for decades to come. Developing a process for these new systems is key to the adoption of state-of-the-art technologies in the Forest Products industry.

This project defined an integrated process model that combines mini-sulfide sulfite anthraquinone (MSS-AQ) pulping and black liquor gasification with a proprietary desulfurization process developed by the Research Triangle Institute. Black liquor gasification is an emerging technology that enables the use of MSS-AQ pulping, which results in higher yield, lower bleaching cost, lower sulfur emissions, and the elimination of causticization requirements. The recently developed gas cleanup/absorber technology can clean the product gas to a state suitable for use in a gas turbine and also regenerate the pulping chemicals needed to for the MSS-AQ pulping process. The combination of three advanced technologies into an integrated design will enable the pulping industry to achieve a new level of efficiency, environmental performance, and cost savings. Because the three technologies are complimentary, their adoption as a streamlined package will ensure their ability to deliver maximum energy and cost savings benefits. The process models developed by this project will enable the successful integration of new technologies into the next generation of chemical pulping mills.

When compared to the Kraft reference pulp, the MSS-AQ procedures produced pulps with a 10-15 % yield benefit and the ISO brightness was 1.5-2 times greater. The pulp refined little easier and had a slightly lower apparent sheet density (In both the cases). At similar levels of tear index the MSS-AQ pulps also produced a comparable tensile and burst index pulps. Product gas composition determined using computer simulations The results demonstrate that RVS-1 can effectively remove > 99.8% of the H<sub>2</sub>S present in simulated synthesis gas generated from the gasification of black liquor. This level of sulfur removal was consistent over simulated synthesis gas mixtures that contained from 6 to 9.5 vol % H<sub>2</sub>S. A significant amount of the sulfur in the simulated syngas was recovered as SO<sub>2</sub> during regeneration. The average recovery of sulfur as SO<sub>2</sub> was about 75%. Because these are first cycle results, this sulfur recovery is expected to improve. Developed WINGems model of the process. The total decrease in variable operating costs for the BLG process compared to the HERB was in excess of \$6,200,000 per year for a mill producing 350,000 tons of pulp per year. This represents a decrease in operating cost of about \$17.7/ton of oven dry pulp produced. There will be additional savings in labor and maintenance cost that has not been taken into account. The capital cost for the MSSAQ based gasifier system was estimated at \$164,000,000, which is comparable to a High Efficiency Recovery Boiler. The return on investment was estimated at 4%.

A gasifier replacement cannot be justified on its own, however if the recovery boiler needs to be replaced the MSSAQ gasifier system shows significantly higher savings.

Before black liquor based gasifier technology can be commercialized more work is necessary. The recovery of the absorbed sulfur in the absorbent as sulfur dioxide is only 75%. This needs to be greater than 90% for economical operation. It has been suggested that as the number of cycles is increased the sulfur dioxide recovery might improve. Further research is necessary. Even though a significant amount of work has been done on a pilot scale gasifiers using liquors containing sulfur, both at low and high temperatures the lack of a commercial unit is an impediment to the implementation of the MSSAQ technology. The

implementation of a commercial unit needs to be facilitated before the benefits of the MSSAQ technology with ZnO absorption will become acceptable to the paper industry.

## Introduction

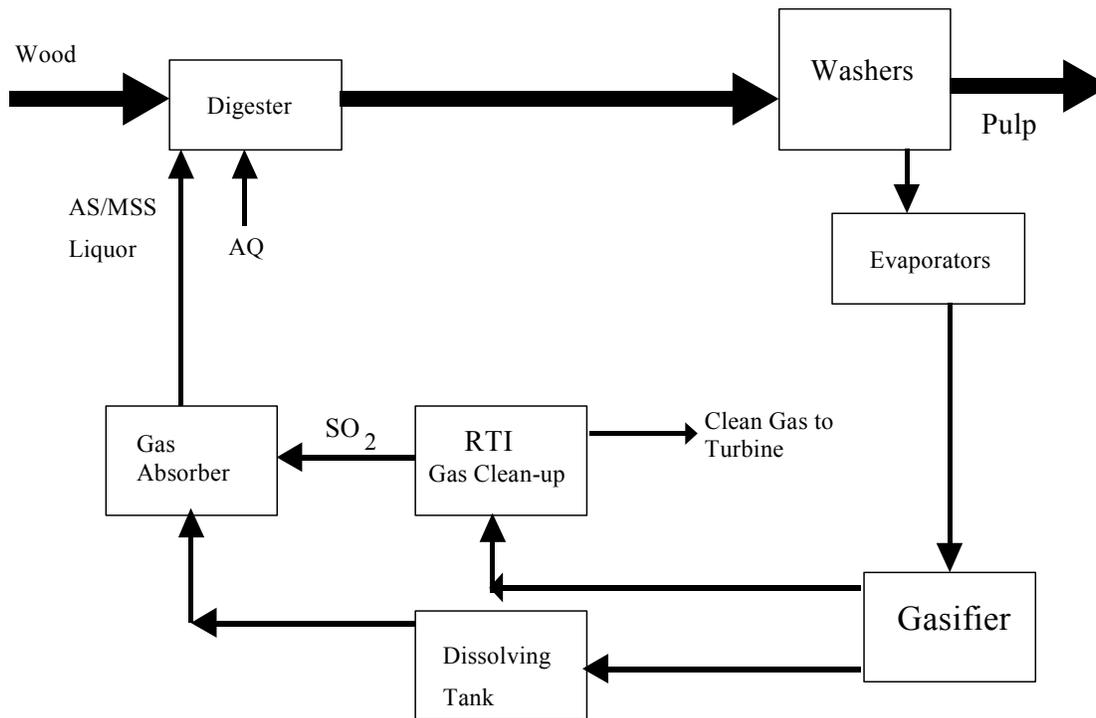
The Mini-Sulfide-Sulfite AQ (MSS-AQ) pulping process was investigated in Sweden in the mid 1980's. The pulping liquor consists of a mixture of sodium sulfide (15% of the total alkali) and sodium sulfite (85% of the total alkali). The MSS-AQ process has some unique features as compared to the existing kraft process, namely:

- Pulp yield is significantly higher at equivalent Kappa number. At a kappa number of 100 (linerboard) the yield from MSS-AQ is 67-69% as compared to 54% for the kraft process.
- The brightness of the MSS-AQ linerboard pulp at 30% ISO is considerably higher than the brightness of the corresponding kraft pulp: 15% ISO. This would be a considerable advantage for high quality printing on corrugated boxes. MSS-AQ pulps also have improved bleachability which will result in significant savings in bleaching chemicals (1-2).
- With black liquor gasification, the chemical recovery process is simplified. The caustic plant and lime kiln are eliminated along with the associated energy usage. This will result in a significant capital savings, especially for greenfield mills and mills with major rebuilds.
- Lower TRS emissions, resulting in a low odor mill.

Despite these very significant advantages, the development of the MSS-AQ processes was not pursued more aggressively because of the lack of an attractive chemical recovery process (3-4).

Black liquor gasification is one emerging technology that would enable the implementation of the MSS-AQ pulping, allowing industry to take advantage of the higher yield, lower bleaching cost, lower TRS and the elimination of causticization requirements described above. However, a bottleneck in the implementation of the black liquor gasification process has been the gas clean-up and regeneration of the pulping chemicals. The recently developed gas cleanup/absorber technology from the DOE/Research Triangle Institute can be integrated into a pulp mill to clean the product gas and also generate the pulping chemicals necessary for the MSS-AQ process. The process schematic is shown in Figure 1. The product gases from the black liquor gasifier are fed to the RTI absorber where the sulfur containing compounds are absorbed in the ZnO bed. The clean gas can then be fed to the turbine generators for high efficiency power generation. When the absorber bed is regenerated using air the sulfur is desorbed as sulfur dioxide which is the source for the active chemical for the alkaline pulping processes. The RTI absorber serves the dual purpose of cleaning up the product gas and also regeneration of the chemicals.

With the successful implementation of black liquor gasification and the RTI gas absorption technology, it would be possible to reinvent the traditional chemical recovery operations of modern pulp mills by eliminating the lime kiln and recausticizing operations. The yield and bleachability improvements from the MSS-AQ process would be additional.



**Figure 1: Schematic of the MSS-AQ Pulping Processes with the RTI Absorber**

This project demonstrates the potential savings and the viability of integrating these three technologies. One shortcoming is that all three of the technologies have to be available on a commercial scale.

## Background

In the conventional kraft recovery cycle, the sodium and the sulfur ratio is fixed by the sulfidity of the liquor. Using black liquor gasification the sodium and the sulfur can be split into two separate fractions. This separation of the sodium and the sulfur creates some opportunities in the pulping process, which can lead to production cost savings or improved operations. The splitting of the sodium and the sulfur can be taken advantages of with the following technologies:

- Split Sulfidity Pulping
- Polysulfide Pulping
- Mini-Sulfide Sulfite AQ Process (MSSAQ)

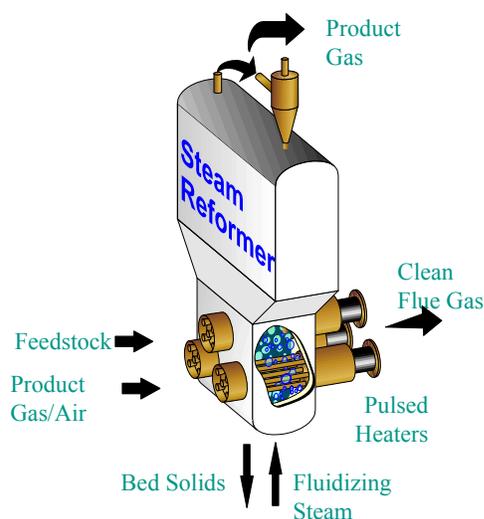
Split sulfidity and polysulfide pulping are the technologies most often discussed in conjunction with black liquor gasification and are being further evaluated in other projects. MSS-AQ pulping would require for a more radical change to the pulping process but the benefits would be much more significant and would represent a breakthrough technology for society and the paper industry.

In this proposal, black liquor gasification is being combined with the RTI gas absorption and MSS-AQ pulping to reinvent the traditional chemical recovery operations of modern pulp mills by eliminating the lime kiln and recausticizing operations and also increasing the pulping yield and improving bleachability.

## *Black Liquor Gasification*

In cooperation with the DOE, MTCI and its affiliate, ThermoChem Recovery International, Inc., have developed a steam reforming technology that is uniquely capable of processing a wide spectrum of organic feedstocks to produce a hydrogen-rich, medium-Btu reformat gas.

The march towards commercialization however has been slow due to softening of pulp prices and a lack of full-scale system in successful commercial operation. Recent DOE awards for full-scale demonstration of this technology however have tilted the balance and are on target to meet the required process performance metrics. A black liquor demonstration project was under way at the Georgia-Pacific Mill in Big Island, Virginia. This demonstration should provide performance, operability, reliability, availability, and maintainability data on the technology and help prospective buyers gain confidence. However this gasifier has been shut down recently. A similar TRI unit is supporting the full mill at Norampac in Trenton, Ontario, Canada.



**Figure 2: PulseEnhanced™ Steam Reformer**

A simplified schematic of the black liquor gasifier system is shown in Figure 2. It consists of a fluidized bed reactor that is indirectly heated by multiple resonance tubes of one or more pulse combustion modules. Feedstock such as spent liquor or biomass is fed to the reactor, which is fluidized with superheated steam from a waste heat recovery boiler. The organic material injected into the bed undergoes a rapid sequence of vaporization and pyrolysis reactions. Higher hydrocarbons released among the pyrolysis products are steam cracked and partially reformed to produce low molecular weight species. Residual char retained in the bed is more slowly gasified by reaction with steam. The sulfur and sodium are separated in that the sulfur reports mostly to the gas stream and the sodium stays in solid form. Product gases are routed through a cyclone to remove bulk of the entrained particulate matter and are quenched and scrubbed in a venturi scrubber. A portion of the medium-Btu product gases is supplied to the pulse combustion modules and combustion of these gases provides the heat necessary for the indirect gasification process. The inorganic chemical in the feedstock is recovered and recombined with sulfur from the gas stream to recycle the product to the mill.

The products of combustion exit from the resonance tubes completely segregated from the reformat product gases. Hot flue gases from the steam reformer are used to generate steam and to preheat the pulsed heater combustion air. Excess fuel gas is exported for use in a boiler or gas turbine or fuel cell.

The process uses only a single reactor; it does not require solids recirculation and handling equipment and it can be easily controlled by varying the gas-firing rate.

#### *Mini-sulfite sulfide AQ (MSS-AQ) Pulping*

The MSS-AQ was developed as a new cooking process at STFI, in which a small amount of sulfide is used in an alkaline sulfite AQ pulping process. The amount of sulfide used can vary from 5-20% as total chemical. The total charge of alkali, at about 22% Na<sub>2</sub>O on OD wood, is higher than for the kraft process (20%). The delignification rate is slower than for the kraft process and higher pulping temperatures (+ 18 F) and addition of anthraquinone (0.15% on OD wood) is required to obtain acceptable pulping rates. Dahlbom et al (2) also showed that at a sulfide-sulfite ratio of about 0.1 resulted in the best pulping rates. The MSS-AQ pulps were shown to have 8-10% higher yield at kappa number of 50-100 (1-2). They also note that the odor from the MSS-AQ process could be 90% less than that of the kraft process.

#### *Research Triangle Institute (RTI) Absorber*

RTI has developed durable zinc oxide based regenerable desulfurization sorbents, and confirmed that these sorbents are reproducible on a commercial scale. Tests of up to 50 cycles of sulfidation and regeneration have been satisfactorily conducted in RTI's Bench Scale High Temperature High Pressure Reactor system. The primary application for the technology has been removal of reduced sulfur compounds from hot coal derived synthesis gases and recovery of concentrated SO<sub>2</sub> streams. Tests were conducted at 260 to 530°C and at pressures from 240 to 2000 kPa. In fixed bed sulfidation reactor tests, inlet H<sub>2</sub>S levels were decreased from percent levels to ppm levels. The sorbent capacity at breakthrough was as high as 17% S. The sorbent was regenerated with 3.5% oxygen at 566°C.

This technology was extended to recover sulfur from black liquor gasification. The conventional approach to processing black liquor is based on combustion of the black liquor in a Tomlinson boiler. The conventional kraft mill processes the ash from the Tomlinson boiler, which contains both alkali minerals and sulfur species, to generate the cooking liquor for pulping. Because the ash contains both alkali minerals and sulfur species, the alkali and sulfur components of the cooking liquor must be processed together. Black liquor gasification separates the alkali minerals into the ash and releases gaseous sulfur species into the syngas.

Initial experiments in RTI's Bench Scale Reactor System tested the ability of RVS-1 sorbent to remove H<sub>2</sub>S from a simulated syngas stream generated from black liquor gasification containing 2 vol% CH<sub>4</sub>, 4 vol% H<sub>2</sub>S, 41.5 vol% H<sub>2</sub>, 5 vol% CO, 22.5 vol% CO<sub>2</sub> and 25 % H<sub>2</sub>O. Results of cycle-by-cycle breakthrough data indicated that the sulfur capacity progressively decreased. This problem was eliminated by introducing a 30 minute reductive regeneration (exposure of the sorbent to a sulfur free syngas) before sulfidation and performing regeneration with 2 vol% O<sub>2</sub> at a starting temperature of 1200°F.

A 20-Cycle test was then conducted at 538°C. The RVS-1 sorbent consistently decreased the inlet H<sub>2</sub>S concentration of 40,000 ppmv to about 30 ppmv. Although there was some initial decline in the sulfur capacity of RVS-1, the sulfur capacity eventually stabilized. A mixture of 2% oxygen/balance nitrogen was used for sorbent regeneration. No significant changes in performance were observed between Cycles 4 and 18.

#### *Project Objectives*

This technology has potential for both unbleached and bleached mills. The proposed target will be a linerboard mill. Work that needs to be done to define the next generation mill process will include definition of the process changes necessary to generate the MSSAQ pulping liquors using black liquor gasification, identification of process conditions and the potential benefits and a preliminary process design.

The followings tasks will need to be completed to meet the above objectives:

1. Define the pulping process conditions necessary to achieve the highest yield and optimum product characteristics
2. Use MSSAQ liquors in the lab scale to define the product gas composition and identify design parameters for a black liquor gasifier system
3. Trials on a pilot scale RTI absorber with the appropriate product gas compositions to quantify the adsorption and desorption characteristics with MSS-AQ product gas compositions and identify design parameters for an absorber
4. Define the process and equipment changes required in an existing batch and continuous digester mill to integrate the MSS-AQ process along with BLG and RTI absorption technology.
5. Develop a WINGems process model for detailed economic evaluation and process impact
6. Provide a conceptual design and economic benefit analysis for the conversion of an existing kraft linerboard mill to the MSS-AQ/BLG/RTI absorber process

## **Body of the Report**

### Objective 1: Define the pulping process conditions necessary to achieve the highest yield and optimum product characteristics

This work was performed by North Carolina State University with help from Andritz and Packaging Corporation of America.

#### *MSSAQ Pulping*

##### *Mini-Sulfide-Sulfite Pulping methods*

A procedure was developed for laboratory pulping exploring methods using anthraquinone. The laboratory cooks consisted of a batch procedure where the pulping liquor and anthraquinone was charged to an M&K digester. The digester was then brought to the selected cooking temperature and maintained at temperature until the desired h factor was reached and the cook terminated. The obtained pulps were defibered by two passes on a disc refiner with gaps 0.010 and 0.005 mm, then screened prior to refrigerated storage.

Standard laboratory Kraft pulps were prepared and used as a baseline for comparisons made from the MSS-AQ pulps. Two MSS-AQ procedures were explored where the amount of NaOH and Na<sub>2</sub>S charged to the system was varied. The breakdown of charged chemicals for the Kraft baseline cooks and the MSS-AQ cooks are shown in Table 1, and outline the differences between the procedures with respect to chemicals used and their relative amounts.

**Table 1. Chemicals charged in Kraft and MSS-AQ Pulping**

Pulping Method	Total Chemical Charge (% as Na <sub>2</sub> O on OD wood)	Component % of total chemical charge				AQ
		Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> S	NaOH	Na <sub>2</sub> CO <sub>3</sub>	
Kraft	17.6% TTA	0	21	64	15	0
MSS-AQ (Different Split) With NaOH						
	22.0% TC	75	10	5	10	0.1
	22.0% TC	75	5	10	10	0.1
	22.0% TC	70	15	5	10	0.1
	22.0% TC	70	10	10	10	0.1
	22.0% TC	65	15	10	10	0.1
MSS-AQ (Different Split) Without NaOH						
	22.0% TC	85	5	0	10	0.1
	22.0% TC	80	10	0	10	0.1
	22.0% TC	75	15	0	10	0.1
	22.0% TC	70	20	0	10	0.1

The amounts of total titratable alkali, TTA, and total chemical, TC, used in these procedures fall in the typical range for each respective pulping method. Kraft pulping utilizes no Na<sub>2</sub>SO<sub>3</sub>, whereas mini-sulfide sulfite pulping employs a mixture of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub> being the major component, but only a small amount or no NaOH. Na<sub>2</sub>CO<sub>3</sub> represents a system dead load not having been converted to active cooking chemical. The amount of AQ charged in each procedure was held constant at 0.1 % on oven dry wood, OD, basis. The most noteworthy difference between the procedures is the amount of NaOH used in the pulping liquor. In the Kraft procedure NaOH makes up 64 % of the total chemical charged and in one of the MSS-AQ procedures no NaOH is used at all. This fact is important as the use of NaOH dictates the required chemical recovery operations and heavily impacts the overall process economics.

Laboratory cooks were aimed at generating linerboard grade pulp with kappa number in the range 90-100. Under the selected operating parameters an h factor of 700 proved to produce pulps in this range. The operating parameters used in each laboratory cook procedure are shown in Table 2. The table displays the system active and total chemical charge, as well as the anthraquinone charge on OD basis. Also shown was the pulping liquor to wood ratio, L/W, cooking temperature and h factor. The difference between active chemical and total chemical is the amount of Na<sub>2</sub>CO<sub>3</sub> present in the pulping liquor.

**Table 2. Operating parameters for Kraft and Mini Sulfide Sulfite AQ Methods**

	Units	Kraft	MSS-AQ
Active Chemical	% Na <sub>2</sub> O	15.0	19.8
Total Chemical	% Na <sub>2</sub> O	17.6	22.0
AQ	% on ODw	0.1	0.1
L/W	n.a.	4	4
Temp.	°C	160	160
h factor	n.a.	700	700

The pulping data obtained through the series of experimental cooks is outlined in Table 3. The table shows the black liquor pH, the total pulp yield, as well as the pulp kappa and brightness. The pH remains high in the Kraft. As expected, the black liquor pH is significantly lower in the MSS-AQ cooks which contain no NaOH than the MSS-AQ cooks with NaOH. However, the black liquor pHs still remain above nine, where recrystallization of lignin becomes a problem.

## RESULTS AND DISCUSSION

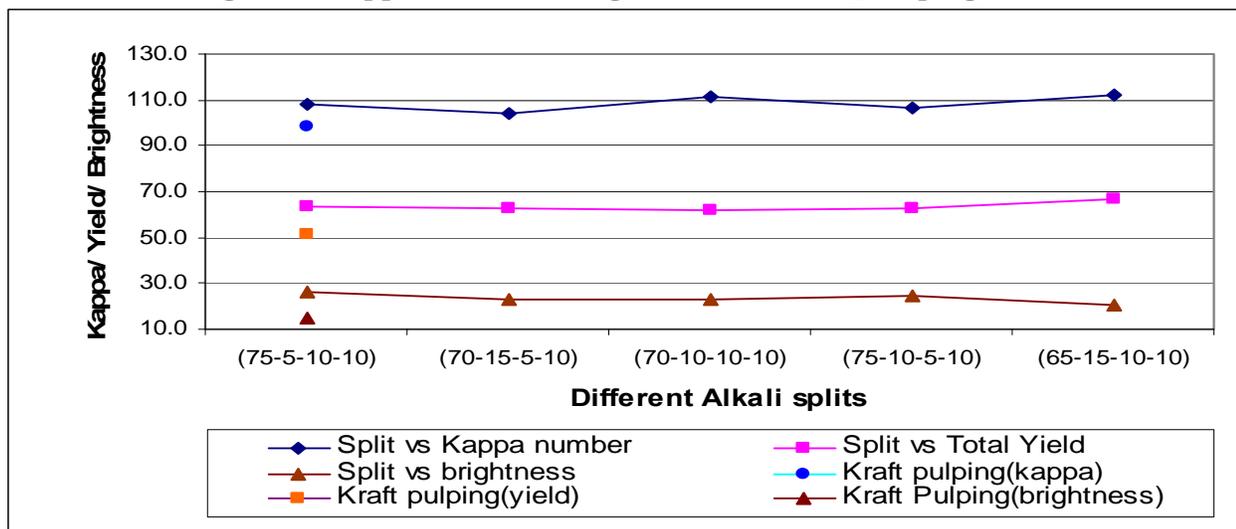
### MSSAQ Pulping

MSS-AQ procedure was modified by varying the NaOH charge, while keeping total chemical 22% constant throughout the experimental series. Target kappa was ~100. Following are the distribution of chemicals.

**Table 3. Results of MSS-AQ Pulping with NaOH**

			Kappa Number	Total Yield	Brightness (Unbleached)	Black liquor
Cook ID		(Na <sub>2</sub> SO <sub>3</sub> /Na <sub>2</sub> S/ NaOH/Na <sub>2</sub> CO <sub>3</sub> )		%	ISO	PH
MSSAQ-1	22%TC	(75-5-10-10)	108.3	63.2	26.4	9.94
MSSAQ-2	22%TC	(70-15-5-10)	104.3	63.1	23.2	10.02
MSSAQ-3	22%TC	(70-10-10-10)	111.0	61.5	22.8	10.10
MSSAQ-4	22%TC	(75-10-5-10)	106.5	62.7	24.7	9.92
MSSAQ-5	22%TC	(65-15-10-10)	112.1	66.5	20.7	10.14
<b>Kraft Baseline</b>	<b>17.6%TTA</b>	<b>Kraft Cook</b>	<b>98.2</b>	<b>51.7</b>	<b>15.22</b>	<b>12.86</b>

**Figure 3 Kappa Yield and Brightness of MSSAQ Pulping with NaOH**



Strength properties measurement shows that MSSAQ-700-22% TC (with NaOH) pulps have comparable tensile and burst index but the tear index still remains lower than the base Kraft pulps.

*MSSA-Q Pulping (without NaOH)*

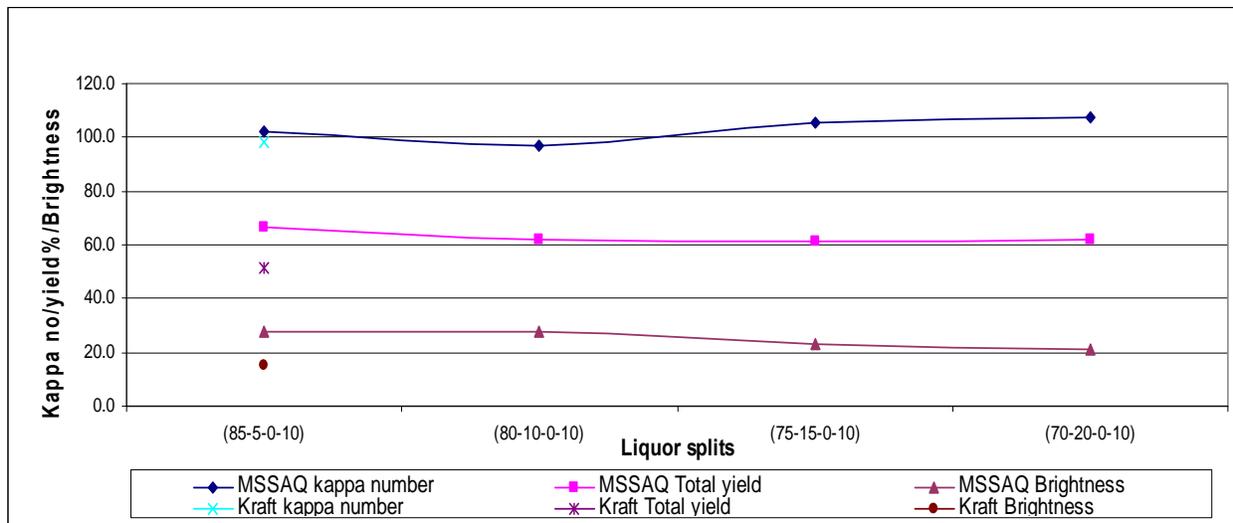
MSSAQ pulps without NaOH were produced, useful for eliminating the lime kiln in the recovery cycle. The results showed improved brightness and strength properties. The chemical splits are shown in Table 4. The total chemical was 22% but there is no sodium hydroxide charged to the cook.

**Table 4. Results of MSSA-Q Pulping without NaOH**

			Kappa Number	Total Yield	Brightness (unbleached)	Black liquor
Cook ID		(Na <sub>2</sub> SO <sub>3</sub> -Na <sub>2</sub> S-NaOH-Na <sub>2</sub> CO <sub>3</sub> )		%	ISO	PH
MSSAQ-1	22%TC	(85-5-0-10)	102.2	66.3	27.44	9.61
MSSAQ-2	22%TC	(80-10-0-10)	97.0	62.3	27.97	9.74
MSSAQ-3	22%TC	(75-15-0-10)	105.5	61.0	23.1	9.98
MSSAQ-4	22%TC	(70-20-0-10)	107.7	61.7	20.8	9.84
<b>Kraft Baseline</b>	<b>17.6%TTA</b>	<b>Kraft Cook</b>	<b>98.2</b>	<b>51.7</b>	<b>15.22</b>	<b>12.86</b>

As shown in Figure 4, the MSSA-Q methods generate pulps yield significantly greater than the Kraft procedure at similar kappa. The MSSA-Q procedures resulted in yield increase ranging from about 10 to 14 % relative the Kraft baseline. The brightness of the MSSAQ-700-22%TC (without NaOH) was 6-12 points higher than the base kraft pulps.

**Figure 4. Kappa Yield and Brightness of MSSAQ pulping without NaOH**



**Table 5. Strength properties of MSSAQ-700-22% TC Pulping**

Pulp ID	Base kraft	Average Values				CSF (mL)
		Apparent density (kg/m <sup>3</sup> )	Tear Index (mN*m <sup>2</sup> /g)	Tensile Index (N*m/g)	Burst Index ((kPa*m <sup>2</sup> /g)	
PFI (revolutions)	Basis Wt. (g/m <sup>2</sup> )					
3000	68.6	499.5	12.2	85.0	4.43	739
6000	67.1	546.9	9.8	99.3	5.36	655
9000	65.0	652.1	9.3	130.1	6.30	456
12000	64.7	657.1	8.2	132.7	6.42	255
Pulp ID	MSSAQ-700-22%TC (75-10-5-10)	With NaOH				
6000	66.4	576.1	10.1	101.1	5.97	688
8000	68.5	633.6	9.5	111.8	5.91	586
10000	67.8	634.1	8.7	112.5	5.87	405
12000	69.4	638.9	7.4	113.2	6.08	316
Pulp ID	MSSAQ-700-22%TC (70-15-5-10)	With NaOH				
3000	72.9	516.5	9.9	90.4	4.92	709
6000	70.9	629.6	9.4	96.7	6.05	638
9000	69.3	667.7	9.2	113.8	6.19	444
12000	70.5	681.5	8.2	114.0	6.25	268
Pulp ID	MSSAQ-700-22%TC (85-5-0-10)	Without NaOH				
3000	71.1	448.2	17.2	66.0	3.28	736
6000	69.5	582.1	15.9	95.6	4.68	684
9000	69.0	584.0	15.0	96.9	4.71	572
12000	68.0	658.6	13.4	111.6	5.66	356
Pulp ID	MSSAQ-700-22%TC (80-10-0-10)	Without NaOH				
3000	70.1	484.1	17.6	86.7	4.30	753
6000	68.5	574.0	16.3	101.0	5.33	693
9000	71.9	642.6	14.7	109.7	5.35	546
12000	68.1	659.5	13.5	118.0	6.32	288
**Pulp ID	MSSAQ-700-22%TC (75-15-0-10)	Without NaOH				
3000	69.4	464.6	21.1	82.0	4.11	746
6000	70.6	542.5	17.2	98.8	5.09	685
9000	68.2	620.2	14.1	116.8	5.80	482
12000	68.3	662.2	13.4	122.1	6.25	284
Pulp ID	MSSAQ-700-22%TC (70-20-0-10)	Without NaOH				
3000	70.2	475.8	21.3	93.9	3.93	744
6000	69.9	547.1	19.1	98.1	5.14	682
9000	67.9	625.7	14.2	116.2	5.79	494
12000	68.2	664.6	14.0	117.3	6.26	285

\*\* MSSAQ-700-22%TC (without NaOH) generate pulps of comparable strength with Kraft pulp

\*\* MSSAQ-700-22%TC (without NaOH) generated pulps selected for further studies

## PHYSICAL PROPERTIES

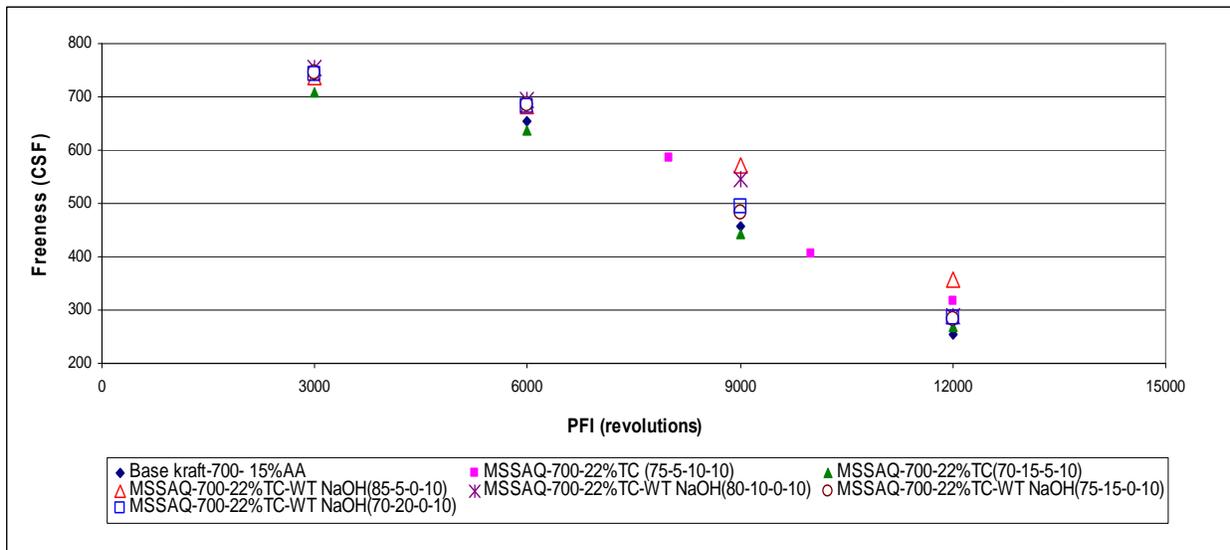
All unbleached pulps were beaten in a PFI-mill and the physical properties tested according to TAPPI

standard. Figure 8 show that the MSSAQ pulps had a slightly lower tear index at a given tensile index than the reference pulp. At a tensile index nearly 100 Nm/g, the MSS-AQ pulp with NaOH had tear index 3% lower but MSS-AQ pulp without NaOH had tear index 50-70% higher than the reference pulp. The differences between the various MSS-AQ pulps were, however, small. Results indicate that, at the same yield, tear-tensile index relationship lies at a higher level for MSS-AQ (without NaOH) pulps than for MSS-AQ (with NaOH).

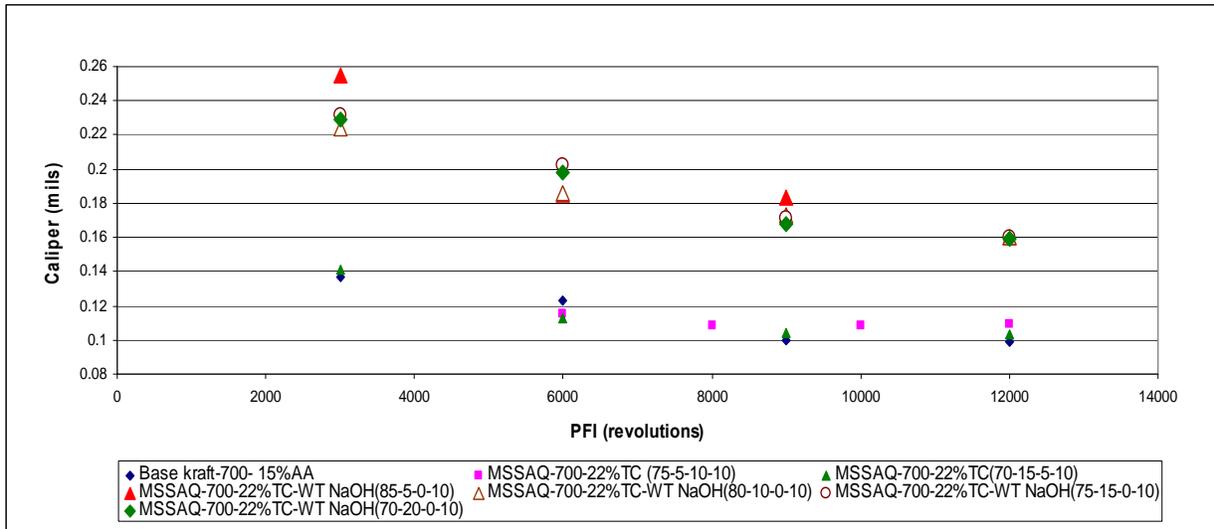
In MSS-AQ (without NaOH) pulps had improved tear index 5-10 point higher than the Kraft pulps. The tear strength of a pulp can in a simplified way be assumed to be dependent on the pulp yield and on the pulp viscosity. The viscosity of the unbleached MSS-AQ pulps lies at a higher level for all pulps and influence the tear strength. An increase in the pulp yield means that the number of load bearing elements per gram of the sheet is reduced. This leads to a reduction in the tear index of the pulp. \*\* MSS-AQ (without NaOH) pulps have, however, higher tear index values (13.2-21.4 mNm<sup>2</sup>/g) at the same yield than MSS-AQ (with NaOH) pulp. The reason for this result is unknown.

As shown in Figure 7, the MSS-AQ pulps freeness response to refining is slightly lower in MSS-AQ pulps than Kraft pulp. The sheet apparent density was calculated from the average hand sheet caliper and its' variation with level of refining is shown in Figure 6&7. The MSS-AQ pulps had an apparent density slightly greater than the Kraft pulp.

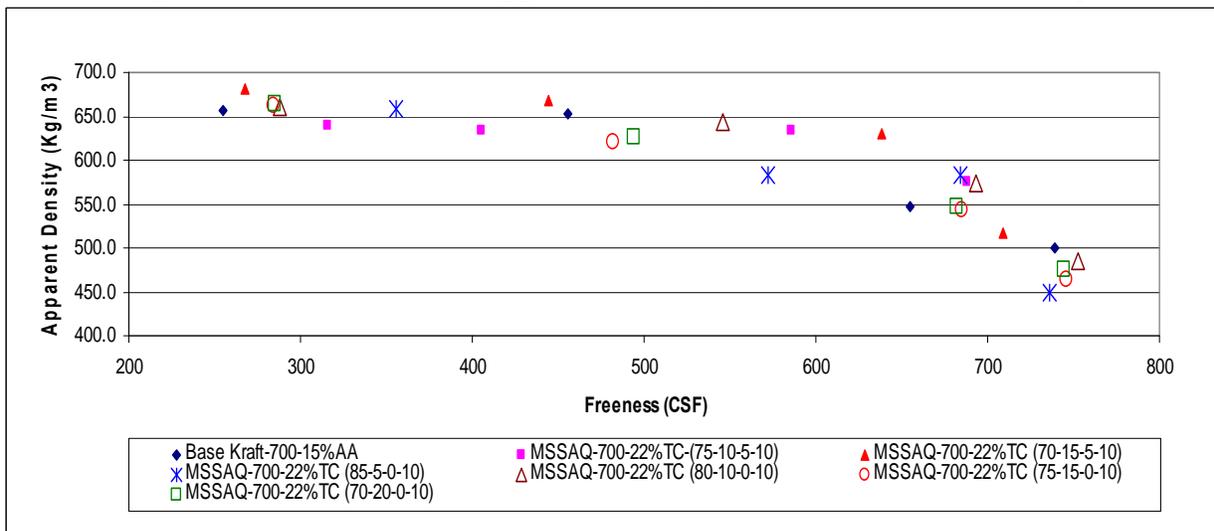
**Figure 5. Freeness vs PFI revolutions for Base and MSSAQ Pulps**



**Figure 6. Caliper vs PFI Revolution for Base and MSSAQ Pulps**

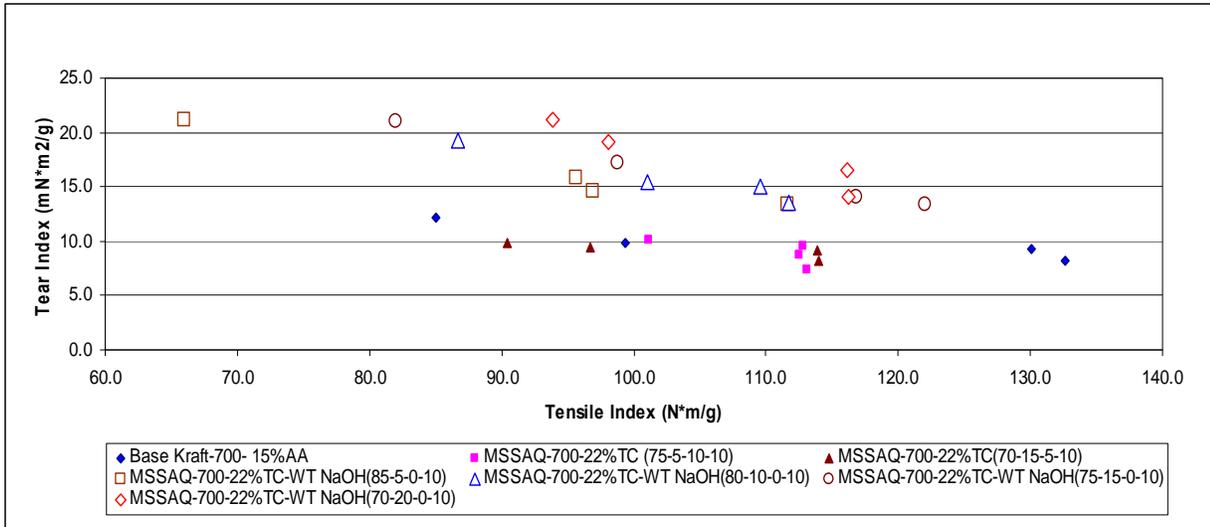


**Figure 7. Freeness vs Apparent Density for Base and MSSAQ Pulps**



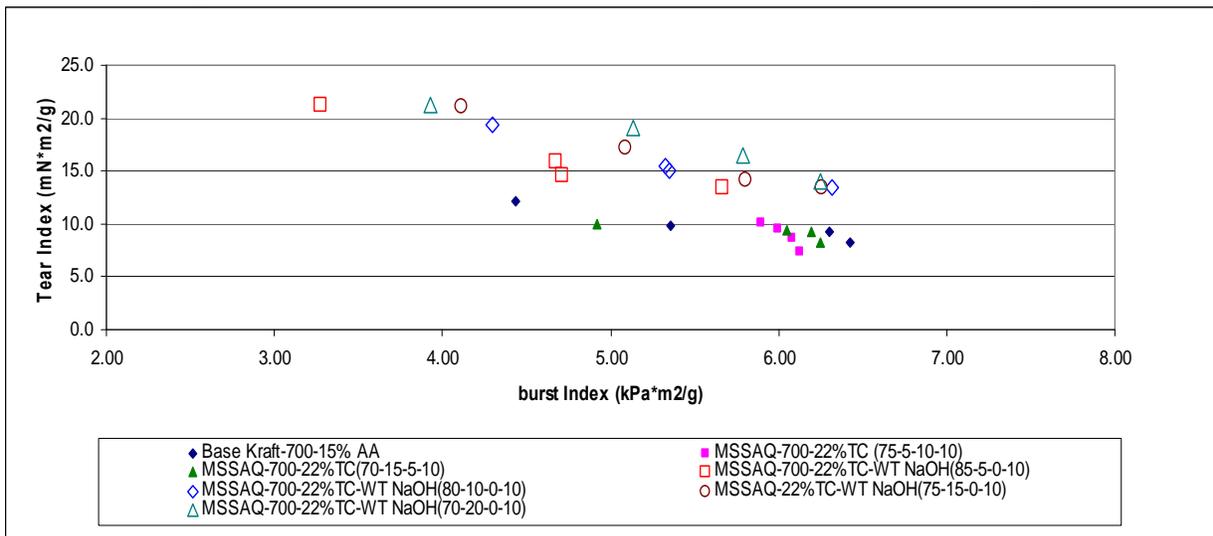
The tensile index was plotted against the tear index for all samples in Figure 8. As shown, a tear index of MSSAQ pulps was lower for the comparable tensile index of kraft pulps. It was also seen that the response of the MSSAQ pulps without NaOH gives higher tear than the base kraft pulps at nearly comparable tensile values. As shown, at a comparable tensile index, the MSSAQ-700-22% TC (75-15-0-10) (without NaOH) generated tear values 6 to 9 mNm<sup>2</sup>/g points greater than those obtained for Kraft pulps. The promising results for tensile and tear index are for MSSAQ-700-22%TC (80-10-0-10) and MSSAQ-700-22%TC (75-15-0-10).

**Figure 8. Tensile Index vs Tear index for Base and MSSAQ Pulps**



The pulp burst index was similarly plotted against the tear index for all pulps. The resulting graph is shown in Figure 9. As shown, The MSSAQ-700-22%TC (without NaOH) generated pulps with comparable burst but higher tear values. Particularly the MSSAQ-700-22% TC (75-15-0-10) had best compared tensile and burst with higher tear index than kraft pulps. MSS-AQ (with NaOH), had tear index somewhat lower than the reference pulp.

**Figure 9. Burst Index vs Tear Index for Base and MSSAQ Pulps**



The results shown in Figures 8 and 9 indicate that the Kraft reference pulp generated sheets of comparable tensile strength, and burst strength relative the MSS AQ-700-22%TC (with NaOH) but lower tear index. MSS-AQ-700-22%TC (without NaOH) procedures produced pulps that were somewhat higher tear index and comparable tensile and burst than the kraft pulp.

## CONCLUSIONS

The purpose of the two different liquor compositions in MSS-AQ pulping was to optimize the effect of NaOH and Na<sub>2</sub>S charge on the pulping procedure and pulp properties. MSS-AQ (with NaOH) pulps had a total chemical 22%. From an operating cost perspective, it would be desirable to minimize the amount of NaOH used in the process, while optimizing the relative amounts of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as to their effect on process operation, output and pulp properties.

When comparing the process output results for the two procedures it is worth noting that there seems to be little difference in the cooking liquor initial pH and the black liquor final pH. Furthermore, when pulping to the same h factor, there is little difference in the resulting pulp yield, kappa and ISO brightness. This indicates that with regard to pulping operations and the listed pulp properties, there is little or no benefit of adding NaOH to the cooking liquor.

When compared to the Kraft reference pulp, the MSS-AQ procedures produced pulps with a 10-15 % yield benefit and ISO brightness 1.5-2 times greater. The pulp refined little easier and had a slightly lower apparent sheet density (In both the cases). At similar levels of tear index the MSS-AQ (without NaOH) pulps also produced a comparable tensile and burst index pulps which was reported to be the main problem in the previous published papers with the MSS-AQ pulping (6-7).

Modifications to the kraft process, using MSS-AQ pulping, can generate comparable rates of delignification, improvements in pulp yield, viscosity and strength properties, but not all at the same time. Further optimization of this technology could have a significant effect on the kraft process. MSS-AQ pulping can generate significant yield benefits and significantly higher brightness. A unique opportunity exists in MSS-AQ pulping where it would be possible to eliminate the causticizing and lime kiln operations in the recovery cycle of black liquor gasification, resulting in very significant cost-savings.

The work summarized here was intended to show the potential of MSS-AQ process, a high yield pulping process. The payback on realizing the potential of these processes would be rather large cost savings due to the increased yield and high brightness therefore saving in pulping and bleaching chemical and have significant cost savings.

It was also determined that the use of AQ should not be a significant problem since many mills are already using AQ. Some mills do see increased scaling which leads to higher boilout frequencies in the evaporators.

Objective 2: Use MSSAQ liquors in the lab scale to define the product gas composition and identify design parameters for a black liquor gasifier system.

In this section computer simulations were used to determine the syngas compositions. This was different than the original proposal because of the total cost and the ability to determine the gas compositions for efficiently. It was also decided that the gas compositions would be reasonably accurate based on past experience. Thermochem Recovery International performed this work.

### *Gas Composition*

Using the pulping results the elemental composition of the black liquor was calculated using an EXCEL model. The elemental composition of the black liquor is as follows:

**Table 6: Elemental Composition of the Black Liquor**

BL Element	Percent by weight
Carbon	29.75%
Hydrogen	3.41%
Oxygen	35.98%
Sulfur	11.57%
Sodium	18.60%
Calcium	0.19%
Silicon	0.14%
Potassium	0.19%
Chlorine	0.17%

The above results will be used by TRI to estimate the gas composition from the gasifier in the next quarter. Following the estimation of the gas composition, trials will be run at RTI to evaluate the potential for removing the sulfur and regenerating it as SO<sub>2</sub>.

The actual measurements are shown below in Table 7. The numbers are in the same order of magnitude.

**Table 7: Actual Analysis of Black Liquor**

ANALYSIS	AS SAMPLED		DRY & GROUND	
Solids	17.12	%		
Carbon	4.05	%	23.66	%
Hydrogen	9.99	%	4.18	%
Sulfur	2.09	%	12.21	%
Total Halogens as Cl	0.22	%	1.28	%
Sodium	3.50	%	20.44	%
Potassium	158	ppm	923	ppm
Oxygen (by difference)	80.15	%	38.23	%
Heat of Combustion	717	Btu/lb	4188	Btu/lb
Inerts	<0.1	%		

TRI used the calculated and actual measurements of the black liquor in a steady state, quasi-equilibrium process model that it has developed and validated on many different organic feedstocks to project product gas composition and yield and reformer performance for the MSSAQ liquor. The model was modified to enable for the simulation of the MSSAQ process. The reformer comprises 2 stages – steam reformer and carbon trim cell. The product gas generated after cleanup appears to be more than self sufficient in that (i) pulse heater firing demand is satisfied (~75% of the gas is utilized) and (ii) excess gas (25%) may be used in downstream process (boiler, gas turbine, synthesis train etc.). The product gas heat recovery can generate ~35,000 lb/hr of Hp steam; additional 55,000 lb/hr HP steam may be generated if the excess gas (item ii) is fired in a boiler. The reformer island required ~45,000 lb/hr of LP steam. The steam generated is significantly lower than that from the conventional process because of the higher pulp yield, which results in a lower organic load to recovery.

The details of the simulation are shown below in Table 8.

**Table 8: Conditions Simulated for Gas Conditions**

BL MOISTURE CONTENT, As Received	25%	
BL solids concentration, by wt	75%	
BLS FEED RATE, Lb/Day	1,500,000	31.25 tph
BL FEED RATE (As Fed), Lb/Day	2,000,000	41.67 tph

The results are summarized in Table 9-11. The most critical results are shown in Table 4, the composition of the syngas.

**Table 9: Components in Different Streams for Gasifier**

		1	4	9	10	12	13
		Black Liquor	LP Superheated Steam	O2-rich Air	LP Superheated Steam	Spent Solids	Syngas
PRESSURE	PSIG	32.0	130.0	21.4	130.0	11.0	10.5
	IN WC						
TEMP	F	240	1,100	322	1,100	1,131	1,131
FLOW	GPM	126.3					
	SCFM		14,228	1,403	1,324		35,396
	ACFM		4,336	859	403		63,155
COMPONENT							
CH4	LB/HR						1,835
C2H6	LB/HR						106
C2H4	LB/HR						709
C3H6	LB/HR						0
C3H8	LB/HR						0
H2S	LB/HR						7,857
CH3SH	LB/HR						61
(CH3)2S	LB/HR						12
(CH3)2S2	LB/HR						12
COS	LB/HR						180
H2	LB/HR						2,487
CO	LB/HR						1,801
CO2	LB/HR						28,968
H2O (v)	LB/HR		40,590		3,777		56,449
NH3	LB/HR						0
O2	LB/HR			3,553			0
N2	LB/HR			3,111			3,423
SO2	LB/HR						0
H2O (l)	LB/HR	20,833					0
H2SO4 (l)	LB/HR						
NO	LB/HR						0
HCl	LB/HR						409

C	LB/HR					40	277
Na <sub>2</sub> CO <sub>3</sub>	LB/HR					21,409	7,139
NaCl	LB/HR					490	172
Na <sub>2</sub> SO <sub>4</sub>	LB/HR					0	0
Na <sub>2</sub> SO <sub>3</sub>	LB/HR						0
NaHSO <sub>3</sub>	LB/HR						0
Na <sub>2</sub> S	LB/HR					21	179
NaHS	LB/HR						0
NaHCO <sub>3</sub>	LB/HR						0
NaOH	LB/HR						0
K <sub>2</sub> CO <sub>3</sub>	LB/HR					76	26
CaCO <sub>3</sub>	LB/HR					0	0
SiO <sub>2</sub>	LB/HR					0	0
Condensables (v)	LB/HR						539
MAF Biomass or BLS	LB/HR						0
Inerts	LB/HR					0	0

**Table 10: Heat Value in the Different Streams**

		1	4	9	10	12	13
		Black Liquor	LP Superheate d Steam	O <sub>2</sub> -rich Air	LP Superheat ed Steam	Spent Solids	Syngas
MASS	LB/H R	83,333	40,590	6,664	3,777	22,036	112,640
HHV	BTU/ HR	261,750,000	0	0	0	565,514	289,619,294
ENTHALP	BTU/ HR	5,656,378	62,766,242	383,81 3	5,840,059	7,058,2 91	113,352,499
TOTAL HEAT	BTU/ HR	267,406,378	62,766,242	383,81 3	5,840,059	7,623,8 05	402,971,793

**Table 11: Syngas Composition and Heat Value**

<b>Comp</b>	<b>Vol% wet</b>	<b>Vol% dry</b>
CH4	2.04%	4.63%
C2H6	0.06%	0.14%
C2H4	0.45%	1.02%
C3H6	0.00%	0.00%
C3H8	0.00%	0.00%
H2S	4.11%	9.33%
CH3SH	0.02%	0.05%
(CH3)2S	0.00%	0.01%
(CH3)2S2	0.00%	0.01%
COS	0.05%	0.12%
H2	21.97%	49.83%
CO	1.15%	2.60%
CO2	11.75%	26.64%
H2O (v)	55.90%	
NH3	0.00%	0.00%
O2	0.00%	0.00%
N2	2.18%	4.94%
SO2	0.00%	0.00%
HCl	0.20%	0.45%
Condensables	0.10%	0.23%
Total	100.00%	100.00%
HHV, BTU/SCF	136	309

The major components of the syngas were methane, hydrogen sulfide, hydrogen, carbon monoxide and nitrogen. The heat value of the syngas was about 310 BTU/SCF. The composition of the syngas was used by RTI to simulate the operation of the ZnO based gas absorption system. It will be critical to see if the sulfur in the syngas can be cleaned up to appropriate levels.

Objective 3: Trials on a pilot scale RTI absorber with the appropriate product gas compositions to quantify the adsorption and desorption characteristics with MSS-AQ product gas compositions and identify design parameters for an absorber

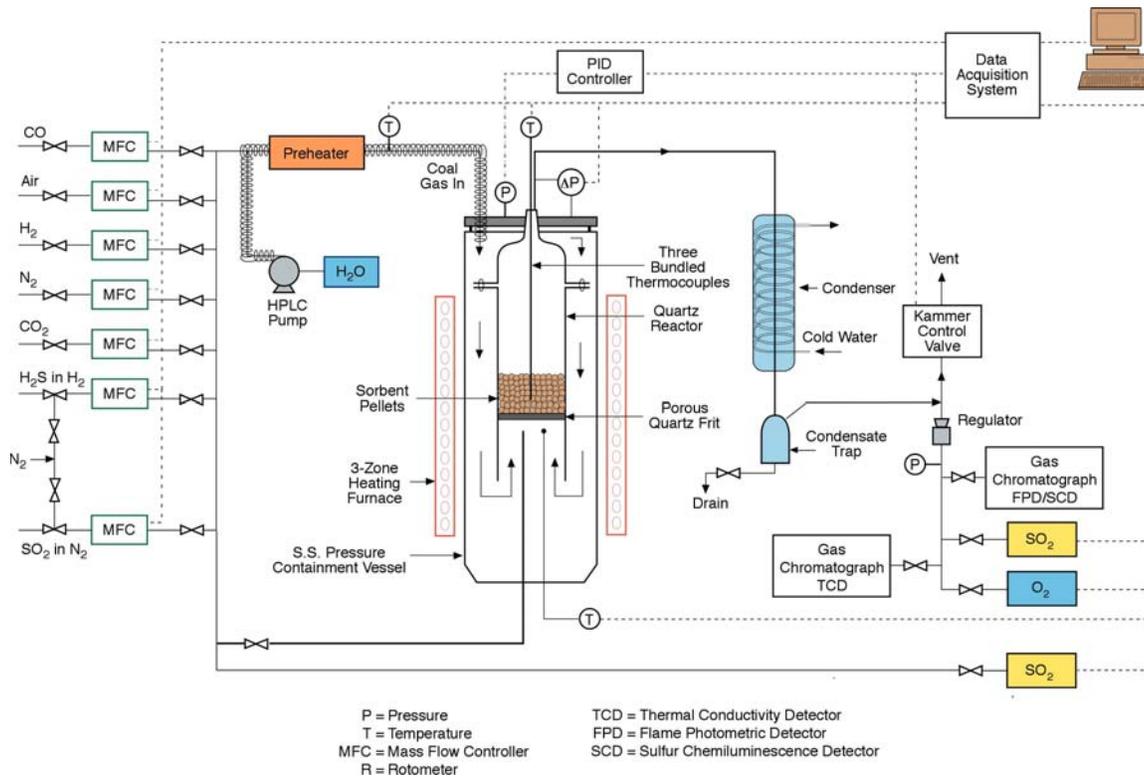
Research Triangle Institute performed this work.

### *Sulfur Recovery*

This section describes testing of RVS-1 with simulated synthesis gas mixtures that would typically be generated by black liquor gasification (8-11). The specific synthesis gas compositions were selected to cover the typical ranges of steam and H<sub>2</sub>S content. These two species were of key importance because previous testing of ZnO-based sorbent has demonstrated that the concentration of these components has the greatest effect on desulfurization performance.

### *Experimental System and Procedure*

The testing was conducted in RTI's High Pressure High Temperature Reactor System, shown in Figure 10. This system includes a 2-inch internal diameter quartz reactor equipped with a porous quartz distributor. The quartz reactor is housed within a 4-inch stainless steel pressure vessel. The stainless steel pressure vessel is heated externally by a 3-zone electric furnace.



**Figure 10. RTI's High Temperature High Pressure Reactor System.**

The desired synthesis gas composition was generated by blending CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and a mixture of H<sub>2</sub>S in H<sub>2</sub>. The steam was added to this raw synthesis gas mixture by vaporizing deionized (DI) water. The amount of steam was controlled by the amount of DI water pumped into the vaporization system. This synthesis gas mixture was further preheated in an external preheater and as the gas passed through the annulus between the heated pressure shell and the quartz reactor. The synthesis gas then flowed upward through a fixed-bed of the sorbent. The effluent from the reactor was cooled to condense the steam. A sample of the dry effluent gas was sent to an HP 5890 gas chromatograph (GC) equipped with a sulfur chemiluminescence detector. The remainder of the dry effluent was scrubbed in a sulfur trap to capture any remaining H<sub>2</sub>S before being vented. The desulfurization cycle was ended when the H<sub>2</sub>S effluent concentration exceeded 5,000 ppmv.

After the desulfurization process, the synthesis gas was shut off and the reactor system purged with nitrogen to remove all traces of synthesis gas. As the reactor system was being purged of synthesis gas, the reactor was heated to the desired regeneration temperature. When all traces of syngas had been removed from the reactor system, the reactor feed was switched to a mixture containing 5 vol% O<sub>2</sub> in N<sub>2</sub> to regenerate the sorbent by burning off the sulfur as SO<sub>2</sub>. Small samples of the reactor effluent were sent to an online SO<sub>2</sub> detector and O<sub>2</sub> sensor. Regeneration conditions were maintained until the effluent SO<sub>2</sub> concentration dropped below 1,000 ppmv. At the end of regeneration, the reactor system was purged with nitrogen and cooled.

Each test in this project consisted of one desulfurization cycle and one regeneration cycle. For each test, a fresh batch of RVS-1 sorbent was loaded into the reactor. The reactor was loaded with approximately 210 g to a bed depth of about 3 in. The specific operating conditions for the desulfurization and regeneration cycle are provided in Table 12. The tests were conducted at 30 psig to provide sufficient gas to ensure stable system operation and sufficient gas flow in the sample lines to the gas chromatograph and analyzers

to ensure representative samples. The specific synthesis gas compositions for each test are provided in Table 13, which were provided by North Carolina State University.

**Table 12. Operating Conditions for Testing with Simulated Synthesis Gas from Black Liquor Gasification**

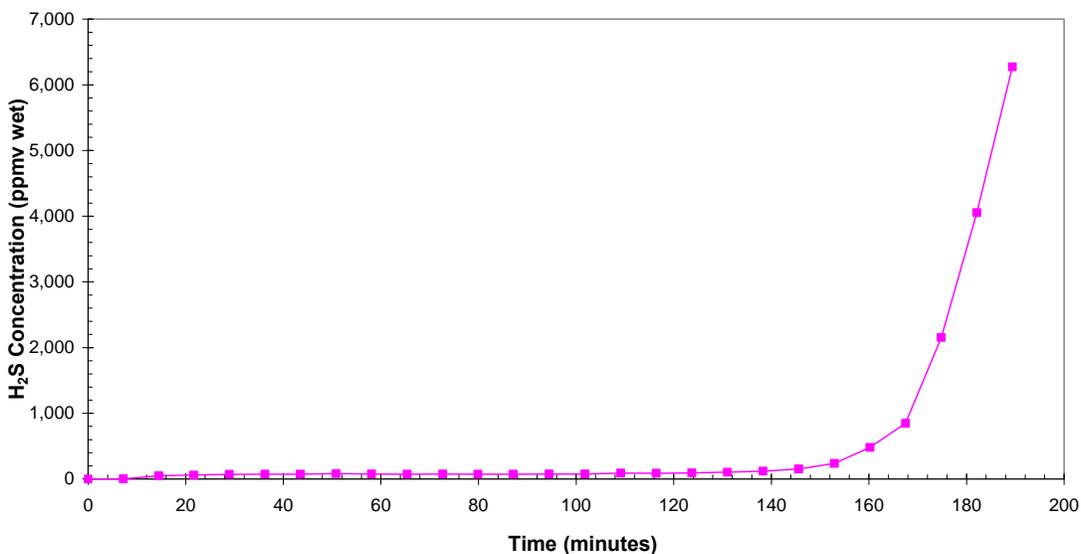
Condition	Desulfurization	Regeneration
Temperature (°C)	540	540
Pressure (psig)	30	30
Space velocity at STP (h <sup>-1</sup> )	780	3,500

**Table 13. Simulated Synthesis Gas from Black Liquor Gasification**

Component	Composition (volume %)				
	Test 1	Test 2	Test 3	Test 4	Test 5
H <sub>2</sub> O	20.0	5.0	10.0	30.0	40.0
H <sub>2</sub> S	8.0	9.5	9.0	7.0	6.0
H <sub>2</sub>	41.6	49.4	46.8	36.4	31.2
CH <sub>4</sub>	4.0	4.8	4.5	3.5	3.0
CO <sub>2</sub>	24.0	28.5	27.0	21.0	18.0
CO	2.4	2.9	2.7	2.1	1.8
Total	100.0	100.0	100.0	100.0	100.0

### *Experimental Results and Discussion*

The sulfur measurements in the reactor effluent during the desulfurization cycle obtained from the GC for Test 1 are provided in Figure 11. Figure 11 shows a typical breakthrough pattern. Initially, essentially none of the sulfur capacity of the RVS-1 sorbent has been used. During this portion of the desulfurization cycle, the RVS-1 sorbent can reduce the H<sub>2</sub>S in the simulated synthesis gas to concentrations approaching the thermodynamic equilibrium value. In Figure 11, the concentration in the reactor effluent during this portion of the desulfurization cycle is about 80 ppmv. Since the H<sub>2</sub>S concentration in the feed was 8.0 vol% ( or 80,000 ppmv), this represents a removal of 99.9%. As the sulfur capacity is consumed, the effluent H<sub>2</sub>S concentration slowly increases. For Test 1, the concentration slowly increased from about 77 ppmv to about 100 ppmv. When the RVS-1 sorbent eventually becomes saturated with sulfur, because the sulfur capacity has been consumed, the H<sub>2</sub>S concentration in the reactor effluent rapidly increases.



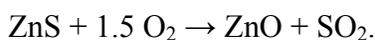
**Figure 11. Effluent H<sub>2</sub>S concentration (wet basis) in reactor effluent as a function of sulfidation time for Test 1.**

From the difference in the H<sub>2</sub>S concentration in the inlet simulated synthesis gas and the reactor effluent, the amount of sulfur captured on the sorbent can be calculated prior to breakthrough. This value represents the sulfur capacity of the sorbent and is typically expressed as the mass of sulfur captured as a percentage of the weight of the fresh sorbent. From Test 1, the sulfur capacity for RVS-1 was calculated to be 20.8 wt%.

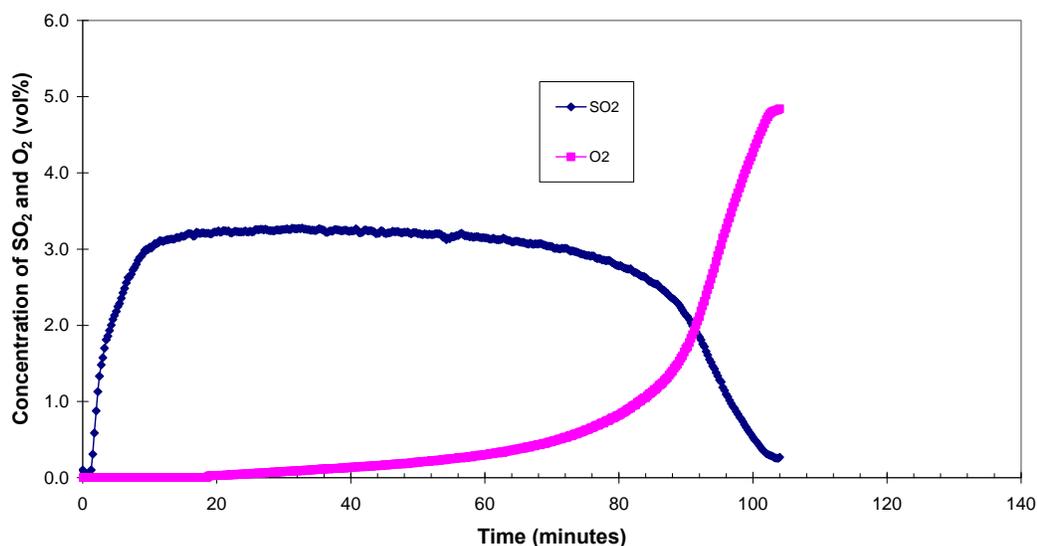
Similar H<sub>2</sub>S breakthrough profiles were generated in each subsequent test. The results for all five tests are summarized in Table 14. The results in Table 14 show that RVS-1 was able to remove > 99.8% of the H<sub>2</sub>S for simulated synthesis gas mixtures from black liquor gasification with H<sub>2</sub>S concentrations between 6 and 9.5 vol%. The sulfur capacity for RVS-1 under these testing conditions was about 20 wt%. No significant effect of synthesis gas composition was noted during these experiments.

Test #	Feed Gas H <sub>2</sub> S Concentration (ppmv, wet basis)	Sulfur Capacity (wt%)	Pre-breakthrough H <sub>2</sub> S Concentration (ppmv, wet basis)	Sulfur Removal Efficiency (%)
1	60,000	20.8	80	99.90
2	70,000	20.8	90	99.87
3	80,000	18.3	100	99.88
4	90,000	20.5	80	99.91
5	95,000	20.3	70	99.93

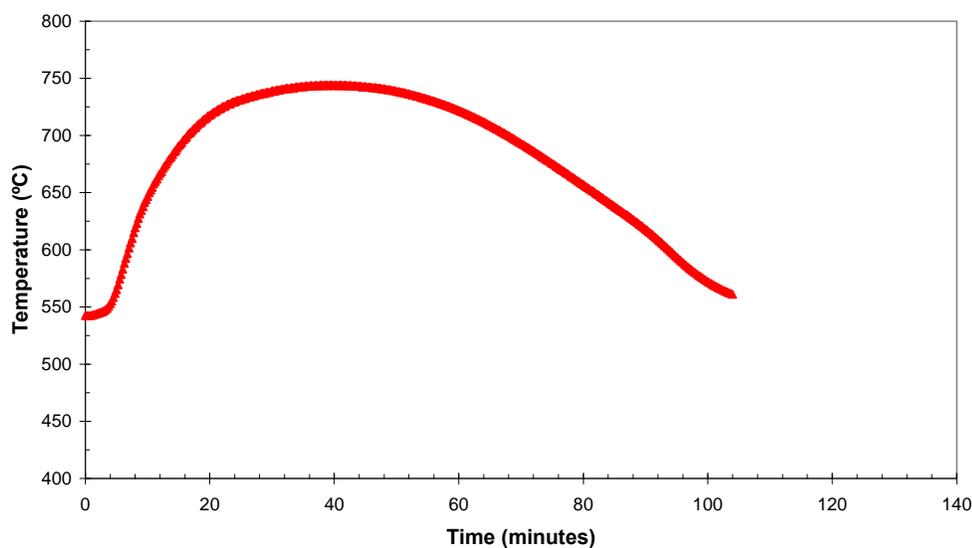
Figure 3 shows the effluent oxygen and SO<sub>2</sub> concentrations during the regeneration cycle for Test 1. As the oxygen reaches the sorbent bed, it oxidizes the sulfided sorbent generating SO<sub>2</sub>. The reaction that takes place for ZnO sorbents like RVS-1 is



Because this is an exothermic reaction, a significant amount of heat is released increasing the temperature of the bed. This temperature rise in the sorbent bed during regeneration for Test 1 can be seen in Figure 13.



**Figure 12. SO<sub>2</sub> and O<sub>2</sub> concentrations at sorbent bed exit as a function of sulfidation time for Test 1.**



**Figure 13. Sorbent bed temperature profile during regeneration in Test 1.**

Initially all of the oxygen is consumed in oxidizing the sulfided sorbent. From Figure 12, the effluent SO<sub>2</sub>

concentration reaches a maximum of slightly over 3 vol%. The effluent concentration based on the reaction stoichiometry should be 3.3 vol%. The slight difference could be associated with an undesired side reaction resulting in sulfate formation and sorbent deactivation. However, even with these operating conditions (that have not been optimized), this side reaction is not very significant. Using the effluent concentration of SO<sub>2</sub>, the total amount of sulfur released during the regeneration cycle can be calculated. These values expressed as a weight fraction of the fresh sorbent are provided in Table 14 for all five tests.

**Table 15. Summary of Sulfur Recovered During Regeneration Cycles**

Test #	Sulfur Recovered (wt%)
1	17.3
2	15.6
3	13.3
4	11.9
5	16.2

The amounts of sulfur recovered in Table 15 are slightly less than the 20 wt% of sulfur loaded onto the sorbent. This occurs because there is inevitably some sulfate formation, and this sorbent typically takes between 1 and 3 cycles for the sorbent performance to stabilize. In spite of these non-optimal conditions, the average recovery of sulfur as SO<sub>2</sub> is about 75%.

Although only the summary results for Tests 2 through 5 have been included in this discussion, the desulfurization and regeneration profile for each Test has been provided in the Appendix. The results shown in these figures are essentially identical to those shown for Test 1 as demonstrated by results shown in the summary tables (Tables 14 and 15).

## CONCLUSIONS

The results demonstrate that RVS-1 can effectively remove > 99.8% of the H<sub>2</sub>S present in simulated synthesis gas generated from the gasification of black liquor. This level of sulfur removal was consistent over simulated synthesis gas mixtures that contained from 6 to 9.5 vol % H<sub>2</sub>S and steam concentrations up to 40 vol %. Even with operating conditions that have not been optimized, this level of sulfur removal is very close to meeting the typical sulfur emission standards for coal-fired power plant (1.4 lb of SO<sub>x</sub>/MWh gross which translates to roughly 60-80 ppmv in the synthesis gas). With suitable optimization of operating and/or process conditions, the sulfur in the desulfurized synthesis gas could meet current emission requirements for SO<sub>x</sub>.

Based on the regeneration results generated during this testing, a significant amount of the sulfur in the simulated syngas was recovered as SO<sub>2</sub> during regeneration. The average recovery of sulfur as SO<sub>2</sub> was about 75%. Because these are first cycle results, this sulfur recovery is expected to improve. In previous testing with RVS-1, between 2 and 5 cycles were required for sorbent desulfurization to stabilize.

Based on these results, the use of regenerable ZnO-based sorbents, like RVS-1, to desulfurize synthesis gas generated by black liquor gasification provides a technically feasible means to improve thermal efficiency of synthesis gas production and use, while recovering the sulfur in the synthesis gas as SO<sub>2</sub>. With these results, a better techno-economic evaluation of the use of warm gas desulfurization of synthesis gas using

regenerable ZnO-based sorbents should be possible.

Objective 4: Define the process and equipment changes required in an existing mill to integrate the MSS-AQ process along with BLG and RTI absorption technology.

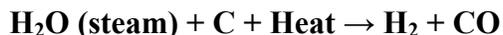
Objective 5: Develop a WINGems process model for detailed economic evaluation and process impact

This work was performed by North Carolina State University, with very significant help from TRI, Andritz and PCA who provided much of the information necessary.

### *Process Simulation*

#### *The Low Temperature Black Liquor Gasifier*

The low temperature black liquor gasifier operates using a fluidized bed. The bed solids, sodium carbonate, are fluidized using superheated steam. As black liquor is sprayed into the gasifier, the liquor coats these solids. The hot temperatures and reducing environment of the gasifier causes the organic material to react through the following sequence of reactions:



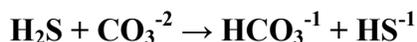
The carbon monoxide reacts further with the steam by the following reaction:



The result of these reactions is a syngas consisting of hydrogen, methane series alkanes, phenolics, carbon monoxide, carbon dioxide and water (1). If kraft or sulfite pulping was utilized hydrogen sulfide and other mercaptans will also be present. Heat for the endothermic reaction is provided by indirect pulse tube heaters. These heaters can be fueled using natural gas or possibly syngas from the reactor. Particulate matter from the syngas is removed using a cyclone and returned to the bed.

### *Chemical Recovery*

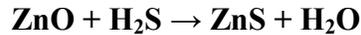
The sulfur and sodium in the black liquor are split inside the gasifier. Virtually all the sulfur exits with the syngas. The sodium is recovered by continually removing a small portion of bed solids from the gasifier. These bed solids are dissolved in water to become green liquor. A small portion of the syngas will be used to generate sodium hydrosulfide. This will be accomplished by scrubbing the syngas with green liquor. The sodium carbonate in the green liquor reacts with the hydrogen sulfide in the syngas to regenerate sodium hydrosulfide through the following reaction:



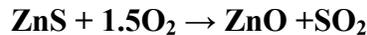
A small portion of clean syngas will remain after sodium hydrosulfide generation. The clean syngas from the hydrogen sulfide scrubber will be used as fuel for the pulse heaters. A portion of the carbon dioxide in the syngas is also adsorbed into the green liquor during hydrogen sulfide scrubbing. The carbon dioxide from the syngas reacts with the sodium carbonate of the green liquor yielding sodium bicarbonate through the following reaction:



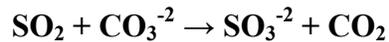
One of the largest impediments to black liquor gasification implementation is an efficient process to economically recover sulfur from the syngas. One possibility for sulfur recovery is a process developed by the Research Triangle Institute (RTI) which uses a ZnO sorbent. The metal oxide reacts with the reduced sulfur compounds through the following reaction:



The sorbent is regenerated using air by the following reaction:



For the process to be continuous, two units would be needed. Having two units would help ensure a sulfur removal system would be operational while one unit was regenerating its sorbent. When the SO<sub>2</sub> is adsorbed in green liquor, sodium sulfite, one of the active pulping chemicals for MSS-AQ pulping, is generated. Sodium sulfite generation occurs through the following reaction:



Alternative sulfur removal processes include scrubbing with amines. One disadvantage of the amine processes not inherent to the RTI process is excessive cooling of the syngas. Excessive cooling of the syngas requires the syngas to be reheated before it can be fed to the gas turbine.

### *Power Generation*

After the sulfur has been removed from the syngas, the clean gas is compressed and fed to the gas turbine. The combusting gas inside the turbine exerts a force on the turbine blades causing the turbine to rotate. The generator to produce electricity uses the resulting shaftwork of the turbine. Heat from the hot exhaust gases of the gas turbine are used to generate steam in a heat recovery steam generator. This steam can either be used to generate more electricity or used for process heat. A coal boiler is utilized to generate the extra steam that would be necessary to meet the mill's heating needs.

### *MSS-AQ Pulping*

MSS-AQ pulping can result in yield increases of 15-20% over traditional kraft pulping. These increases in yield diminish at lower kappa numbers but this would not be a problem for a linerboard mill since linerboard is made from high kappa pulp. Slower delignification rates require the use of higher temperatures, +18°F, and the use of anthraquinone. Additionally, a higher chemical charge, 22% as Na<sub>2</sub>O, is required when using the MSS-AQ pulping process (the charge for most kraft pulps is around 19% as Na<sub>2</sub>O). Despite the many benefits associated with MSS-AQ pulping such as reduced wood cost, elimination of the lime kiln and reduced odor, the process has yet to be implemented industrially due to the lack of an attractive chemical recovery process. Black liquor gasification with RTI clean-up would allow for the generation of the pulping chemicals needed to achieve the benefits of MSS-AQ pulping.

### *Method*

### *Base Case*

A kraft linerboard mill was established as the base case. This mill consists of the traditional unit operations found at most kraft mills. The pulp mill contains a digester, knot screens and brownstock washers. The recovery area contains multiple effect evaporators, concentrator, recovery boiler and smelt dissolving tank. The recausticization area contains a slaker, causticizer, white liquor clarifiers, and lime kiln.

Modifications for the BLG case involved removing the recovery section after the concentrator. The old recovery process was replaced by the following sets of unit operations: a black liquor gasifier, a sulfur recovery process and combined cycle power generation. Changes were also made in the pulp mill to reflect the different composition of the pulping liquor charged and the different yield obtained from MSS-AQ pulping. The following changes are discussed in more detail in the following sections.

### *Pulping*

Pulping assumptions for both the base and BLG cases are summarized in Table 16. Production was set to 1000 ODmt/day for both the base and BLG cases. Controlling the production for both cases is important to ensure fair comparison during the economic analysis. Production was set to a fixed value by applying a proportional controller to the amount of wood entering the digester. A pulping temperature increase of 18°C and a yield increase of 15% were assumed for MSS-AQ pulping. Additionally, it was also assumed that 0.15% AQ would be needed for MSS-AQ pulping. It was also determined that there was no increased loading to the washers because of the higher yield. The digester feed system will have a lower loading.

**Table 16-Pulping Assumptions for Simulation**

	<b>Base Case</b>	<b>MSS-AQ</b>
Production (mt/day)	1000	1000
Temperature (°C)	155	173
Yield (%)	50	65
AQ (%)	0	0.15
NaOH (kg as Na <sub>2</sub> O/ODt pulp)	226	0
Na <sub>2</sub> S (kg as Na <sub>2</sub> O/ODt pulp)	74	32
Na <sub>2</sub> CO <sub>3</sub> (kg as Na <sub>2</sub> O/ODt pulp)	53	32
Na <sub>2</sub> SO <sub>3</sub> (kg as Na <sub>2</sub> O/ODt pulp)	0	261

(1)

### *Liquor Charge*

The assumptions for the charging of liquor are summarized in Table 16. The amount of NaOH, Na<sub>2</sub>S, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub> needed per ODt pulp was presented in Table 17. This information was used to calculate the active alkali, effective alkali, sulfidity and causticity for the base case. Since kraft pulping was used for the base case, the standard WinGEMS “CTRL” block was used to calculate make-up chemicals. For the base case, sulfur was added back to the system by adding salt cake to the black liquor prior to the recovery furnace and soda was added back to the system by adding sodium hydroxide to the white liquor before the digester. For MSS-AQ pulping, sulfur was added to the system by adding sodium sulfate to the black liquor before the gasifier. The ratio of sodium sulfide to sodium sulfite was controlled by varying the ratio of syngas sent to the RTI process versus the hydrogen sulfide scrubber. The amount of makeup sulfur and the sodium sulfide to sodium sulfite ratio were both controlled in WinGEMS using compute functions

**Table 17-Liquor Charge Assumptions for Simulation**

Base Case		MSS-AQ	
AA (%)	15.0	Na <sub>2</sub> S (kg/ODt wood)	33
EA (%)	13.1	Na <sub>2</sub> CO <sub>3</sub> (kg/ODt wood)	22
Sulfidity (%)	0.247	Na <sub>2</sub> SO <sub>3</sub> (kg/ODt wood)	143
Causticity (%)	0.810	kg Na <sub>2</sub> S / (kg Na <sub>2</sub> S + kg Na <sub>2</sub> SO <sub>3</sub> )	0.1875

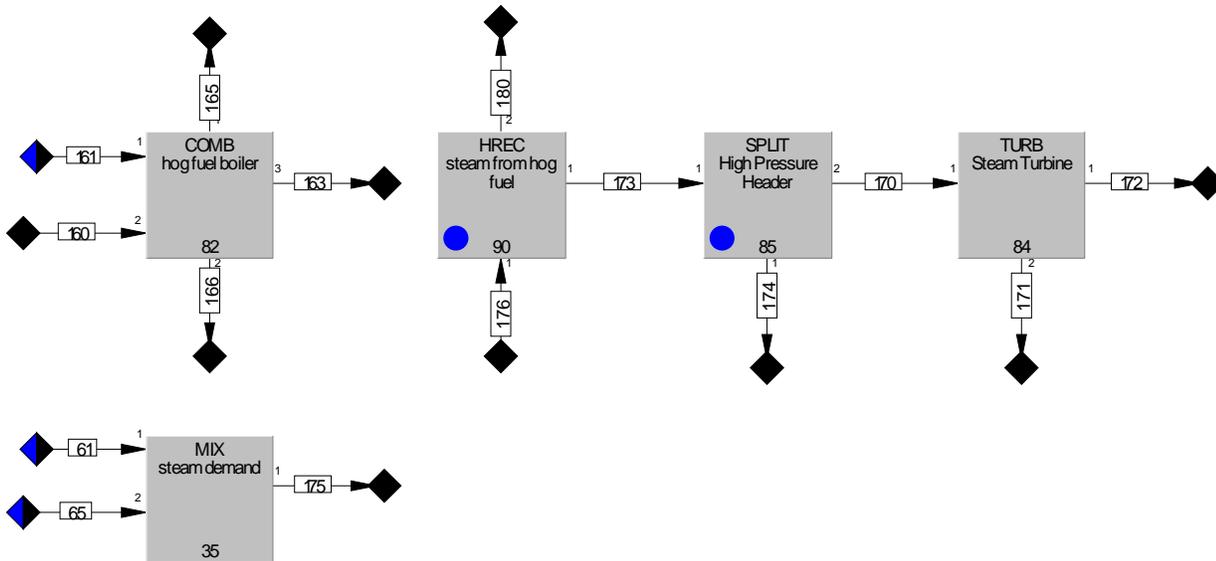
(1)

*Combined Cycle Power Generation*

It was necessary for both the base and BLG cases to meet the low and high pressure steam demands of the mill. For the base case, steam was generated in an “HREC” block from the energy given off by the recovery boiler and a power boiler. The power boiler was modeled using a “COMB” block that combusts hog fuel. The high pressure steam produced by the two boilers is expanded in a steam turbine to generate electricity. However, all of the high pressure steam generated by the boilers is not used by the turbine alone. A mill needs a certain amount of high pressure steam to operate boiler feedwater pumps, for use in soot blowers and for steam turbines that drive the paper machines. In reality, there are actually six or seven different pressures of steam that are used in mills for various functions. But for this simulation, it is assumed that there is only high and low pressure steam. A high pressure steam demand of 0.46 kg steam / kg paper was assumed (5). Thus, a fraction of the high pressure steam was split using a “SPLIT” block and a compute function to meet this high pressure steam demand. The mill also has to meet a low pressure steam demand as well. The low pressure steam source is the turbine exhaust. The low pressure steam demand is determined by summing together all of the steam streams for the pulp mill and recovery area and adding this to the steam needed for the paper machines. It was assumed that 5.16 kg steam / kg paper were used by the paper mill (5). These two values were added together using a “MIX” block to give the total mill steam demand for low pressure steam. The low pressure steam demand was met using a proportional controller on the hog fuel entering the “COMB” block. A summary of the steam and electric demands along with the steam temperatures and pressures is presented in Table 18. The WinGEMS simulation for these unit operations is seen in Figure 14.

**Table 18-Base Steam and Electric Demand and Steam Properties**

Production	OD mt/hr	41.7
Low Pressure Steam	mmHg	2844
	kg/kg paper	5.162
	kg/hr	215083
Electric Use	kW-hr/mt paper	1406
	kW-hr/hr	58583.33
High Pressure Steam	mmHg	51715
	°C	540
	kg/kg paper	0.4608
	kg/hr	19200



**Figure 14-Power Generation for Base Case**

The difference in power generation for the BLG case was the addition of a gas turbine and heat recovery/steam generation from the gas turbine’s flue gases. Other than this difference, the power generation processes are very similar. In both cases the mill’s high and low pressure steam demands are met by varying the amount of hog fuel fed to a power boiler. Electrical output from the turbines is given as an output parameter from the blocks.

The energy available for power generation from the syngas in the gas turbine was input into the “GASTURB” block using a compute function. Linear mixing rules were assumed and the heats of combustion for each component were calculated using heats of formation. The heats of combustion for each syngas product were multiplied by their corresponding mass flow rate in the stream entering the turbine. The heats of combustion for the syngas products are summarized in Table 19.

**Table 19-Syngas Heats of Combustion**

<b>Heat of Combustion (Mcal/kg)</b>	
Methane	-11.99
Ethane	-5.60
Phenol	-7.62
Hydrogen	-57.80
Carbon Monoxide	-2.42
Ethylene	-11.29
Propene	-10.96
Acetone	-6.96
Hydrogen Sulfide	-3.65

The gas turbine efficiency and exhaust temperature was determined from the General Electric website for gas turbines (12). A gas turbine efficiency of 34% and exhaust temperature of 613°C were used for this simulation. Higher efficiencies are possible, but only for turbines that are utility scale. The energy available from the hot flue gases of the gas turbine available for steam generation was determined using a compute function inside an “HREC” block. The energy was calculated using the formula,  $Q = mC_p\Delta T$ . The change in temperature was the difference between the turbine exhaust temperature and the flue gas temperature as it leaves the heat recovery/steam generator unit. The exhaust temperature was assumed to be 400°C. Again, linear mixing rules were applied, multiplying each component’s specific heat by its mass flow rate. Specific heat values were assumed not to vary significantly with temperature and were calculated at 500°C using data from Smith, Van Ness and Abbot (10). The specific heat values of the flue gas components are tabulated in Table 20.

**Table 20-Gas Turbine Flue Gas Specific Heat Values**

<b>Component</b>	<b>C<sub>p</sub> (Mcal/kg)</b>
H <sub>2</sub>	0.003566
N <sub>2</sub>	0.000266
O <sub>2</sub>	0.000248
H <sub>2</sub> O	0.000509
CO	0.000270
CO <sub>2</sub>	0.000274

The combined cycle process modeled in WinGEMS is seen in Figure 14. Steam from the “HREC” block is combined with steam created by the power boiler in a “STMIX” block. A portion of this high pressure steam is then removed using a “SPLIT” block. The remaining steam goes to a “TURB” block which generates electricity and outputs low pressure steam to meet the mill’s heating needs. Just like the base case, the steam demand is met by varying the hog fuel fed to the power boiler.

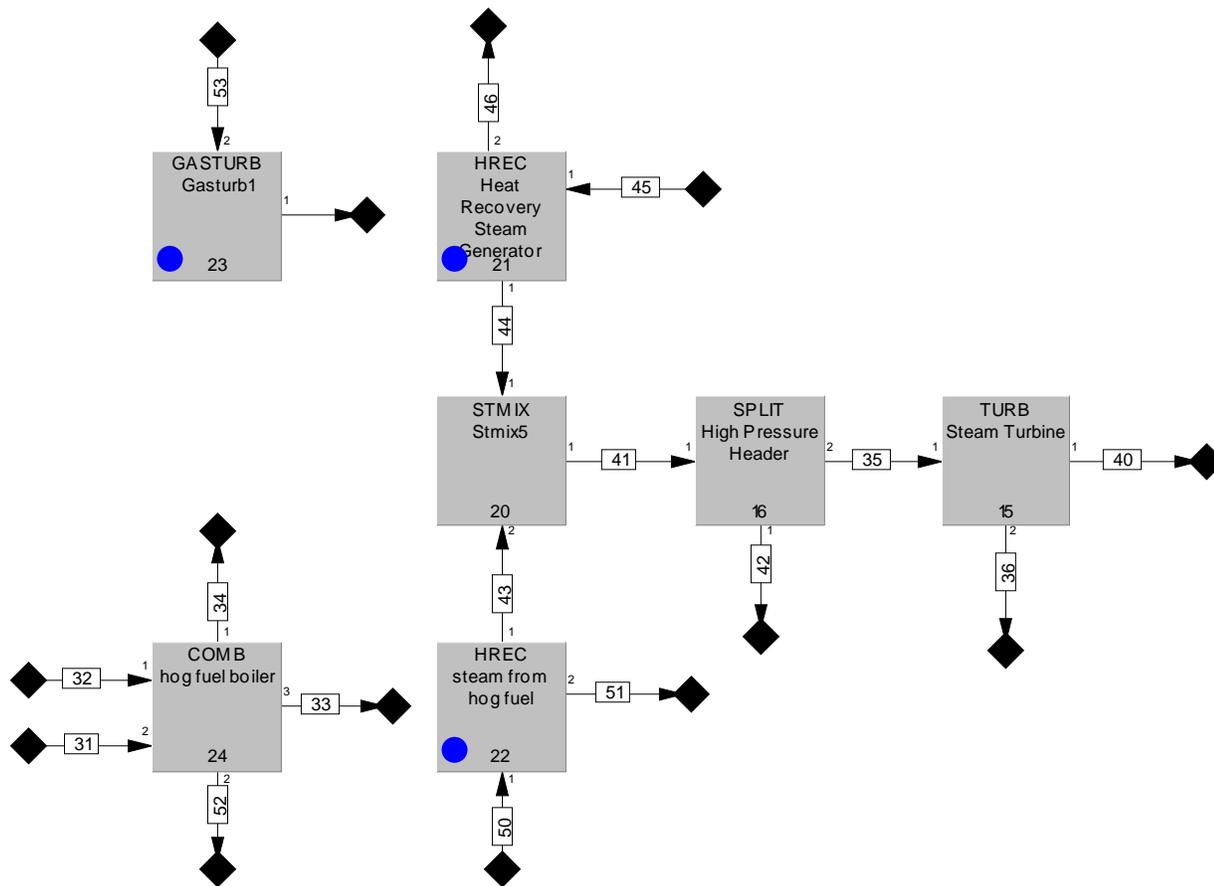
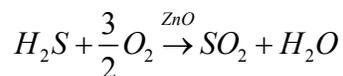
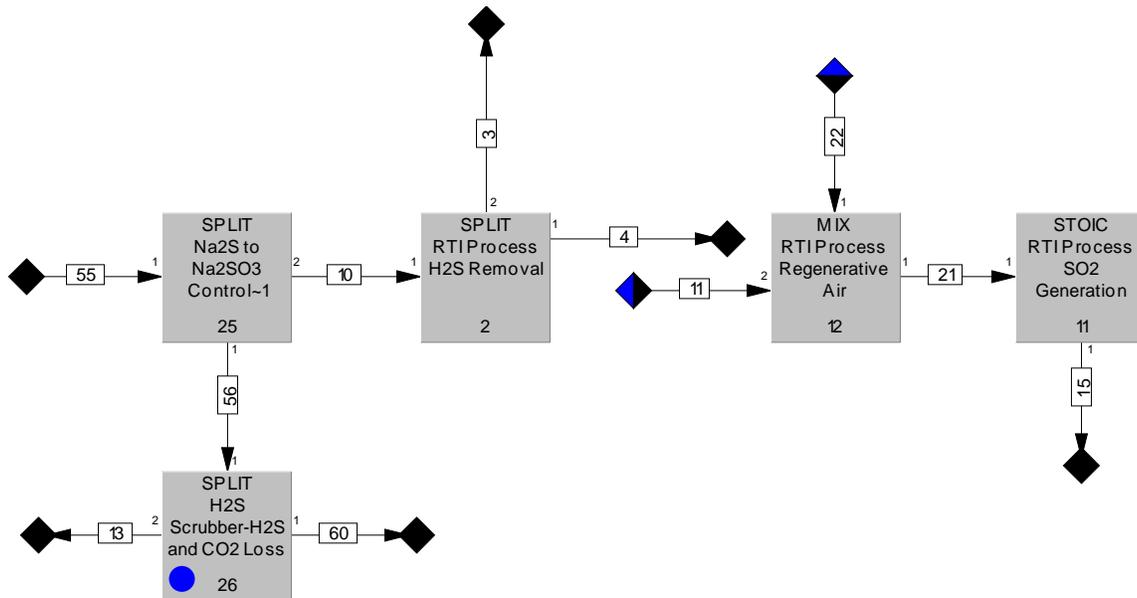


Figure 14-BLG Combined Cycle Layout

### Sulfur Recovery

The sulfur recovery process consists of the following four basic unit operations: a syngas split, a hydrogen sulfide scrubber, the RTI process and a sulfur dioxide scrubber. The first step of sulfur recovery involves a split of the syngas. In the actual process this would be accomplished by simply having one pipe split into two pipes and using a valve to control the relative flow rates. In WinGEMS, the split is made using a “SPLIT” block and a compute function. A proportional controller is used to achieve the desired ratio of sodium sulfide to sodium sulfite in the pulping liquor. This value was determined to be 0.07 kg Na<sub>2</sub>S / kg Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> (5). This value corresponded to 0.048 kg HS<sup>-1</sup> / kg HS<sup>-1</sup> and SO<sub>3</sub><sup>-2</sup>, which was the value input into WinGEMS. The largest portion of the syngas leaving the “SPLIT” block will enter the RTI process, seen in Figure 23. This process is represented by “SPLIT,” “MIX” and “STOIC” blocks. In the “SPLIT” block, 99.5% of the H<sub>2</sub>S is removed and is sent to the “MIX” block. The remaining syngas, free from H<sub>2</sub>S, goes to the gas turbine via stream 3. Air is added to the process using a mix block. A stoichiometric amount of air is calculated using a compute function on stream 22. The H<sub>2</sub>S exiting the split block (stream 4) is copied to stream 11 because stream 4 is a gas stream and stream 11 needs to be a liquor stream. The “STOIC” block is used to generate SO<sub>2</sub> from the H<sub>2</sub>S. This block represents the following reaction which takes place inside the RTI process:





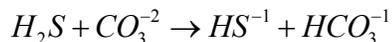
**Figure 15 RTI Process Gas Absorption Process**

A significant amount of costs is expected to be needed to regenerate the sorbent used in the RTI process. Therefore, estimation of the amount of sorbent needed for regeneration is a critical component of calculating variable operating costs. The amount of cycles needed between sorbent replacement and the space time of the reactor were provided by RTI and can be seen in Table 21. The space time along with the flowrate of syngas were used to calculate the total amount of sorbent needed in the RTI reactor. The total sorbent mass and the syngas flowrate were used to determine how much syngas could be cleaned per cycle. This information was then used to determine how much sorbent had to be replaced per metric ton of syngas cleaned.

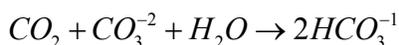
**Table 21-RTI Sorbent Replacement Assumptions**

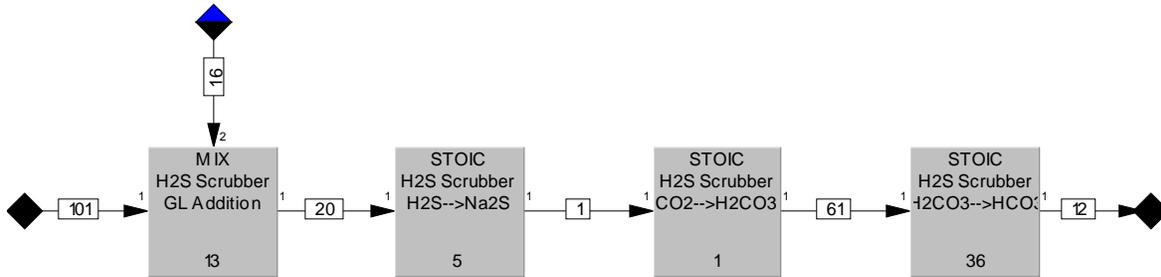
Sorbent Replacement (cycles)	500
Space Time (hr)	2000
Syngas Cleaned per cycle (mt)	93500
ZnO in bed (mt)	10100
Sorbent Replacement Rate (kg ZnO/mt syngas cleaned)	0.216

The portion of syngas leaving the bottom of the first “SPLIT” of Figure 16 enters a series of blocks that make up the H<sub>2</sub>S scrubber. The first “MIX” block combines green liquor from the smelt dissolving tank with the hydrogen sulfide and carbon dioxide absorbed from the syngas. The next “STOIC” block models the reaction of hydrogen sulfide with carbonate in the green liquor:



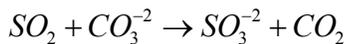
The next two “STOIC” blocks model the reaction of carbon dioxide with the carbonate in the green liquor. Two blocks had to be used since a “STOIC” block can only accept two products and two reactants. Thus, two reactions, that had a total sum of the desired reaction, were used in each block. The overall reaction which was modeled by these two blocks is the following:



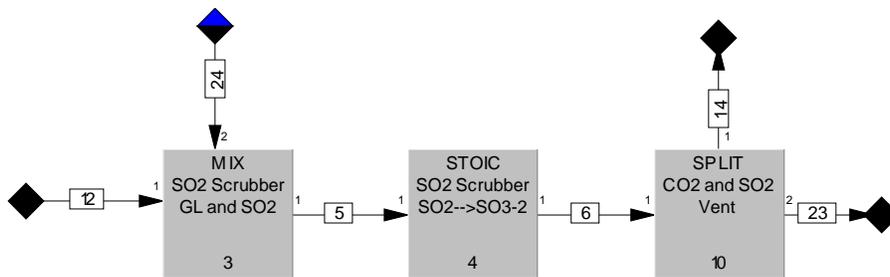


**Figure 16-H<sub>2</sub>S Scrubber Layout**

The blocks that model the sulfur dioxide scrubber are depicted in Figure 17. The sulfur dioxide produced by the RTI process is combined with the green liquor in a “MIX” block. A “STOIC” block then models the following reaction between sulfur dioxide and carbonate:



The MSS pulping liquor is now regenerated, containing both hydrosulfide and sulfite ions. Before the pulping liquor goes to the digester, remaining unreacted gases are vented to the atmosphere using a “SPLIT” block.



**Figure 17-SO<sub>2</sub> Scrubber Layout**

### Gasification Assumptions

The composition of the syngas was based on experimental data from TRI. The composition of the syngas was adjusted slightly to account for the extra sulfur that would be associated with MSSAQ pulping. The compositions of the syngas used for the simulation are summarized in Table 22 and were taken from the data provided by TRI.

**Table 22-Syngas Composition Dry Vol%**

Component	%
CH <sub>4</sub>	4.6
C <sub>2</sub> H <sub>6</sub>	0.2
C <sub>2</sub> H <sub>4</sub>	1.0
C <sub>3</sub> H <sub>6</sub>	0
H <sub>2</sub> S	9.3
H <sub>2</sub>	49.8
CO	2.6
CO <sub>2</sub>	26.6
HCl	0.45

The flowrates of syngas produced, natural gas needed for the pulse heaters and steam needed to fluidize

the bed were also determined from the same experimental set of data. The bed solids available to make green liquor were determined by a material balance around the gasifier. The assumptions used to model the gasification process are summarized in Table 23.

**Table 23-Black Liquor Gasification Assumptions**

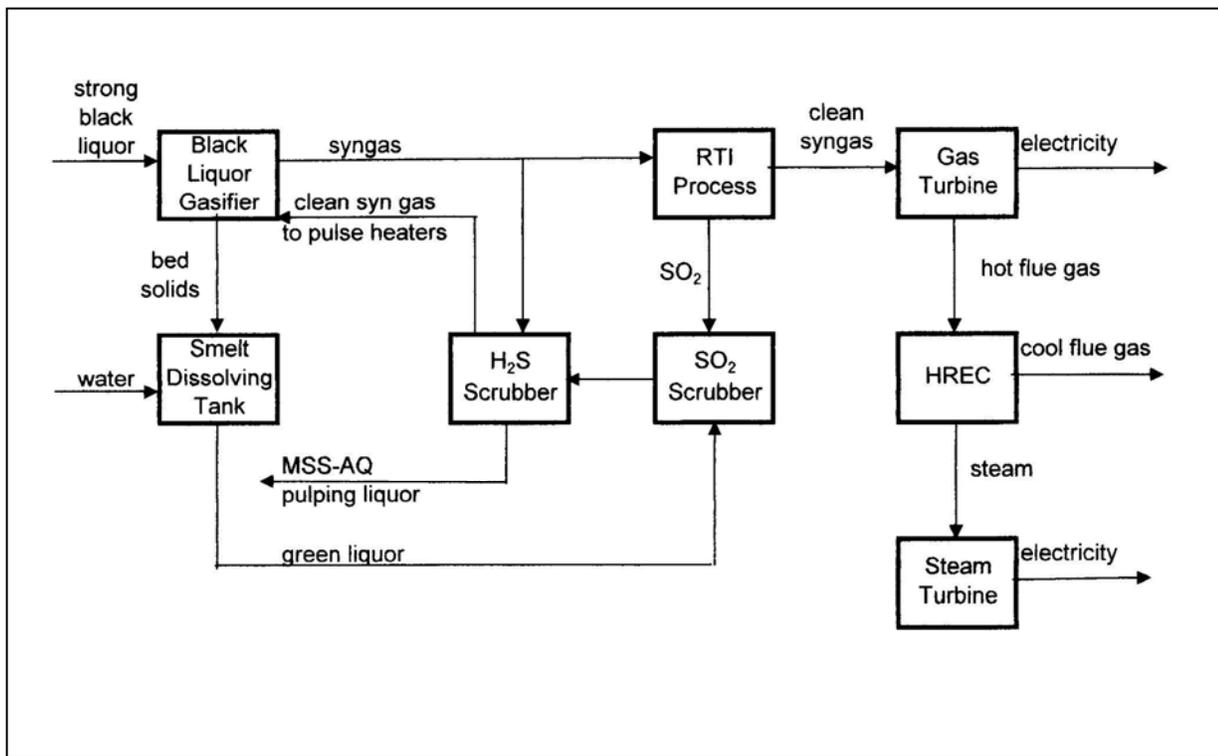
Black Liquor Solids (%)	70
Syngas Produced (mt/mt BLS)	0.60
Natural Gas to Pulse Heaters (mt/mt BLS)	0.10
Steam to Gasifier (mt/mt BLS)	0.19
Bed Solids (mt/mt BLS)	0.59

Objective 6: Provide a conceptual design and economic benefit analysis for the conversion of an existing kraft linerboard mill to the MSS-AQ/BLG/RTI absorber process

This work was performed by NCSU with input from Andritz, RTI and TRI.

*The Low Temperature Black Liquor Gasification Process*

In general terms, the black liquor gasification process gasifies black liquor and then combusts the resulting syngas in a gas turbine to produce electricity. Heat from the hot combustion gases are recovered and used to produce steam for a steam turbine and process heat. A sulfur recovery system is needed to remove sulfur from the syngas and return it to the cooking liquors. An overview of this process is depicted in Figure 18.



**Figure 18-Black Liquor Gasification with Chemical Recovery and Power Generation**

### *Capital Cost and Operating Cost*

The major equipment purchases needed to install a BLG process include the following: an H<sub>2</sub>S scrubber, an SO<sub>2</sub> scrubber, the RTI process, a gas turbine, the heat recovery/steam generation system, and the gasifier. A steam turbine will not need to be purchased because one is already present in the base system. Furthermore, it is assumed that extra capacity in the coal and hog fuel boiler already exists and can handle the extra throughput of coal and wood refuse needed to meet the increased steam for the BLG case. Total equipment costs are shown in Table 24. For both scrubbers, the flow to the unit was determined from the WinGEMS simulation and then a scaling factor of 0.6 was used to scale the equipment costs. For the scrubbers, the material used was assumed to be 316 stainless steel since sulfur is a very corrosive material.

The type of scrubber was assumed to be wet dynamic. Once each individual cost was determined, the total purchased equipment cost was determined by summing the individual costs. Cost estimate is based on a process that essentially mimics the conditions under which the sorbent was previously tested at RTI. In the tests at RTI, the sulfur capture from the syngas was based on a space velocity at standard temperature and pressure conditions (STP, 0° C and 14.7 psia) of 780 h<sup>-1</sup>. For a flow rate of 35,396 SCFM, 2749 ft<sup>3</sup> of sorbent would be required for desulfurization. As this would be a relatively large reactor vessel, we propose to divide the total syngas flow into five equal flows of about 7,080 SCFM. Each of these five syngas streams is desulfurized in a 3.5 ft ID reactor with 60 ft of packed sorbent length. Each of these reactors holds about 580 ft<sup>3</sup> of sorbent. While one set of reactors is being used to desulfurize the syngas, a second set of five reactors is undergoing regeneration and a third set of five reactors is being cooled and prepared for desulfurization. Thus, the total number of reactors required is 15.

During sorbent testing at RTI, regeneration of the sorbent was performed at a much higher space velocity than desulfurization. However, in a larger commercial bed, the heat from the exothermic regeneration can result in very high temperatures that have detrimental consequences to the sorbent and reactor. Rather than actively removing this heat, the rate of reaction is slowed by lowering the oxygen concentration in the regeneration gas (assumed 2 vol% rather than 5 vol%) and reducing the space velocity which reduces the reaction rate by reducing the supply of oxidation gas. For this cost estimate, it was assumed that the regeneration and subsequent cooling of the reactors take the same time to complete as the desulfurization. This assumption results in a set of reactors for regeneration and cooling/preparation for desulfurization

Using cost data from Loh and Lyons (Process Equipment Cost Estimation: Final Report, DOE/NETL-2002/1169, January 2002), which provides estimated capital cost and cost factors for key process equipment for gasification, the bare cost of these vessels (with a 150 psig rating, which is more than adequate for this desulfurization process) is \$51,000/ea (1998\$). Stainless steel will be required with a cost factor of 2.90 over carbon steel. Installation costs (including foundation, structural, buildings, insulation, electrical, piping, and miscellaneous) is estimated at \$98,369/ea, using Loh's factors applied to the carbon steel price (because the cost of installation of a stainless vessel should not be any greater than a carbon steel vessel).

The installed cost of each vessel is estimated at \$246,000; 15 vessels would cost \$3.69 million (1998\$). This cost, escalated to 2009\$ with the Chemical Engineering Process Equipment index (550/289.5) is \$5.22 million. Sorbent (580 ft<sup>3</sup> x 15) will also be required at \$560/ft<sup>3</sup>, or \$4.85 million for a total installed 2009 cost of \$10 million.

As you can see from the description of this cost estimate, the lion's share of the cost can be traced to the large amount of sorbent and number of reactors required. Potential reductions in capital cost could be

achieved if the desulfurization could be performed at a higher space velocity and the exothermic heat of regeneration effectively removed. Because neither of these issues was addressed in the parametric testing performed at RTI, I have used a space velocity that was been experimentally demonstrated in the testing at RTI for this capital cost estimate.

The cost of the gasifier and the HRSG unit were provided by Thermochem and has been escalated for 2009.

**Table 24-Installed Equipment Costs For Gasifier Based MSSAQ System**

<b>Equipment</b>	<b>Cost, 2009 \$</b>
H <sub>2</sub> S Scrubber	125,000
SO <sub>2</sub> Scrubber	475,000
RTI Process	10,000,000
Gas Turbine	32,500,000
Heat Recovery/Steam Generator	57,860,000
Gasifier	62,800,000
<b>Total Installed Equipment Costs</b>	<b>163,760,000</b>

The total capital investment needed for replacing the old recovery boiler with a high efficiency recovery boiler is estimated at \$170 million based on estimates from suppliers. It is being estimated that the capital cost for a new HERB and the Gasifier based MSSAQ recovery system is expected to be comparable and no credit was taken for the lower capital cost because of the uncertainty in the cost of the gasifier based system.

### *Operating Costs*

The main variable operating costs for both the base case and gasifier case are presented in Table 25. These costs are not inclusive of all costs that would be incurred but are expected to be the most significant cost related to these cases.

**Table 25-Variable Operating Costs for Eastern North Carolina**

Item	Cost	Units
Wood (OD)	75	\$/dry mt
NaOH	650	\$/mt
Na <sub>2</sub> SO <sub>4</sub>	122.5	\$/mt
Lime	61.4	\$/mt
AQ	3.31	\$/kg
Water	0.53	\$/mt
Waste Water Treatment	0.53	\$/mt
Boiler Feed Water	0.9	\$/mt
Fuel Oil Kiln	11.93	\$/MMBTU
Natural Gas Gasifier	6.95	\$/MMBTU
Coal for Boiler	2.05	\$/MMBTU
Disposal	8.05	\$/mt
Purchased Electricity	0.07	\$/kWh
Sold Electricity	0.05	\$/kWh
ZnO Sorbent for RTI Process	5	\$/lb

The change in total variable operating costs from the base case to the gasifier case for 1000 ODmt/day production is summarized in Table 26. A significant cost reduction in wood results for the gasifier case due to the higher yield associated with MSS-AQ pulping. Furthermore, a reduction in caustic make-up is also experienced since the MSS-AQ process does not use any caustic soda. However, saltcake make-up increased substantially which offset the savings from wood and caustic soda make-up. An annual savings of \$150,000 resulted from eliminating the need to purchase lime for the gasifier case. However, anthraquinone use needed for MSS-AQ pulping increased the variable operating costs by almost \$2,300,000 per year. The elimination of the lime kiln resulted in an annual savings of over \$7,800,000 from the purchase of fuel oil. However, natural gas needed for the pulse heaters resulted in an increase in natural gas costs of \$9,700,000 per year. It was assumed that the extra fuel needed to meet the steam demand would come from burning extra coal fuel. It is possible that that the existing boiler might not have the capacity to meet this extra throughput. In such a case the capacity of the hog fuel boiler will also have to be evaluated. The BLG case did result in an increase in electrical generation. Mill water and boiler feed water were reduced but the resulting savings were not significant compared to the other variable operating costs. Solid waste cost were reduced by about \$400,000 per year for the BLG case through less amounts of knots, and the elimination of dregs, grits and mud losses. However, the sorbent regeneration amounted to an increase in costs of \$1,000,000 per year. The net total change in variable operating costs for the gasifier compared to the HERB was an decrease of \$6,200,000 per year. This amounts to a reduction in operating cost of \$17/OD ton of pulp. This is a very significant saving and would have a very large impact on the overall operating cost. Additional saving would result from decreased labor and maintenance cost.

**Table 26- Savings in Operating Costs from Base with HERB to Low Temperature Gasifier**

	Base with HERB			MSSAQ with Gasifier			Difference
Item	Quantity Per ODT	\$/year		Quantity Per ODT	\$/year		\$/ODT
Wood (OD)	1.9428	50998500		1.5192	39879000		\$11119500
NaOH	0.0137	3116750		0	0		\$3116750
Na <sub>2</sub> SO <sub>4</sub>	0.0072	308700		0.08763	3757136.25		\$-3448436.30
Lime	0.0117	251433		0	0		\$251433
AQ	0	0		2	2317000		\$-2317000
Water							\$56000
Waste Water Treatment							\$12000
Boiler Feed Water							\$-11000
Fuel Oil Kiln	1.88	7849940		0	0		\$7849940
Natural Gas Gasifier	0	0		4	9730000		\$-9730000
Coal for Boiler				3.87	2776725		\$-2776725
Disposal	210	591675		62	174685		\$416990
Purchased Electricity	107	2621500					\$2621500
Sold Electricity							
ZnO Sorbent for RTI Process					1000000		\$-1000000
Total							\$6161275.50

## CONCLUSION

As expected, the addition of the low temperature black liquor gasifier with MSS-AQ pulping resulted in significant savings in purchased wood costs, kiln fuel and electricity. However, there were increases in saltcake make-up, natural gas, coal for the boiler and sorbent that were associated with the BLG process. The total decrease in variable operating costs for the BLG process compared to the HERB was in excess of \$6,200,000 per year for a mill producing 350,000 tons of pulp per year. This represents a decrease in operating cost of about \$17.7/ton of oven dry pulp produced. There will be additional savings in labor and maintenance cost that has not been taken into account.

The total capital investment for the BLG process was similar to that for the High Efficiency Recovery Boiler. However, the BLG process has yet to be successfully implemented at any pulp mill in North America containing sulfur and is thus an unproven technology.

The return on investment was estimated at 4%. A gasifier replacement cannot be justified on its own, however if the recovery boiler needs to be replaced the MSSAQ gasifier system shows a higher savings than replacement with a conventional recovery system.

## Accomplishments

Objective	Assessment of Success	Accomplishment
Define the pulping process conditions necessary to achieve the highest yield and optimum product characteristics	<p>Yield increase of 10-15% over kraft</p> <p>Comparable strength properties to kraft</p> <p>Increased brightness</p>	<ul style="list-style-type: none"> <li>• When compared to the Kraft reference pulp, the MSS-AQ procedures produced pulps with a 10-15 % yield benefit</li> <li>• ISO brightness 1.5-2 times greater.</li> <li>• The pulp refined little easier and had a slightly lower apparent sheet density (In both the cases). At similar levels of tear index the MSS-AQ (without NaOH) pulps also produced a comparable tensile and burst index pulps</li> <li>• Results presented at TAPPI Engineering Conference</li> </ul>
Trials with MSSAQ liquors in the lab scale to define the product gas composition and identify design parameters for a black liquor gasifier system	Completion of objective	Product gas composition determined using computer simulations
Trials on a pilot scale RTI absorber with the appropriate product gas compositions to quantify the adsorption and desorption characteristics with MSS-AQ product gas compositions and identify design parameters for an absorber	<p>98.5%+ removal of the sulfur from the product gas</p> <p>If removal is:</p> <ul style="list-style-type: none"> <li>• ~90% further trials will be recommended</li> <li>• less than 70%, project terminated</li> </ul>	<ul style="list-style-type: none"> <li>• The results demonstrate that RVS-1 can effectively remove &gt; 99.8% of the H<sub>2</sub>S present in simulated synthesis gas generated from the gasification of black liquor. This level of sulfur removal was consistent over simulated synthesis gas mixtures that contained from 6 to 9.5 vol % H<sub>2</sub>S.</li> <li>• A significant amount of the sulfur in the simulated syngas was recovered as SO<sub>2</sub> during regeneration. The average recovery of sulfur as SO<sub>2</sub> was about 75%. Because these are first cycle results, this sulfur recovery is expected to improve.</li> </ul>
Define the process and equipment changes required in an existing batch and continuous digester mill to integrate the MSS-AQ process along with BLG and RTI absorption technology	Completion of objective	Identified major changes necessary for the process

<p>Develop a WINGems process model for detailed economic evaluation and process impact</p>	<p>Confirm energy savings of 2.6 million BTU/ton of pulp and cost savings of \$25-30/ODTP.</p> <p>ROI should be greater than 20+%</p>	<ul style="list-style-type: none"> <li>• Developed WINGems model of the process.</li> <li>• The total decrease in variable operating costs for the BLG process compared to the HERB was in excess of \$6,200,000 per year for a mill producing 350,000 tons of pulp per year. This represents a decrease in operating cost of about \$17.7/ton of oven dry pulp produced. There will be additional savings in labor and maintenance cost that has not been taken into account.</li> <li>• The capital cost for the MSSAQ based gasifier system was estimated at \$164,000,000 which was comparable to a High Efficiency Recovery Boiler</li> <li>• The return on investment was estimated at 4%. A gasifier replacement cannot be justified on its own, however if the recovery boiler needs to be replaced the MSSAQ gasifier system shows a higher savings.</li> </ul>
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## Conclusions

The purpose of the two different liquor compositions in MSS-AQ pulping was to optimize the effect of NaOH and Na<sub>2</sub>S charge on the pulping procedure and pulp properties. MSS-AQ (with NaOH) pulps had a total chemical 22%. From an operating cost perspective, it would be desirable to minimize the amount of NaOH used in the process, while optimizing the relative amounts of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as to their effect on process operation, output and pulp properties.

When comparing the process output results for the two procedures it is worth noting that there seems to be little difference in the cooking liquor initial pH and the black liquor final pH. Furthermore, when pulping to the same h factor, there is little difference in the resulting pulp yield, kappa and ISO brightness. This indicates that with regard to pulping operations and the listed pulp properties, there is little or no benefit of adding NaOH to the cooking liquor.

When compared to the Kraft reference pulp, the MSS-AQ procedures produced pulps with a 10-15 % yield benefit and ISO brightness 1.5-2 times greater. The pulp refined little easier and had a slightly lower apparent sheet density (In both the cases). At similar levels of tear index the MSS-AQ (without NaOH) pulps also produced a comparable tensile and burst index pulps which was reported to be the main problem in the previous published papers with the MSS-AQ pulping.

Modifications to the kraft process, using MSS-AQ pulping, can generate comparable rates of delignification, improvements in pulp yield, viscosity and strength properties, but not all at the same time. Further optimization of this technology could have a significant effect on the kraft process. MSS-AQ pulping can generate significant yield benefits and significantly higher brightness. A unique opportunity

exists in MSS-AQ pulping where it would be possible to eliminate the causticizing and lime kiln operations in the recovery cycle of black liquor gasification, resulting in very significant cost-savings.

The work summarized here was intended to show the potential of MSS-AQ process, a high yield pulping process. The payback on realizing the potential of these processes would be rather large cost savings due to the increased yield and high brightness therefore saving in pulping and bleaching chemical and have significant cost savings.

TRI used the calculated and actual measurements of the black liquor in a steady state, quasi-equilibrium process model that it has developed and validated on many different organic feedstocks to project product gas composition and yield and reformer performance for the MSSAQ liquor.

The major components of the syngas were methane, hydrogen sulfide, hydrogen, carbon monoxide and nitrogen. The heat value of the syngas was about 310 BTU/SCF. The composition of the syngas was used by RTI to simulate the operation of the ZnO based gas absorption system. It was critical to see if the sulfur in the syngas can be cleaned up to appropriate levels.

The results demonstrate that RVS-1 can effectively remove > 99.8% of the H<sub>2</sub>S present in simulated synthesis gas generated from the gasification of black liquor. This level of sulfur removal was consistent over simulated synthesis gas mixtures that contained from 6 to 9.5 vol % H<sub>2</sub>S and steam concentrations up to 40 vol %. Even with operating conditions that have not been optimized, this level of sulfur removal is very close to meeting the typical sulfur emission standards for coal-fired power plant (1.4 lb of SO<sub>x</sub>/MWh gross which translates to roughly 60-80 ppmv in the synthesis gas). With suitable optimization of operating and/or process conditions, the sulfur in the desulfurized synthesis gas could meet current emission requirements for SO<sub>x</sub>.

Based on the regeneration results generated during this testing, a significant amount of the sulfur in the simulated syngas was recovered as SO<sub>2</sub> during regeneration. The average recovery of sulfur as SO<sub>2</sub> was about 75%. Because these are first cycle results, this sulfur recovery is expected to improve. In previous testing with RVS-1, between 2 and 5 cycles were required for sorbent desulfurization to stabilize.

Based on these results, the use of regenerable ZnO-based sorbents, like RVS-1, to desulfurize synthesis gas generated by black liquor gasification provides a technically feasible means to improve thermal efficiency of synthesis gas production and use, while recovering the sulfur in the synthesis gas as SO<sub>2</sub>. With these results, a better techno-economic evaluation of the use of warm gas desulfurization of synthesis gas using regenerable ZnO-based sorbents should be possible.

As expected, the addition of the low temperature black liquor gasifier with MSS-AQ pulping resulted in significant savings in purchased wood costs, kiln fuel and electricity. However, there were increases in saltcake make-up, natural gas, coal for the boiler and sorbent that were associated with the BLG process. The total decrease in variable operating costs for the BLG process compared to the HERB was in excess of \$6,200,000 per year for a mill producing 350,000 tons of pulp per year. This represents a decrease in operating cost of about \$17.7/ton of oven dry pulp produced. There will be additional savings in labor and maintenance cost that has not been taken into account.

The total capital investment for the BLG process was similar to that for the High Efficiency Recovery Boiler. However, the BLG process has yet to be successfully implemented at any pulp mill in North America containing sulfur and is thus an unproven technology. The return on investment was estimated at 4%. A gasifier replacement cannot be justified on its own, however if the recovery boiler needs to be

replaced the MSSAQ gasifier system shows a higher savings than replacement with a conventional recovery system.

It has been demonstrated that the three technologies necessary are capable of delivering significant savings. For commercialization the following need to be considered:

**MSSAQ Pulping:** The barriers for pulping are minimal, some metallurgical issues will need to be corrected if the digesters are made of carbon steel. There were no major equipment limitations identified. The TRS collection system should also be adequate.

**TRI Gasifier:** A commercial unit based on soda liquor is in operation, however no commercial unit for liquors containing sulfur is in operation. This probably is the biggest limitation to implementation of this technology. Operation of pilot scale gasifiers with sulfur containing liquors has been demonstrated.

**RTI ZnO based absorber:** This system has been commercially implemented for cleanup application in coal gasification. The results demonstrate that RVS-1 can effectively remove > 99.8% of the H<sub>2</sub>S present in simulated synthesis gas. The major barrier is the low sulfur recovery. Further research is necessary to improve the SO<sub>2</sub> recovery.

## **Recommendations**

Before black liquor based gasifier technology can be commercialized more work is necessary in the following areas:

- The recovery of the absorbed sulfur in the absorbent as sulfur dioxide is only 75%. This needs to be greater than 90% for economical operation. It has been suggested that as the no of cycles is increased the sulfur dioxide recovery might improve. Further research is necessary.
- Even though a significant amount of work has been done on a pilot scale for a gasifier using liquors containing sulfur, both at low and high temperatures the lack of a commercial unit is an impediment to the implementation of the MSSAQ technology. The implementation of a commercial unit needs to be facilitated before the benefits of the MSSAQ technology with ZnO absorption can be taken advantage of.

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