

ABSTRACT

LINDSTRÖM, ERIK VILHELM MATHIAS. Integrating Black Liquor Gasification with Pulping – Process Simulation, Economics and Potential Benefits. (Under the direction of Dr. Hasan Jameel and Dr. Adrianna G. Kirkman.)

Gasification of black liquor could drastically increase the flexibility and improve the profit potential of a mature industry. The continuous efforts made in the area of black liquor gasification (BLG) are bringing this technology closer to commercial realization and potential wide-spread implementation. Research exploring the integration of BLG into the kraft process and the potential of BLG enabled modified pulping technologies on modern pulping operations is important to support this effort. The following effort is focused on such research, utilizing laboratory pulping experiments and process simulation. The separation of sodium and sulfur achieved through gasification of recovered black liquor can be utilized in processes like modified continuous cooking, split sulfidity and green liquor pretreatment pulping, and polysulfide-anthraquinone pulping to improve pulp yield and properties. Laboratory pulping protocols have been developed for these modified pulping technologies and different process options evaluated. The process simulation work around BLG has led to the development of a WinGEMS module for the low temperature MTCI steam reforming process, and case studies comparing a simulated conventional kraft process to different process options built around the implementation of a BLG unit operation into the kraft recovery cycle. The implementation of gasification, functioning as the core of wood pulping recovery operations in a biorefinery, would enable the application of modified pulping technologies while creating a synthetic product gas that could be utilized in the production of value added products in addition to wood pulp. The evaluated modified pulping technologies have indicated the potential of yield increases of 1-3% points with improved product quality, and the potential for capital and operating cost savings relative to the conventional kraft process. Process simulation work has shown that the net variable operating cost for a pulping process using BLGCC is highly dependent on the cost of lime kiln fuel and the selling price of green power to the grid. Under the initial assumptions taken in the performed case study, the BLGCC process combined with split sulfidity or PSAQ pulping operations had net variable operating cost 2-4% greater than the kraft reference. When comparing the BLG cases to the MCC reference, the net variable operating cost break even point based on lime kiln fuel cost is about \$47/barrel for the split sulfidity and lower charge polysulfide processes, and about \$38/barrel for the higher polysulfide charge process. This is significantly lower than assumed kiln fuel price of \$60/barrel used in this work. If the sales price for power to the grid could be increased through green power credits from 3.5 to 6 ¢/KWh cost savings of about \$40/ODtP could be realized in the investigated BLG processes. Other alternatives to improve the process economics around BLG would be to modify or eliminate the lime kiln unit operations, utilizing high sulfidity green liquor pretreatment, PSAQ with auto-causticization, or converting the process to mini-sulfide sulfite-AQ.

**INTEGRATING BLACK LIQUOR GASIFICATION WITH PULPING – PROCESS
SIMULATION, ECONOMICS AND POTENTIAL BENEFITS**

by
ERIK VILHELM MATHIAS LINDSTRÖM

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

WOOD AND PAPER SCIENCE

Raleigh, North Carolina
2007

APPROVED BY:

Dr. Michael Overcash

Dr. Hou-min Chang

Dr. Hasan Jameel
Chair of Advisory Committee

Dr. Adrianna Kirkman
Co-chair of Advisory Committee

For my wife, my mother and father, and for all those that have believed in me...

...change is good...

BIOGRAPHY

The author was born in Stockholm, Sweden in 1975. He graduated from Nacka Gymnasium in 1995, after having spent one year (1992-1993) in Flint, MI, as an AFS exchange student. While in Flint he attended Flint Northern HS, participating in the Magnet Program and lettering in 4 sports. Upon completion of the Swedish "*Studenten*", he returned to the US, matriculating at Wittenberg University in Springfield, OH. He received a Bachelor of Arts in chemistry with a minor in music theory and composition in 1999. He then went on to Miami University, Oxford, OH, where he completed a Master of Science in Paper Science and Engineering, working with Dr. Bill Scott. He now lives with his wife Amy Joyce in Garner, NC and has accepted a position with MeadWestvaco in Raleigh, NC, where he will begin his career upon completion of this degree.

ACKNOWLEDGMENTS

The following work is the result of my own relentless persistence and invaluable assistance from a group of very important people. First and foremost, I would like to thank my wife Amy Joyce, for not abandoning me during this long process, and for her endless support! I also would like to express my deepest regards and gratitude for my advisors, Dr. Hasan Jameel and Dr. Adrianna Kirkman. Without their guidance, efforts and great patience, this undertaking would never have succeeded! They have helped me grow as a problem solver, researcher, and person beyond what I could ever have expected! I would also like to thank my other committee members, members of the faculty and staff, and all my new found friends, for their support and optimism; especially Dr. Sunkyu Park, and Dr. Ved Naithani and Jim McMurray without whom the pulping effort would have fallen short. I would also like to acknowledge TRI, MTCI and the US Department of Energy, for their financial and technical support of this project that allowed me to learn so much about so many things.

E.V.M.L., Raleigh, 2007

TABLE OF CONTENTS

LIST OF TABLES.....	viii
LIST OF FIGURES.....	x
1 INTRODUCTION.....	1
1.1 Review of black liquor gasification development.....	2
<i>1.1.1 Low Temperature Gasifier/Steam Reformer.....</i>	<i>3</i>
<i>1.1.2 High Temperature Gasifier.....</i>	<i>4</i>
<i>1.1.3 Current Status of BLG Technologies.....</i>	<i>5</i>
1.2 Review of kraft pulping chemistry.....	6
<i>1.2.1 Lignin structure and kraft pulping reactions.....</i>	<i>7</i>
<i>1.2.2 Carbohydrate structure and kraft pulping reactions.....</i>	<i>11</i>
1.3 Review of modified kraft pulping processes.....	15
<i>1.3.1 Modified continuous cooking.....</i>	<i>15</i>
<i>1.3.2 Green liquor pretreatment.....</i>	<i>16</i>
<i>1.3.3 Split sulfidity pulping.....</i>	<i>16</i>
<i>1.3.4 Kraft polysulfide pulping with anthraquinone.....</i>	<i>18</i>
2 STATEMENT OF OBJECTIVES.....	19
2.1 Objectives for laboratory pulping work.....	20
2.2 Objectives for process simulation work.....	20
3 SUMMARY, CONCLUSIONS AND FUTURE WORK.....	20

3.1 Review of laboratory pulping results	20
3.1.1 <i>Green liquor pretreatment</i>	20
3.1.2 <i>Split sulfidity pulping</i>	21
3.1.3 <i>Polysulfide-anthraquinone pulping</i>	22
3.2 Process simulation	23
3.2.1 <i>Development of BLG model for WinGEMS</i>	24
3.2.2 <i>Simulation of the effects of BLG integration on kraft mill operations</i>	25
3.3 Conclusions	25
3.3.1 <i>Conclusions from split sulfidity pulping</i>	25
3.3.2 <i>Conclusions from green liquor pretreatment pulping</i>	25
3.3.3 <i>Conclusions from polysulfide pulping with anthraquinone</i>	26
3.3.4 <i>Conclusions from WinGEMS simulation work</i>	26
3.4 Future work	27
4 REFERENCES	28
5 ECONOMICS OF INTEGRATING BLACK LIQUOR GASIFICATION WITH PULPING: PART I – EFFECT OF SULFUR PROFILING	32
6 EFFECTS ON PULP YIELD AND PROPERTIES USING MODIFIED PULPING PROCEDURES INVOLVING SULFUR PROFILING AND GREEN LIQUOR PRETREATMENT	47
7 THE EFFECT OF INTEGRATING POLYSULFIDE PULPING AND BLACK LIQUOR GASIFICATION ON PULP YIELD AND PROPERTIES	64
8 THE EFFECT OF INTEGRATING POLYSULFIDE PULPING AND BLACK LIQUOR GASIFICATION ON PULP YIELD AND DELIGNIFICATION	81
9 THE DEVELOPMENT AND VALIDATION OF A LOW-TEMPERATURE BLACK LIQUOR GASIFIER MODEL FOR USE IN WINGEMS©	93
10. WINGEMS SIMULATION OF NET PROCESS VARIABLE OPERATING COSTS RESULTING FROM BLG INTEGRATION WITH SPLIT SULFIDITY AND POLYSULFIDE PULPING	102
11 INTEGRATING BLACK LIQUOR GASIFICATION AND PULPING AND A REVIEW OF CURRENT TECHNOLOGY	113
12 APPENDICES	134

12.1 Notes on pump calibration and operation	135
12.2 Protocol for simulated MCC pulping	136
12.3 Protocol for Polysulfide generation.....	137

LIST OF TABLES

Table 1.1	Demonstration of sulfur utilization as Na ₂ S (kraft) or Na ₂ S/PS (kraft-PS) and the system sulfur availability for PS generation	19
Table 3.1	Total yield improvement from PS procedures compared to 25% S MCC pulp	23
Table 5.1	Effect of Black Liquor Gasification and the H ₂ S to CO ₂ Co-absorption on the Process	41
Table 5.2	Effect of Black Liquor Gasification and the H ₂ S to CO ₂ Co-absorption on Cost	42
Table 5.3	Effect of Split Sulfidity and Yield Increase on the Process	43
Table 5.4	Effect of Split Sulfidity and Yield Increase on Cost	44
Table 5.5	Effect of using Na ₂ CO ₃ for Pretreatment and %EA Use on the Process	45
Table 5.6	Effect of using Na ₂ CO ₃ for Pretreatment and %EA Use on Cost	46
Table 6.1	Parameters for MCC protocol	50
Table 6.2	Outline of collection scheme for digester liquor samples	50
Table 6.3	Parameters for Split Sulfidity protocols, high initial and low initial alkali (SS_HIA/SS_LIA)	51
Table 6.4	Parameters for Green Liquor Pretreatment protocols, high initial and low initial alkali (GLPT_HIA/GLPT_LIA)	51
Table 6.5	MCC baseline pulp yield, kappa and viscosity	54
Table 6.6	Split Sulfidity baseline pulp yield, kappa and viscosity	55
Table 6.7	Green liquor pretreatment baseline pulp yield, kappa and viscosity	57
Table 6.8	Pulp strength properties for low kappa range cooks	60
Table 6.9	Pulp strength properties for high kappa range cooks	60
Table 7.1	Parameters for MCC protocol	66
Table 7.2	Demonstration of sulfur utilization and system availability for PS generation	67
Table 7.3	Parameters for Polysulfide-Anthraquinone (PSAQ) cooks	67
Table 7.4	Parameters for medium (MIA) and high (HIA) initial alkali PSAQ cooks	67
Table 7.5	Summary of cooks performed using 25% sulfidity	68
Table 7.6	Summary of cooks performed using 40% sulfidity	70
Table 7.7	Pulp strength properties for 25% sulfidity cooks	75

Table 7.8	Pulp strength properties for 40% sulfidity cooks	77
Table 8.1	Parameters for MCC protocol	83
Table 8.2	Outline of cooks performed using 25% and 40% sulfidity	84
Table 8.3	Outline of cooks performed at zero initial alkali exploring the effect of alkali profiling	84
Table 9.1	BLG user defined block parameters.....	97
Table 9.2	Algorithm for BLG material balances	98
Table 9.3	Predicted BLG process streams and comparisons to MTCI process data	100
Table 10.1	Input parameters and key assumptions for WinGEMS case study.....	106
Table 10.2	Comparison of fiber line process parameters for each simulated case.....	107
Table 10.3	Comparison of chemical recovery process parameters for each simulated case.....	108
Table 10.4	Comparison of power and steam process variables for each simulated case	109
Table 10.5	Comparison of case study variable operating cost parameters and net cost per ODtP produced	109
Table 11.1	Demonstration of sulfur utilization as Na ₂ S (kraft) or Na ₂ S/PS (kraft-PS) and the system sulfur availability for PS generation	124
Table 11.2	Total yield improvement from PS procedures compared to 25% S MCC pulp	124
Table 11.3	Chemical Requirements for Selected Options for production of 1 ODtP (all chemicals as Na ₂ O) converted to kg/ton.....	126
Table 11.4	Estimated Cost Comparisons of Tomlinson and BLGCC Power/Recovery Systems Relative the Tomlinson BASE (index = 100), (68).....	128
Table 11.5	General Comparison of BLG Enabled Pulping Technologies	129

LIST OF FIGURES

Figure 1.1	Simplified representation of BLGCC power/recovery systems.....	3
Figure 1.2	Schematic of MTCI Steam Reformer	4
Figure 1.3	Formation of the Quinone-Methide Intermediate (QMI) under alkaline conditions and outline of lignin degradation reactions (13)	8
Figure 1.4	Nucleophilic (HS ⁻) addition to the QMI and cleavage of the β -aryl ether bond (13).....	9
Figure 1.5	Formaldehyde elimination from the QMI generating an enol ether structure and subsequent condensation between formaldehyde and enol ether resulting in diaryl-methane structures (13) ...	9
Figure 1.6	Electron-transfer reaction reducing the QMI with cleavage of the β -aryl ether bond leading to the generation of coniferyl-type structures (13)	10
Figure 1.7	Alkaline degradation of non-phenolic lignin structures with epoxide ring opening through nucleophilic attack generating stable lignin-carbohydrate complexes (LCC) (13).....	10
Figure 1.8	Outline of the alkaline carbohydrate end-wise peeling reaction (13)	13
Figure 1.9	Outline of the carbohydrate stopping reaction (13)	13
Figure 1.10	Oxidative peeling reaction through β -alkoxy elimination at the C2 position (13).....	14
Figure 1.11	Alkaline (Random) hydrolysis of carbohydrate glycosidic bonds generating a new reducing end group or levoglucosan (13).....	15
Figure 1.12	Outline of process using green liquor pretreatment	16
Figure 1.13	Schematic of unit operations in split sulfidity pulping	17
Figure 1.14	Outline of process using polysulfide	18
Figure 3.1	Obtained results for pulping using green liquor pretreatment procedure.....	21
Figure 3.2	Delignification and yield results for split sulfidity pulping	22
Figure 3.1	Input and output stream structure for BLG model.....	24
Figure 5.2	Schematic of a MTCI Steam Reformer	35
Figure 5.3	Schematic for the Production of Conventional White Liquor with BLG	37
Figure 5.4	Schematic for the Production of Sulfide Lean and Sulfide Rich White Liquor with BLG.....	37
Figure 5.5	Schematic for using NaHS and Na ₂ CO ₃ in Pretreatment with BLG	39
Figure 6.1	Residual Effective Alkali (REA) profiles for MCC procedure.....	52

Figure 6.2	Residual Effective Alkali (REA) profiles for SS_HIA procedure	53
Figure 6.3	Residual Effective Alkali (REA) profiles for SS_LIA procedure	53
Figure 6.4	Residual Effective Alkali (REA) profiles for GLPT modified procedure	54
Figure 6.5	Kappa number versus final h factor for the MCC baseline, SS_HIA and SS_LIA cooks	55
Figure 6.6	Total yield versus kappa for the MCC baseline, SS_HIA and SS_LIA cooks	56
Figure 6.7	Viscosity versus kappa for the MCC baseline, SS_HIA and SS_LIA cooks.....	56
Figure 8.	Kappa number versus final h factor for the MCC baseline, GLPT_HIA, GLPT_LIA and GLPT modified cooks	57
Figure 9.	Total yield versus kappa for the MCC baseline, GLPT_HIA, GLPT_LIA and GLPT modified cooks.....	58
Figure 6.10	Viscosity versus kappa for the MCC baseline, GLPT_HIA, GLPT_LIA and GLPT modified cooks.....	58
Figure 6.11	Refining response for low kappa pulps.....	59
Figure 6.12	Refining response for high kappa pulps	59
Figure 6.13	Tensile index versus tear index for low kappa pulps	61
Figure 6.14	Burst index versus tear index for low kappa pulps.....	61
Figure 6.15	Tensile index versus tear index for high kappa pulps.....	62
Figure 6.16	Burst index versus tear index for high kappa pulps.....	62
Figure 7.1	Kappa number versus AA charge for the MCC baseline and PS cooks at 25% sulfidity	69
Figure 7.2	Total yield versus kappa for the MCC baseline and PS cooks at 25% sulfidity	69
Figure 7.3	Viscosity versus kappa for the MCC baseline and PS cooks at 25% sulfidity	70
Figure 7.4	Kappa number versus AA charge for 25% and 40% sulfidity cooks.....	71
Figure 7.5	Total yield versus kappa for 25% and 40% sulfidity cooks.....	71
Figure 7.6	Viscosity versus kappa for 25% and 40% sulfidity cooks	72
Figure 7.7	Kappa number versus AA charge for the MCC baseline and PS cooks at 40% sulfidity	72
Figure 7.8	Total yield versus kappa for the MCC baseline and PS cooks at 40% sulfidity	73
Figure 7.9	Viscosity versus kappa for the MCC baseline and PS cooks at 40% sulfidity	73
Figure 7.10	Refining response for 25% sulfidity pulps	74
Figure 7.11	Refining response for 40% sulfidity pulps	74

Figure 7.12	Tensile index versus tear index 25% sulfidity cooks.....	75
Figure 7.13	Burst index versus tear index for 25% sulfidity cooks	76
Figure 7.14	Tensile index versus tear index for 40% sulfidity cooks	78
Figure 7.15	Burst index versus tear index for 40% sulfidity cooks	78
Figure 8.1	Kappa number versus initial alkali charge for 25% sulfidity pulps	85
Figure 8.2	Normalized total yield versus initial alkali charge for 25% sulfidity pulps.....	85
Figure 8.3	Kappa number versus initial alkali charge for 40% sulfidity pulps	86
Figure 8.4	Normalized total yield versus initial alkali charge for 40% sulfidity pulps.....	86
Figure 8.5	Comparing the effect of alkali profiling on delignification rate and pulp yield for zero initial alkali PSAQ cooks (25% and 40% sulfidity).....	87
Figure 8.6	The effect of alkali profiling on residual effective alkali for MCC at 25% S.....	88
Figure 8.7	The effect of alkali profiling on residual effective alkali for PSAQ at 25% S.....	88
Figure 8.8	The effect of alkali profiling on REA using for PSAQ 25% S at zero initial alkali charge.....	89
Figure 8.9	The effect of alkali profiling on residual effective alkali for MCC at 40% S.....	89
Figure 8.10	The effect of alkali profiling on residual effective alkali for PSAQ at 40% S.....	90
Figure 8.11	The effect of alkali profiling on REA using for PSAQ 40% S at zero initial alkali charge.....	90
Figure 9.1	Schematic of a MTCI Steam Reformer	96
Figure 9.2	Stream structure for BLG model	96
Figure 9.3	WinGEMS simulation using integrated BLG block model	99
Figure 10.1	Schematic of a MTCI Steam Reformer	104
Figure 10.2	Stream structure for BLG model	105
Figure 10.3	The effect of lime kiln fuel price on net variable operating cost, keeping all other cost factors constant (assuming green power sales price at €3.5/KWh)	110
Figure 10.4	The effect of green power sales price on net variable operating cost, keeping all other cost factors constant (assuming lime kiln fuel price at \$60/barrel).....	111
Figure 11.1	Simplified representation of BLGCC power/recovery systems.....	115
Figure 11.2	Schematic of MTCI Steam Reformer	117
Figure 11.3	Schematic of unit operations in split sulfidity pulping	120
Figure 11.4	Delignification and yield results for split sulfidity pulping	121

Figure 11.5	Outline of process using green liquor pretreatment	122
Figure 11.6	Obtained results for pulping using green liquor pretreatment	122
Figure 11.7	Outline of process using polysulfide	123
Figure 11.7	Total pulp yield and ISO Brightness versus kappa for Kraft, AS-AQ and MSS-AQ	126
Figure 11.8	Schematic of the alkaline sulfite pulping processes with the RTI absorber.....	127

LIST OF ABBREVIATIONS

AQ	anthraquinone
BAR	benzylic acid rearrangement
BL	black liquor
BC	base case (reference for case study comparison)
BLG	black liquor gasification, and BL gasifier module in WinGEMS
BLGCC	black liquor gasification combined cycle
CC	combined cycle (power production)
DP	degree of polymerization
CPS	centipoises (unit)
GL	green liquor
HIA	high initial alkali charge
HRSG	heat recovery steam generator
KFURN	kraft recovery furnace module in WinGEMS
LIA	low initial alkali charge
MCC	modified continuous cooking
MIA	medium initial alkali charge
OD	oven dry
ODtP	oven dry <u>metric</u> ton pulp
PS	polysulfide
PSAQ	polysulfide anthraquinone (pulping)
SS	split sulfidity (pulping)
WINGEMS	windows version of “general energy and mass balance system” (software name)
ZAP	zero effective alkali in pretreatment

1 INTRODUCTION

The kraft or sulfate process is the dominant chemical pulping technology employed in the paper industry today. The competitive advantage that has led to its position is the capability to convert most wood species to high strength pulp combined with an efficient chemical recovery based around the Tomlinson recovery boiler. There are approximately 280 Tomlinson recovery boilers in operation in North America, according to the Black Liquor Recovery Boiler Advisory Committee of the American Forest and Paper Association (AF&PA). Many of these boilers are nearing the end of their useful life, and will either need to be upgraded or replaced in the near future. Black liquor gasification (BLG) is one technology that could be implemented into the kraft process to replace a mature technology, while creating new opportunities in process operations and the potential for enhanced competitiveness.

The underlying fundamental for implementation of any new technology is the impact it will have on overall process economics. Some deciding factors that will influence the implementation of BLG involve the cost-benefits associated with power generation and other high-value products that can be derived from the syngas. Another area of importance is the potential cost-savings that can be realized through process modifications and optimization. The effect on wood, chemical and fuel demand from changes in the pulping process can have a significant effect on the variable operating cost, capital investment and maintenance costs. Therefore, research exploring the impact of BLG on pulping technologies will be of great importance for the eventual implementation of this technology. The following effort explores the potential benefits realizable through the implementation of BLG integrated with the modified pulping technologies that it enables.

Presently, in a typical chemical pulp mill the black liquor is concentrated to greater than 65% dissolved solids and burned in a recovery boiler. The pulping chemicals are recovered in the smelt and the heat energy is converted to steam, which is used in a steam turbine generator to produce electricity. The typical thermal efficiency of a recovery boiler is generally 65-70%, and the thermal efficiency of the Rankine cycle for the conversion of steam to electricity varies from 30-38%, depending on the temperature and pressures of the different streams in the cycle. These values result in an overall system thermal efficiency of about 23% (1). On the other hand, if the black liquor is gasified, the syngas can after cleanup be combusted in a combined cycle for production of electricity. Combined cycle power generation entails the sequential utilization of a gas turbine followed by a steam turbine. The fuel gas is first burned in a gas turbine to produce electricity. The hot exhaust gas from the turbine is then passed through a heat exchanger to produce steam which is then used in a power-producing steam turbine. Implementing a gasifier with combined cycle cogeneration of power will increase the electricity production of the mill. A conventional steam cycle produces about 120-180 kWh/ton of steam, but a gasifier along with combined cycle power generation has the potential to generate 600-1000 kWh/ton of steam (2). Such a production of power would turn a pulp mill into a net exporter of electricity, and this potential is the main motivation for the implementation of black liquor gasification.

In addition to the increased energy efficiency, gasification of black liquor has several other benefits relative to the traditional combustion recovery process. The BLG process operation is inherently very stable and flexible with regard to feedstock and load requirements. It is possible to process almost any biomass material and stable operation can be maintained despite upset feedstock flows, even complete interruptions. BLG has the potential to revolutionize the chemical recovery cycle and, through the separation of sodium and sulfur, enable the utilization of modified pulping technologies such as:

- **Green Liquor Pretreatment**
- **Split Sulfidity Pulping**
- **Polysulfide Pulping**

These pulping technologies will increase yield or reduce wood demand, improve product quality, decrease chemical usage and more importantly simplify the chemical recovery process. A simplification of the chemical recovery process will decrease the operating and capital costs for recovery. BLG would also decrease the malodor associated with the kraft process. Besides power generation, the resulting syngas can be used to generate bio-derived liquid fuels, bio-derived chemicals for the synthetic chemical and pharmaceutical industries, as well as H₂ for use in fuel cells.

Despite these benefits and opportunities, high capital cost and risk associated with new process implementation are impeding the implementation of BLG technologies in the industry. However, the synergy between BLG as an increased energy generator and as an enabler of advanced pulping processes should increase the financial attractiveness of these new process concepts.

1.1 Review of black liquor gasification development

Figure 1.1 shows the typical process elements included in the gasification of black liquor. The black liquor is initially introduced into a process vessel, the black liquor gasifier, which can either be pressurized or operate under atmospheric pressure. In general terms, the process involves the conversion of hydrocarbons and oxygen to hydrogen and carbon monoxide while forming separate solid and gaseous product streams.

The inorganic material, including all sodium salts, leaves as a bed solid or smelt depending on the gasifier operating temperature. The bed solids or smelt is then slaked and recausticized to form a caustic solution. The volatiles, including most of the reduced sulfur species, leave as a syngas of medium BTU value. The major components of the syngas are H₂S, CO₂, CO, H₂O, and H₂. To prepare the syngas for other applications and to regenerate the pulping liquor, all sulfur must be separated from the syngas, and dissolved into the caustic solution prepared from the bed solids. The clean product gas is burned in a gas turbine and the hot flue gases are combined and used to generate steam in heat recovery steam generators (HRSGs). This steam is then used in a steam turbine and other process applications.

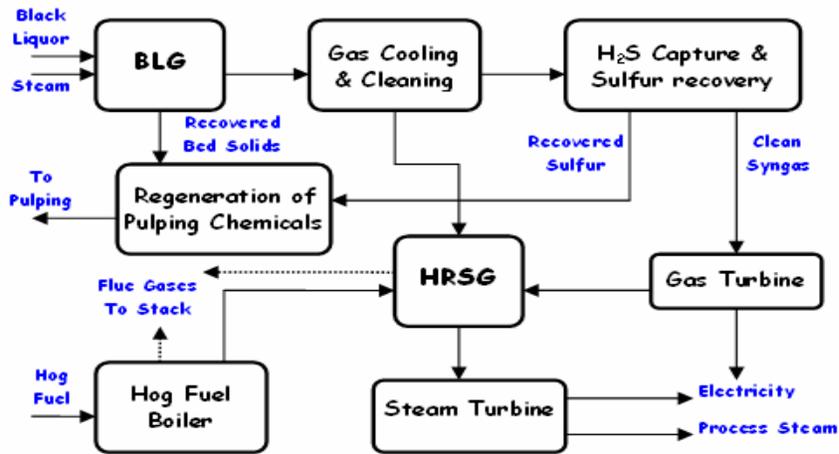


Figure 1.1 Simplified representation of BLGCC power/recovery systems

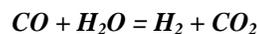
Whitty and Verrill has given a review of the development of alternative recovery technologies to the Tomlinson recovery boiler (3). The following discussion will focus on the gasification processes currently in commercial operation. As suggested by Stigsson, black liquor gasification technologies can be classified by the operating temperature (4). High temperature gasifiers operate at about 1000°C and low temperature gasifiers operate at less than 700°C. In the high temperature gasifier, the inorganic material forms a smelt and leaves in the molten form, while in the low temperature system, they leave as solids. The fuel value of the syngas produced is also dependent on the gasifying technology. Typically, gasification produces a fuel gas with heating values of 3-4 MJ/Nm³ using air and 89 MJ/Nm³ using oxygen (5).

1.1.1 Low Temperature Gasifier/Steam Reformer

The development of low temperature fluidized bed gasifiers is being pursued by ThermoChem Recovery International (TRI) in the USA and by ABB in Sweden. The TRI system uses steam reforming to generate the product gases. As opposed to exothermic incineration or combustion technologies, steam reforming is an endothermic process. The steam reforming vessel operates at atmospheric pressure and at a medium temperature. The organics are exposed to steam in a fluidized bed in the absence of air or oxygen with the following reaction:



The carbon monoxide produced in this first reaction then reacts with steam to produce more hydrogen and carbon dioxide.



The result is a synthesis gas made up of about 65% hydrogen.

The TRI Steam Reformer technology, as shown in Figure 1.2, consists of a fluidized bed reactor that is indirectly heated by multiple resonance tubes of one or more pulse combustion modules. Black liquor is directly fed to the reactor, which is fluidized with superheated steam. The black liquor uniformly coats the bed solids, producing a char and volatile pyrolysis products which are steam cracked and reformed to produce a medium BTU gas. The residual char retained in the bed is more slowly gasified by reaction with steam. The sulfur and sodium are separated in that the sulfur becomes part of the gas stream and the sodium stays in solid form. Bed temperatures are maintained at 605-610 °C, thereby avoiding liquid smelt formation and the associated smelt-water explosion hazards.

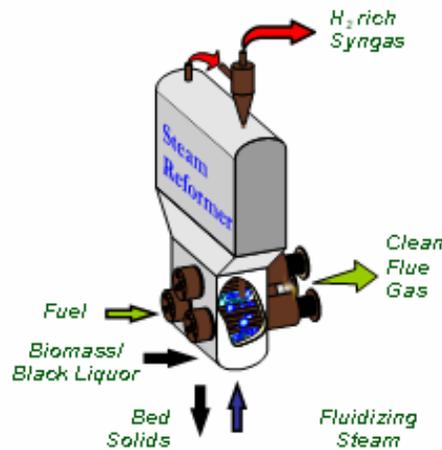


Figure 1.2 Schematic of MTCI Steam Reformer

Product gases are routed through a cyclone to remove the bulk of the entrained particulate matter and are subsequently quenched and scrubbed in a Venturi scrubber. A portion of the medium-Btu product gases can be supplied to the pulse combustion modules, and the combustion of these gases provides the heat necessary for the indirect gasification process. Low temperature gasification leads to complete separation of the sulfur and sodium in kraft black liquor to the gas and solid phases, respectively. Bed solids are continuously removed and mixed with water to form a carbonate solution. The inorganic chemical in the bed solids as well as the sulfur from the gas stream are recovered and used as cooking liquors for the mill. The product gas residence time in the fluid bed is about 15 seconds because of the deep bed (20 ft) used, while the solids residence time is about 50 hrs. These conditions promote extensive tar cracking and carbon conversion. In summary the steam reforming reactor vessel has three inputs; fluidizing steam, black liquor, and heat, and has three outputs; bed solids, hydrogen rich product gas, and flue gas (6).

1.1.2 High Temperature Gasifier

High temperature gasification stems from work initiated by SKF in the 1970s. The original patent for the technology was issued in 1987, and it has since been developed through a sequence of demonstration

projects. The gasifier, as developed by Chemrec, is a refractory-lined entrained-flow reactor. In high temperature gasification (900-1000 °C), concentrated black liquor is atomized, fed to the reactor and decomposed under reducing conditions using air or oxygen as the oxidant. The initial chemical reactions involve char gasification and combustion, and are influenced by physical factors like droplet size, heating rate, swelling, and the sodium and sulfur release phenomena. The resulting products, smelt droplets and a combustible gas, are then brought into direct contact with a cooling liquid in a quench dissolver. The two phases are separated as the smelt droplets dissolve in the cooling liquid, forming green liquor. The exiting product gas is subsequently scrubbed and cooled for use in other unit operations. The split of sodium and sulfur between the smelt and gas phase is dependent on the process conditions. Typically, most of the sulfur leaves with the product gas and essentially all of the sodium with the smelt (7,8,9).

1.1.3 Current Status of BLG Technologies

The TRI steam reformer has been installed in two locations in North America, at the Norampac Mill at Trenton, New Jersey and the Georgia Pacific Mill at Big Island, Virginia. The Trenton mill produces 500 tpd of corrugating medium using a sodium carbonate based pulping process. Prior to the start-up of the low-temperature black liquor gasifier in September 2003, the mill had no chemical recovery system. For over forty years the mill's spent liquor was sold to local counties for use as a binder and dust suppressant on gravel roads. This practice was discontinued in 2002. The capacity of the spent liquor gasification system is 115 tpd of black liquor solids, and the syngas is burned in an auxiliary boiler (6).

Georgia-Pacific's mill at Big Island, produces 900 tpd of linerboard from OCC and 600 tpd of corrugating medium from mixed hardwoods semi-chemical pulp. Like the Trenton mill, the Big Island mill uses a sodium carbonate process. In the past, the semi-chemical liquor was burned in two smelters providing chemical recovery but no energy recovery. Instead of replacing the smelters with a traditional recovery boiler Georgia-Pacific decided to install a low temperature black liquor gasification process. One difference between the two systems is that unlike Trenton, Big Island burns the generated product syngas in the pulsed combustors, so the product gas exiting the reformer vessel is cleaned prior to combustion (6). The Big Island BLG project was terminated in the fall of 2006.

The evolution of the high temperature gasifier has taken the technology from an air-blown process near atmospheric pressure to a high pressure (near 30 atm.) oxygen-blown process. Benefits realized through high pressure oxygen-blown operation are higher efficiencies, higher black liquor throughput and improved compatibility with down stream unit operations such as combined cycle power generation.

An air-blown pilot plant at Hofors, Sweden, was developed to verify the possibility of gasifying black liquor using an entrained-flow reactor operating at 900-1000 °C. The project showed that green liquor of acceptable quality could be generated; and the plant was dismantled in 1990. The Frövi, Sweden plant was

designed as a capacity booster for the AssiDomän facility and was operated from 1991 to 1996, demonstrating the potential for black liquor gasification at a commercial scale. During its operation several technical problems were encountered and addressed. The identification of a suitable material for the refractory lining remained a problem. A subsequent commercial project was initiated in 1996 at the Weyerhaeuser plant in New Bern, North Carolina. The black liquor gasifier was more or less a scale-up of the Frövi plant, designed for a capacity of 300 tons of dissolved solids/day. In 1999 the process maintained greater than 85% availability. However, over the course of the project the plant experienced several technical problems, mainly related to the refractory lining, and it was shut down after cracks in the reactor vessel were discovered in 2000. After detailed studies and re-engineering, the gasifier operation at New Bern was resumed in the summer of 2003 (7). During the rebuild, it was retrofitted with spinel refractory materials developed at Oakridge National Labs in cooperation with other partners. The refractory material is in its second year of operation. The gasifier can burn up to 730,000 lb/day of solids or about 20% of the mill production (10). The syngas generated in the gasifier is currently burned in a boiler.

A pressurized air-blown demonstration project was established at the Stora Enso plant at Skoghall, Sweden, in 1994. The project showed the capability of a pressurized system to generate acceptable quality green liquor while maintaining high carbon conversion ratios. The process was converted to an oxygen-blown operation in 1997 resulting in a capacity increase of more than 60%. A second pressurized demonstration plant was completed in Piteå, Sweden, in 2005. The purpose of the project is to demonstrate high pressure operation (near 30 atm.) with associated gas cooling and sulfur handling unit operations required for a full-scale BLG process. Funding has been obtained for a scale-up project of the Piteå facility. The plant is designed for a capacity of 275-550 tDS/day and encompasses all the required unit operations, including the power island, for a BLG process with combined-cycle power generation (7).

1.2 Review of kraft pulping chemistry

To liberate the cellulose fiber contained in wood, lignin, the “glue” which holds the wood together, must be degraded and solubilized into the pulping liquor. In kraft pulping, this is achieved by heating the wood in the presence of an alkaline pulping liquor containing nucleophiles that attack the lignin polymer. The active chemical agents in kraft pulping chemistry are the hydroxide (OH^-) and hydrosulfide (HS^-) anions. While these chemicals act to degrade wood lignin, the alkaline conditions and elevated temperatures also degrade the wood carbohydrates, cellulose and hemicelluloses, resulting in overall pulp yield losses. Several reviews of kraft pulping chemistry and its effects on wood component degradation and pulp yields have been given (11,12,13). Delignification in kraft pulping has three distinct phases: a rapid initial phase, followed by the bulk phase where most of the lignin is degraded and solubilized, and the final residual phase (14). In the initial phase a substantial amount of hemicelluloses undergo deacetylation and dissolution resulting in significant yield losses (15). Phenolic lignin structures also undergo some degradation while the effect on cellulose is minor. In the bulk phase about 70% of the lignin is degraded, while the carbohydrates undergo further degradation through

peeling and alkaline hydrolysis reactions. Methanol and hexenuronic acid are formed during this phase. Delignification reaches the residual phase when about 90% of the lignin has been removed. At this point, delignification reactions slow down as reactive lignin moieties have been depleted, and the remaining alkali generates rapid carbohydrate degradation (16). Thus, there is a state of diminishing returns for lignin removal from wood in kraft pulping relative to overall yield losses from carbohydrate degradation. A great deal of research has been performed discerning the reactivities of lignin, cellulose and hemicellulose, generating knowledge that can be applied to improve lignin degradation while protecting the cellulose and hemicellulose and improving pulp yield and properties. The following is a brief review of the chemistries involved in lignin and carbohydrate degradation during the kraft process.

1.2.1 Lignin structure and kraft pulping reactions

The lignin macromolecule has been shown to consist of a complex three-dimensional network of 9-carbon phenylpropane subunits, mainly p-hydroxyphenylpropane, guaiacylpropane and syringylpropane. The corresponding hydroxycinnamyl alcohols, or monolignols, involved in lignin biosynthesis are p-coumaryl (4-hydroxy-cinnamyl), coniferyl (3-methoxy-4-hydroxy-cinnamyl) and sinapyl (3,5-dimethoxy-4-hydroxy cinnamyl) (17,18,19,20). These lignin precursors are synthesized through the phenylpropanoid pathway (21). In lignin biosynthesis these subunits are polymerized through radical coupling reactions forming a globular polyphenol macromolecule. The relative proportions of guaiacylpropane (G), syringylpropane (S) and p-hydroxyphenyl propane (H), vary between different wood species, different tissue types and also within the cell wall layers. This variation results in very different reactivities of lignin during chemical pulping of different types of wood. The major component in softwood lignin is guaiacyl (G-lignin), whereas hardwood lignin contains as much as 50% syringyl (S-lignin). Softwood lignin is generally described as fairly uniform, and values for the ratios of G, S and H lignin (G:S:H) in softwood have been reported for pine (*Pinus taeda*) (95:1:5) and spruce (*Picea abies*) (86:2:13). Hardwood lignin is described as having a greater variability in lignin composition with syringyl levels varying from 20 to 60%. The relative composition of lignin in Beech (*Fagus sylvatica*) has been reported as (56:40:4), indicating a much higher level of syringyl groups relative to softwood lignin. Also involved in lignin biosynthesis is the addition of water and carbohydrates to quinone-methide intermediates. The combination of lignin and carbohydrates form a nonphenolic lignin-carbohydrate complex, which is more difficult to degrade during chemical pulping (13).

Lignin degradation is achieved by cleaving the linkages that bind lignin subunits within the lignin macromolecule. The reactivity of these different lignin moieties is dependent on their structure and chemistry. The majority of these inter-lignin bonds are β -O-4 and α -O-4 ether linkages between different phenylpropane units. Other linkage types are the 4-O-5 ether linkage between phenyl carbons, and carbon-carbon bonds like 5-5, β -1, β -5, and β - β . The basic reaction sequence involved in lignin degradation during kraft pulping is initial ionization of a free phenolic hydroxyl group, followed by cleavage of the β -O-4 and α -O-4 ether linkage and the liberation of additional free phenolic groups (16). Under typical kraft pulping conditions, which are strongly

alkaline (pH 11-14), ionization of the lignin C4 free phenolic hydroxyl group ($pK_a \approx 10.9$) readily takes place. If the α -carbon of the formed phenolate anion is not directly linked to another carbon atom, the charged species undergoes β -elimination of the aryl substituent at the α -position forming a para-quinone methide intermediate. This structure is the key-intermediate in lignin degradation reactions (22). After formation of the quinone methide several types of reactions may occur. These reaction pathways can be divided into nucleophilic addition reactions, elimination reactions, and electron transfer reactions. The general outline of lignin degradation is outlined in Figure 1.3. Competing with these lignin degrading reaction pathways are lignin

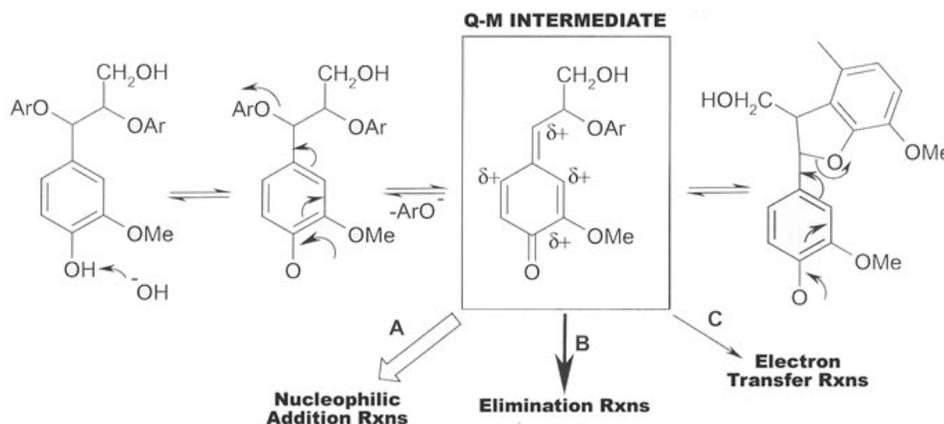


Figure 1.3 Formation of the Quinone-Methide Intermediate (QMI) under alkaline conditions and outline of lignin degradation reactions (13)

condensation reactions where carbon-carbon bonds are formed between the quinone methide and reactive carbon species present in the pulping liquor, like the phenoxide anion and formaldehyde (16).

Cleavage of the α - and β -O-4 ether linkages by nucleophilic addition reactions has been proposed as the major reaction pathway during the initial phase of the cook (16). In nucleophilic addition reactions, all nucleophiles present in the pulping liquor compete for the available quinone methide. In kraft pulping the strongest available nucleophile is HS^- , followed by OH^- and weaker nucleophiles like phenoxide anions and other anionic species originating from carbohydrates. The reaction pathway is shown in Figure 1.4. After HS^- addition to the quinone methide α -position, the intermediate undergoes intramolecular attack at the β -carbon forming a thiirane intermediate (episulfide). The episulfide intermediate is decomposed forming elemental sulfur, which reacts with HS^- to form small amounts of polysulfide, and unsaturated coniferyl-type structures (13).

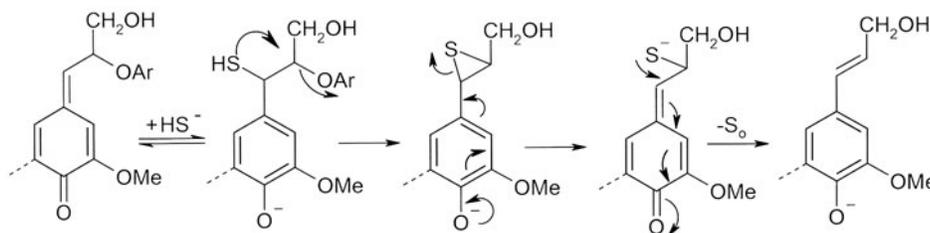


Figure 1.4 Nucleophilic (HS^-) addition to the QMI and cleavage of the β -aryl ether bond (13)

Elimination of the γ -hydroxymethyl group from the quinone methide intermediate produces formaldehyde and an enol-ether structure without significant cleavage of the β -aryl ether bond. This reaction pathway, shown in Figure 1.5, is predominant in soda pulping, where HS^- is not present, but has been observed at the beginning of the bulk phase in kraft pulping (23). The resulting β -aroxy styrene-type structures and diaryl-methane-type structures formed from condensation with liberated formaldehyde are very stable in alkali solutions. The β -hydrogen can also undergo base-induced elimination reactions. The presence of HS^- also causes partial demethylation of lignin methoxyl groups. The resulting methyl mercaptans reacts further as nucleophiles combining with an additional methoxyl group to form dimethyl mercaptans, which is extremely volatile and produces the odor typically associated with kraft mills.

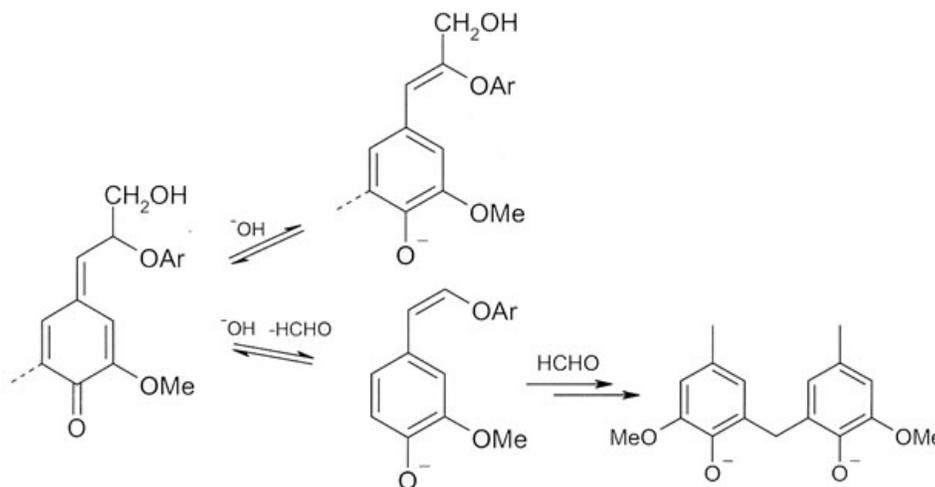


Figure 1.5 Formaldehyde elimination from the QMI generating an enol ether structure and subsequent condensation between formaldehyde and enol ether resulting in diaryl-methane structures (13)

The quinone methide can also undergo electron-transfer reactions with reducing compounds present in the pulping liquor, like carbohydrates and anthrahydroquinone when used as an additive. The proposed reaction mechanism, outlined in Figure 1.6, involves single-electron transfer and radical intermediates, resulting in cleavage of the β -aryl linkage and formation of coniferyl-type structures (24).

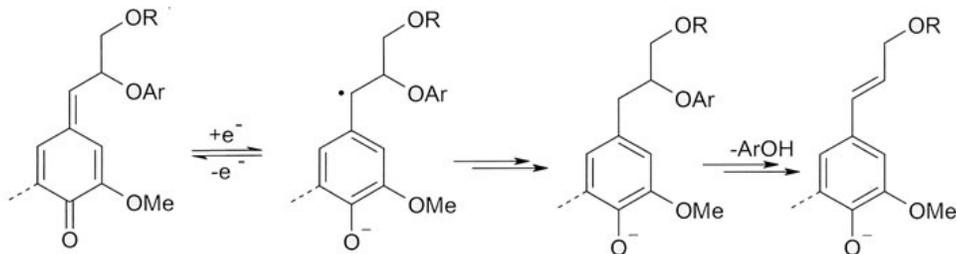


Figure 1.6 Electron-transfer reaction reducing the QMI with cleavage of the β -aryl ether bond leading to the generation of coniferyl-type structures (13)

In addition to the degradation of phenolic lignin structures previously described, non-phenolic lignin structures also undergo degradation in kraft pulping, but demand higher temperatures and alkalinity. This means that most of the non-phenolic lignin degradation takes place in the bulk phase of the cook. The proposed reaction mechanism, outlined in Figure 1.7, involves ionization of the lignin α -hydroxyl group followed by formation of an oxirane (epoxide) intermediate and cleavage of the β -aryl ether bond through internal nucleophilic substitution (S_N1). The epoxide can then be opened by nucleophilic attack (S_N2) by HS^- , OH^- , or hydroxyl groups of carbohydrates present in the liquor. The reaction with carbohydrates leads to the formation of lignin-carbohydrate ether bonds that are somewhat stable during bulk delignification conditions (25).

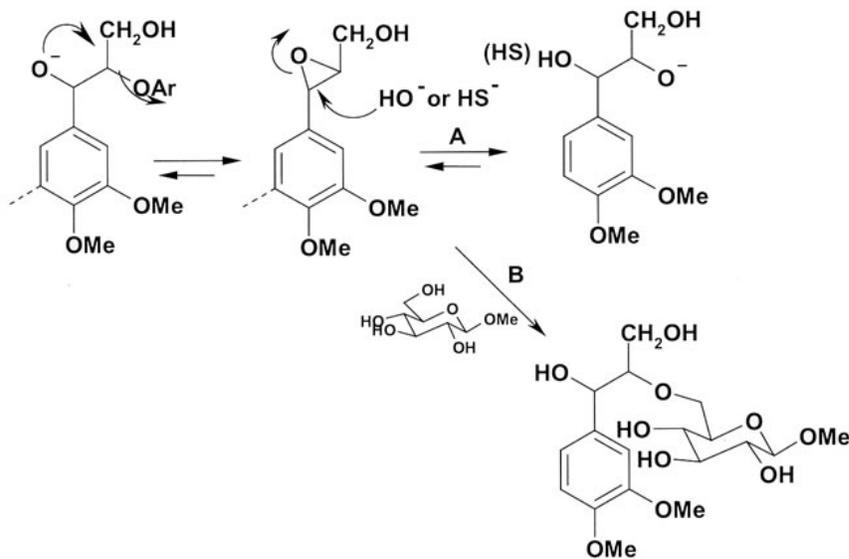


Figure 1.7 Alkaline degradation of non-phenolic lignin structures with epoxide ring opening through nucleophilic attack generating stable lignin-carbohydrate complexes (LCC) (13)

In practice kraft pulping operations are typically interrupted during the bulk phase of delignification to prevent excessive degradation of carbohydrates, which would result in overall yield loss and poor pulp quality.

The residual lignin, typically about 4-5% for softwood and 3% for hardwood, can be removed during subsequent oxygen delignification, or addressed during bleaching operations (16).

1.2.2 Carbohydrate structure and kraft pulping reactions

The carbohydrates in wood consist of cellulose and hemicellulose. The structures and chemistry of cellulose and hemicelluloses in wood has been established and studied in detail. The following discussion is a brief synopsis based on several reviews creating a foundation for ensuing discussions regarding modified pulping technologies aimed at yield improvement (12,13,16,26).

Cellulose is a linear homopolymer consisting of β -1,4-glucosidic linked D -glucopyranose units. The cellobiose disaccharide, consisting of two glucose molecules, is the basic repeating unit in the polymer chain, which in typical papermaking fibers has a weight averaged degree of polymerization of 600-1500. The terminal C1 group of the cellulose polymer is present in the form of a hemiacetal generating a reducing hydroxyl group at the C1 position. The other terminal C4 hydroxyl is nonreducing. Although at first look a very simple polymer, the supramolecular structure of cellulose is a complex matrix containing parallel homoglucon chains that exhibit intermolecular hydrogen bonds. These intermolecular bonds cause a varying degree of organization, where highly ordered domains exhibit a distinct X-ray pattern. These domains are called crystallites or crystalline regions, and the less-ordered domains amorphous or noncrystalline regions. The crystalline regions are more stable than the amorphous regions to alkaline degradation. Cellulose encountered in wood consists of microfibrils, which are rod-like structures of parallel homoglucon chains exhibiting a two-fold screw symmetry around the chain axis. The helical shape is due to the repeating β -1,4-glucosidic linkages between the glucose molecules in the polymer (26).

Wood hemicelluloses are in general terms short linear heteropolymers of different monosaccharides with typical DP of 50 to 200. The polymer backbone can be made up of one repeating sugar unit (e.g. the xylan homopolymer) or with two or more (e.g. the glucomannan heteropolymer). Various substituents can be linked to these polymer chains creating a variety of different types of hemicelluloses. The relative quantity, structure and composition of xylan and glucomannan hemicelluloses encountered in softwoods are different than those encountered in hardwoods. O-acetylgalactoglucomannan is the major constituent in softwood hemicelluloses, making up as much as 18% of the wood, and arabino-4-O-methylglucuronoxylan is the minor constituent, representing about 10% of the wood. In hardwoods, however, O-acetyl-4-O-methylglucuronoxylan is the most prevalent hemicellulose, making up 20-35% of the wood, with glucomannan a minor constituent of 2-4% (13). Due to the prevalence of side chain substituents, xylans are more stable to alkaline degradation than glucomannans. However, compared to cellulose, hemicelluloses are more susceptible to peeling reactions at low temperatures. Combined with their small DP, this leads to very high losses of hemicelluloses in kraft cooking, especially during the initial stages of the cook where little degradation of lignin and cellulose takes place.

During the course of a kraft cook, wood carbohydrates undergo various reactions that lead to polymer degradation and dissolution which results in overall pulp yield loss and decreased pulp viscosity. As wood carbohydrates are degraded during the cook, a substantial amount of carboxyl groups are liberated which consumes available alkali resulting in a lower pH. Thus, the process environment is somewhat dynamic with regard to alkali concentration and temperature, resulting in a complex environment where alkaline lignin degradation competes with less desirable carbohydrate degradation. Focusing on carbohydrate reactions, the strongly alkaline environment and elevated temperatures generate a progression of reactions beginning with deacetylation of hemicelluloses at temperatures below 70 °C. As the temperature is increased, reactions leading to degradation of both hemicellulose and cellulose are initiated. There are three primary reaction types: end-wise peeling of the polymer reducing end, oxidative peeling which cleaves the polymer backbone randomly, and alkaline hydrolysis, or secondary peeling, which also involves direct cleavage of the polymer chain but requires temperatures above 140 °C (13,16). As the normal pulping temperatures are well above these levels, the reactions may take place simultaneously and their relative rates are dependent on the polymeric structures of available carbohydrates, alkalinity and temperature. Competing with these degradation reactions are so called stopping reactions which stabilize carbohydrate polymers against peeling through oxidation. Other reactions that take place in kraft pulping are fragmentation reactions, dissolution of hemicellulose, the elimination of methanol from 4-O- methylglucuronic acid and the generation of hexenuronic acid. In the final stages of the cook, some dissolved hemicelluloses also re-precipitate on the fiber surface, improving the pulp yield and altering the fiber mechanical properties (27).

The end-wise peeling reaction, shown in Figure 1.8, is initiated by an alkali catalyzed rearrangement of the carbohydrate nonreducing end group, forming an enediol anion intermediate. The intermediate undergoes elimination of the cellulose chain in the β -position, producing a cleaved dicarbonyl species. This dicarbonyl is very unstable under alkaline conditions, and undergoes further degradation reactions resulting mainly in the formation of isosaccharinic acid or 2,5-dihydroxypentanoic acid. The initial rearrangement of the carbohydrate reducing end group is the rate-limiting step for the endwise peeling reaction. The enolization is promoted by higher OH⁻ concentrations (15).

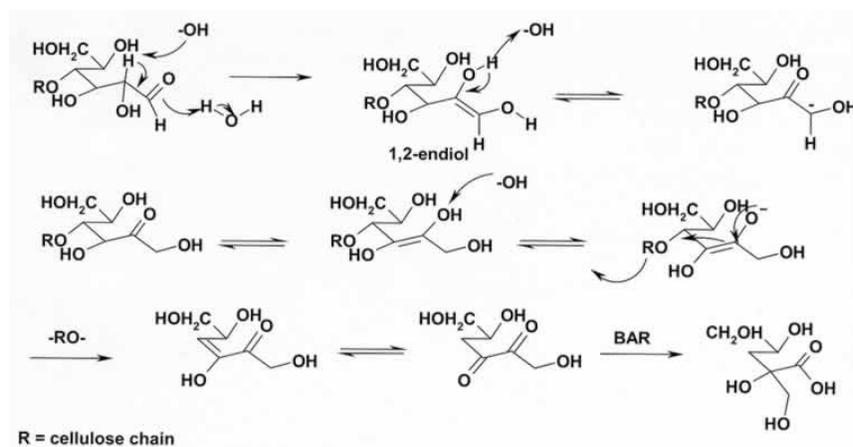


Figure 1.8 Outline of the alkaline carbohydrate end-wise peeling reaction (13)

Competing with the peeling reaction is the stopping reaction, displayed in Figure 1.9. In the stopping reaction, the reducing end group can be stabilized either through oxidation forming its corresponding aldonic acid, or through conversion to metasaccharinic acid or 2-hydroxy-2-methyl-3-alkoxy-propanoic acid. The relative reaction rates of peeling and stopping reactions leads to peeling of about 50 to 60 monosaccharides prior to stabilization by the stopping reaction (13).

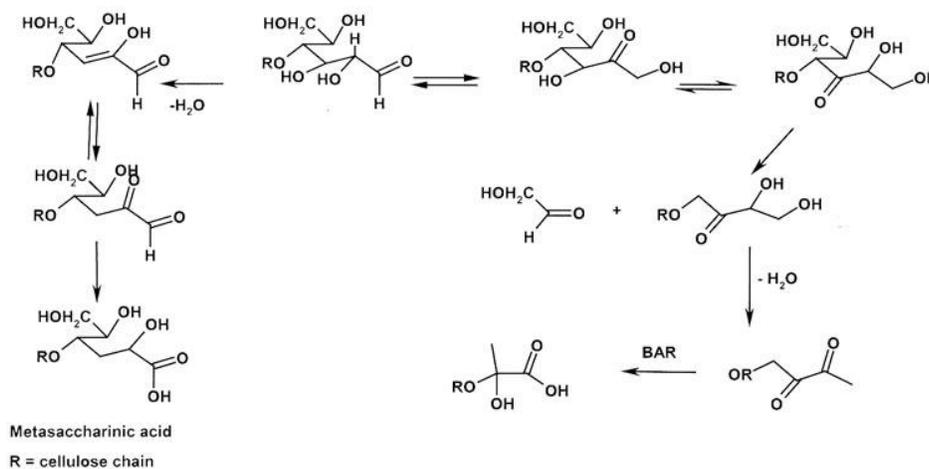


Figure 1.9 Outline of the carbohydrate stopping reaction (13)

The oxidative peeling reaction is facilitated by the presence of oxidized groups contained in the polymer chain. Keto groups or aldehyde groups in the C2, C3, or C6 position of the carbohydrate monomers can undergo alkali catalyzed β -alkoxy elimination, resulting in cleavage of the polymer chain. In addition, elimination reactions induced by C2 keto groups and aldehydes at the C6 or anomeric carbon leads to generation of new reducing end groups. These can undergo further end-wise peeling reactions, resulting in

increased carbohydrate degradation. Figure 1.10 shows the mechanism for oxidative peeling through β -alkoxy elimination at the C2 position (13,16).

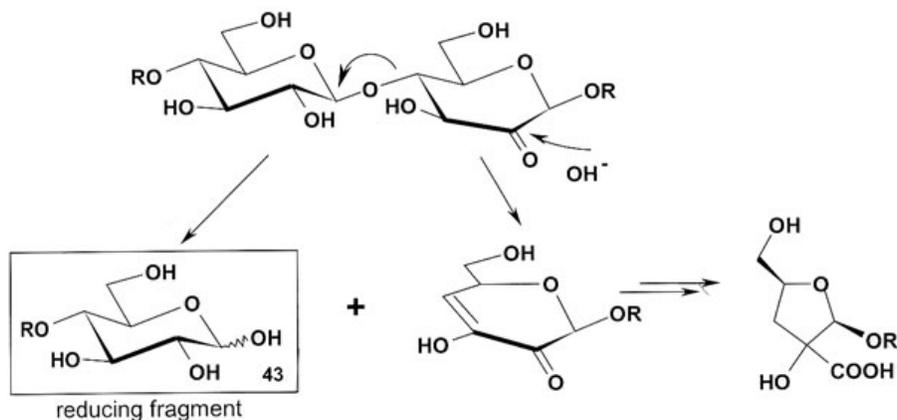


Figure 1.10 Oxidative peeling reaction through β -alkoxy elimination at the C2 position (13)

Alkaline hydrolysis reactions, also called random hydrolysis, take place at temperatures above 140 °C. They involve the cleavage of the glycosidic linkage of the carbohydrate polymer backbone, resulting in new reducing end groups that can undergo further degradation through (secondary) peeling. Although this degradation reaction has little effect on overall pulp yield, it is responsible for the majority of cellulose degradation in the kraft process, leading to lower degrees of polymerization, and associated losses in fiber strength. The reaction, outlined in Figure 1.11, is initiated by alkali induced ionization of the C2 hydroxyl group. The high temperature promotes a conformational change in the reacting monomer from ${}^4\text{C}_1$ to ${}^1\text{C}_4$ structure. This change results in the rearrangement from equatorial to axial positions of all monomer substituents, leading to internal nucleophilic displacement ($\text{S}_{\text{N}}1$) where the ionized C2 hydroxyl group forms an oxirane (1,2-epoxide) with elimination of the cellulose chain from C1. The 1,2-epoxide intermediate formed can undergo further reactions resulting in a new reducing end group, either through reaction with OH^- , or through further rearrangement with the ionized C6 hydroxyl group producing levoglucosan (13).

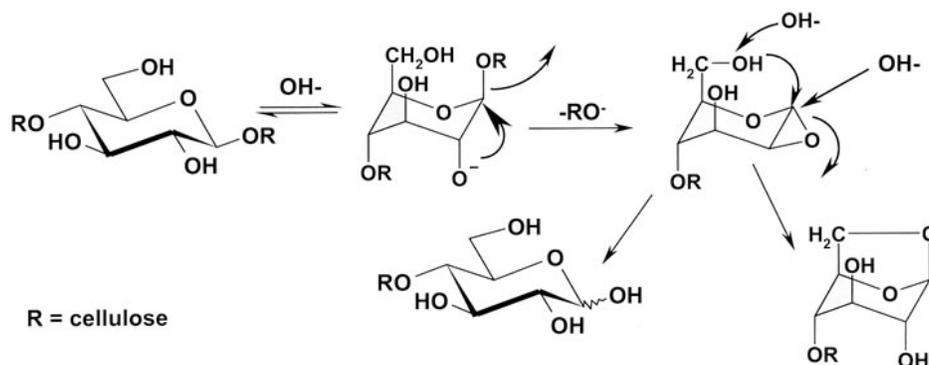


Figure 1.11 Alkaline (Random) hydrolysis of carbohydrate glycosidic bonds generating a new reducing end group or levoglucosan (13)

The carbohydrate degradation reactions that occur during heat-up and the early stages of the cook liberate or produce a substantial amount of uronic, acetic and sugar acids. As a consequence, by the time the cook reaches cooking temperature and the bulk delignification phase, a substantial amount of the available alkali has already been consumed to neutralize the acids formed. This means that a much smaller amount of alkali is available for lignin degradation than what was initially charged. Kraft process modifications that would optimize the efficiency of alkali utilization could thus lead to improved delignification rates, while decreasing the negative effects of alkali promoted carbohydrate degradation (16).

1.3 Review of modified kraft pulping processes

The major areas within the kraft process that drive efforts for process improvement are the following:

- **Low pulp yield relative other pulping processes**
- **High capital requirements necessary to build new pulp mills and to rebuild or maintain current mill operations**
- **Environmental concerns stemming from the use of sulfur and chlorinated compounds during pulping and bleaching operations.**

Process modifications that work within the pre-existing process unit operations and equipment can significantly improve process economics or be devised to meet new environmental regulations without the need for additional capital expenditure.

1.3.1 Modified continuous cooking

Modified kraft pulping processes have gained widespread acceptance, because they can be used either to extend delignification or to enhance the yield and pulp properties at a given kappa number. The basic principles of modified extended delignification consist of a level alkali concentration throughout the cook, a high initial sulfide concentration, low concentrations of lignin and Na^+ in the final stage of the cook, and lower

temperature in the initial and final stages of the cook (28). This process approach has been developed by Kamyr around their continuous digester. Using conventional kraft recovery operations the generated white liquor is split into different feed streams applied during feed, transfer circulation and a countercurrent cooking zone. The process modifications have resulted in the potential for higher yield or improved delignification with improved viscosity and bleachability properties.

1.3.2 Green liquor pretreatment

One alternative to avoid the increase in causticization requirements would be to pre-treat wood with green liquor. Previous work has demonstrated the feasibility of using green liquor in the impregnation stage, without increasing overall chemical usage (29,30). It has also been shown that the amount of sulfur adsorbed during the pretreatment decreases with higher $[OH^-]$ (31). By impregnating chips with high sulfidity, low pH liquor, a mill may enhance yield and further decrease the causticizing load. Figure 1.12 outlines the unit operations for a possible green liquor pretreatment process in conjunction with BLG.

Comparing conventional kraft pulping with the green liquor pretreatment described above, the greatest relative cost-benefit from a decrease in causticization using green liquor pretreatment would be achieved in a situation where the level of TTA was the same in both processes. This requires that similar pulp kappa numbers must be attainable through both processes at the same TTA charge.

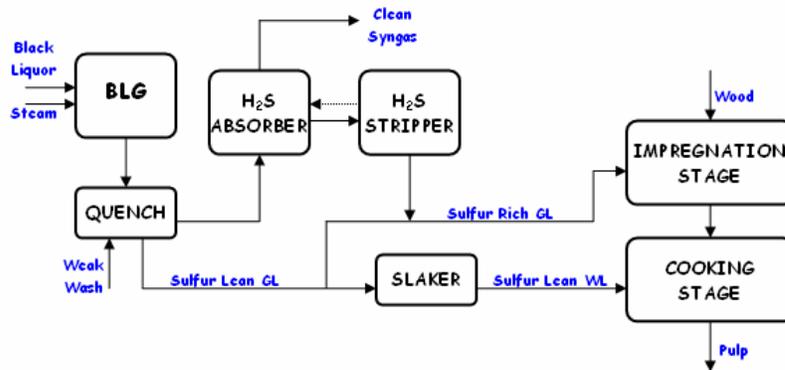


Figure 1.12 Outline of process using green liquor pretreatment

1.3.3 Split sulfidity pulping

BLG would enable a mill to generate a high sulfidity liquor which can be used to provide a high sulfide concentration during the initial phase of the cook. In split sulfidity pulping, it would be necessary to generate two streams of white liquor – one that is sulfide-rich and another that is sulfide-lean. Sulfur profiling would be the lowest capital cost process to implement to modify the pulping process especially for mills with a modified continuous or batch pulping process. Figure 1.13 shows the basic concept design for generating liquors of different sulfide concentrations.

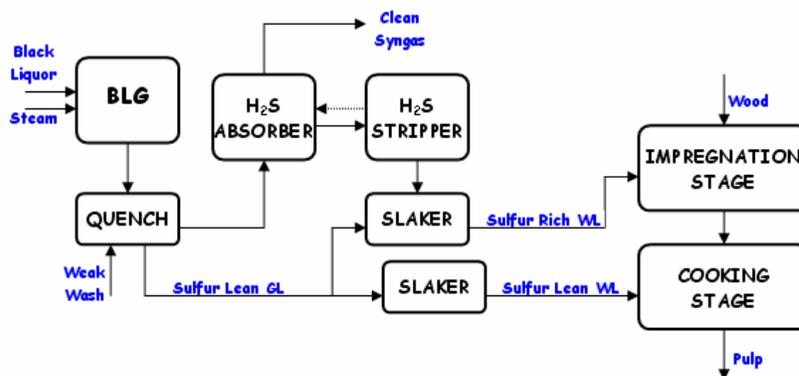


Figure 1.13 Schematic of unit operations in split sulfidity pulping

The concept of sulfur profiling, or split sulfidity pulping, employing a sulfur-rich stream in the rapid initial phase, followed by a sulfur-lean stream in the bulk and residual phase, has been investigated as a method for extending delignification or increasing yield (29,32,33,34,35). Compared to conventional kraft cooks of similar H-factor, split sulfidity pulping has been shown to enhance selectivity of the pulping reactions, resulting in increases in both lignin removal and pulp viscosity. Moreover, split sulfidity pulping has been shown to increase pulp yield and strength properties (36,37,30).

The effects of multiple stage cooking using sulfur profiling, has also been studied. The process showed a significant improvement in selectivity (38,39). Increased sulfide sorption resulted in both higher lignin-free yields and increased viscosities. At 30% overall sulfidity, the lignin-free yield was 0.6 to 0.9% higher and viscosity 8.89 to 10.4 mPa higher than conventional kraft. At increasing overall sulfidities, the yield advantage was reduced. Screened yield increased only slightly with higher sulfidity levels during impregnation. Similar findings were reported in subsequent work (40). Pulping work conducted at STFI found that sorption of sulfide increases with increasing hydrosulfide concentration, time, temperature and concentration of positive ions, but decreases with an increasing concentration of hydroxide ions (41). The potential for modifying softwood kraft pulping by sulfur profiling was also investigated. When all of the sulfide was added to the beginning of the cook, a high hydrosulfide concentration could be maintained both in the initial phase and near the transition point from the initial to the bulk delignification phase (42).

The work described above is difficult to implement in a mill that utilizes conventional recovery technologies. However, BLG generates separate streams of sulfur and sodium, which will allow for independent sulfur and alkali profiling. Thus, the alkali profile can be adjusted independent of the sulfur concentration at any point in the cook. These opportunities were investigated at NC State University, exploring split sulfidity pulping of southern pine with different initial alkali concentrations. Based on a modified continuous cooking (MCC) laboratory procedure, different approaches were devised to explore split sulfidity and different initial alkali profiles (43,44). Two levels of initial alkali were investigated where a fraction of the

available hydroxide was charged in the initial stage. The low initial alkali procedure used 11% of the alkali; the corresponding value for the high initial alkali procedure was 33%.

1.3.4 Kraft polysulfide pulping with anthraquinone

The effect on pulping chemistry of polysulfide (PS), often in conjunction with anthraquinone (AQ) as additives to the Kraft process, has been explored for some time (45,46,47,48,49,50). Its effectiveness has been established, and it is typically reported that each percent of PS added increases the pulp yield by one percent (51,52). However, efficiently generating high concentrations of PS within the Kraft chemical recovery cycle is difficult. There are currently three primary competing processes available for PS generation: Chiyoda, MOXY™ and Paprilox® (53). These processes, in general terms, produce pulping liquors with PS concentrations of five to eight grams per liter and PS selectivities ranging from 60 to 90 percent (54,55,56,57). This results in a PS limit of about 1% PS charge on oven dry wood for a mill operating at 25% sulfidity. However, a chemical recovery system based around BLG would allow for different pathways to generate PS liquors which would enable higher charges of polysulfide. In addition, the separation of sodium and sulfur would allow for alkali profiling in conjunction with PS utilization. Figure 1.14 shows a schematic of PS process unit operations with BLG.

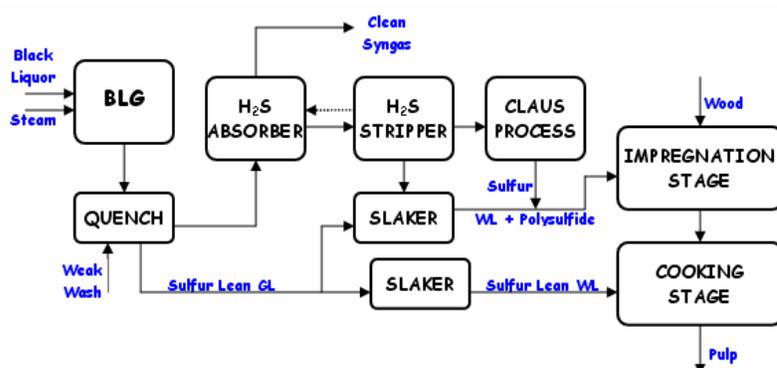


Figure 1.14 Outline of process using polysulfide

Research efforts in the area of PS have generally been in one of two major areas; work on PS pulping associated with PS utilization in Kraft process operations and/or associated PS generation technologies (54,55,56,57,58,59,60,61) and work investigating optimum parameters for PS pulping (62,63,64). A smaller area of work has been based around the potential implementation of BLG and the opportunities created by the unrestricted management of sulfur and sodium as separate entities. The splitting of sulfur and sodium enables the application of polysulfide, sodium sulfide and sodium hydroxide independently of each other. Two processes have been described based on this concept. The ZAP process (Zero effective alkali in pretreatment), entails a two-stage pulping procedure, where the sulfur-containing cooking chemicals (Na_2S and PS) are charged along with AQ to the wood in the pretreatment stage (65). In the subsequent cooking stage, NaOH is added and the temperature increased. The obtained results using PS without AQ, indicate a potential yield

benefit of 1% relative to conventional PS pulping at kappa 30. With the addition of AQ, the yield benefit was increased to 1.5-2%. Additional results indicate even greater yield benefits at kappa 90. The other process is called hyperalkaline polysulfide pulping (66). The process utilizes two pretreatment stages followed by a cooking stage. In the first stage, alkali is charged to the wood at elevated concentrations, neutralizing the acids formed during the temperature elevation. PS is then charged in the second stage, followed by the cooking stage. The process resulted in a higher delignification rate, increased pulp viscosities and yield improvements of 1.5% as compared to modified pulping without PS. Worth noting is that the bleachability and measured tear strength of the hyperalkaline PS pulps were similar to those of the Kraft reference pulp.

In addition to the capability for independent profiling of NaOH and PS, the implementation of BLG would allow for the conversion of all the sulfur in the cooking liquor to PS. This would enable higher PS charges than available through conventional technologies. The total amount of sulfur that is available is dependent on the sulfidity of the pulping liquor. Table 1 illustrates this balance displaying two examples of the partitioning of the total sulfur available in the system at 25 and 40% sulfidity. As seen in the table, PS charges slightly exceeding 2 % on wood are possible at 19.5% AA with 25% sulfidity. To enable higher PS charges the sulfidity must be increased, and as shown in the table the corresponding value at 40% sulfidity is between 3 and 4% PS on wood.

Table 1.1 Demonstration of sulfur utilization as Na₂S (kraft) or Na₂S/PS (kraft-PS) and the system sulfur availability for PS generation

<i>Cook Procedure</i>	25% Sulfidity			40% Sulfidity		
	<i>Tot. avail.</i>	<i>S req.</i>	<i>S avail.</i>	<i>Tot. avail.</i>	<i>S req.</i>	<i>S avail.</i>
	<i>Sulfur (S)</i> <i>(kg/ton)</i>	<i>for PS</i> <i>(kg/ton)</i>	<i>as Na₂S</i> <i>(kg/ton)</i>	<i>Sulfur (S)</i> <i>(kg/ton)</i>	<i>for PS</i> <i>(kg/ton)</i>	<i>as Na₂S</i> <i>(kg/ton)</i>
MCC	25.2	0	25.2	40.3	0	40.3
1% PS	25.2	10.0	15.2	40.3	10.0	30.3
2% PS	25.2	20.0	5.2	40.3	20.0	20.26
3% PS	25.2	30.0	- 4.8	40.3	30.0	10.3
4% PS	25.2	40.0	- 14.8	40.3	40.0	0.3

2 STATEMENT OF OBJECTIVES

The focus of the work explored in this project was the effects that the implementation of black liquor gasification might have on conventional pulping operations. A two pronged approach was pursued: to investigate modified pulping technologies that BLG implementation would enable, and to explore potential process modifications to a kraft mill through process simulation. The first approach entailed laboratory pulping experiments exploring different modified or advanced pulping technologies based on the separation of sodium and sulfur in chemical recovery. The second entailed the generation of a BLG model, its integration into the

WinGEMS software package, and process simulation exploring the combined effects of BLG integrated with the different pulping technologies outlined above on process economics.

2.1 Objectives for laboratory pulping work

Different opportunities arise in the application of pulping chemicals to wood during pretreatment and digestion when sulfur and sodium are separated during chemical recovery operations. The capability to independently charge sulfur and sodium was explored through laboratory pulping using green liquor pretreatment, split sulfidity pulping, and polysulfide pulping with and without anthraquinone. The objective for the pulping work was to establish the potential benefits with regard to total pulp yield, delignification, pulp viscosity and physical properties as compared to pulps generated using conventional kraft pulping methods.

2.2 Objectives for process simulation work

When considering the implementation of new technologies, it is of great benefit to use process simulation as a tool to predict the potential effects of process modifications on overall process operation and economics. To make possible WinGEMS process simulation of the integration of BLG and BLG enabled modified pulping operations into kraft pulping, it was necessary to generate a BLG WinGEMS model. The objective of the simulation work was to initially generate a BLG model. This model was then to be integrated into the WinGEMS software package, and used to explore the effects of retrofitting BLG into kraft pulping on process operation and economics.

3 SUMMARY, CONCLUSIONS AND FUTURE WORK

The results obtained throughout this project have been reported in several articles and conference proceedings, manuscripts of which have been included in sections 8.1 – 8.5. The ensuing discussion is a review of the obtained results outlining the efforts undertaken in laboratory pulping as well as the work performed to generate a BLG model and its application in process simulation. Laboratory procedures for pulping experiments have been described in the manuscripts, and brief outlines have been included in the appendices.

3.1 Review of laboratory pulping results

The following sections discuss the results obtained through laboratory pulping experiments exploring green liquor pretreatment, split sulfidity pulping and polysulfide pulping with anthraquinone.

3.1.1 Green liquor pretreatment

Green liquor pretreatment pulping has been investigated and presented (section 6.2). Pulping results show that green liquor pretreatment would return pulps of higher kappa at the same level of total titratable alkali, as shown in Figure 3.1. However, as shown in the figure it would be possible to achieve similar kappa number at the same level of system TTA by pulping to a higher H factor. Another option for decreasing the kappa number would be to increase the system TTA. Experiments performed with a 10% increase in TTA,

labeled Hi-TTA, also resulted in a higher kappa number than the MCC baseline. In this study, if the TTA is increased by 20% the active alkali is the same in both processes, and the no causticizing benefits exist. The resulting pulp yield did not show any improvement with green liquor pretreatment, but the green liquor pretreated pulps had higher viscosity. These results did not show the yield benefit reported elsewhere, and may be the result from differences in pulping procedures (30).

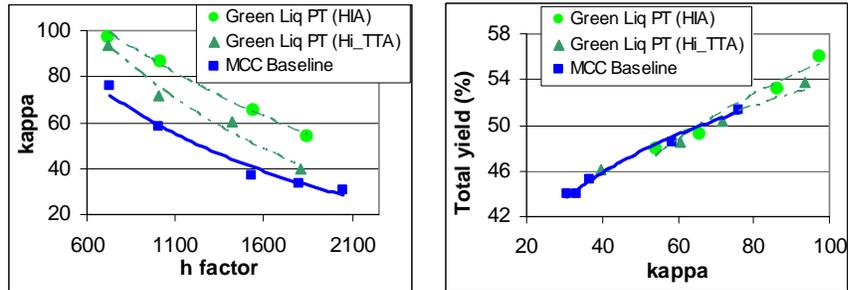


Figure 3.1 Obtained results for pulping using green liquor pretreatment procedure

3.1.2 Split sulfidity pulping

The effects of split sulfidity and different levels of initial alkali on delignification and total pulp yield are presented in Figure 3.2 (section 6.2). As shown, split sulfidity pulping produced lower kappa pulps at similar H factors relative the MCC procedure. The high initial alkali cooks generated pulps of lower kappa number compared to those of low initial alkali. The split sulfidity procedures produced pulp yields 1-2% greater than the MCC procedure, and the difference is more pronounced at higher kappa. Since the high initial alkali approach produced higher yields and lower kappa numbers than the low initial alkali approach, this would be the preferred option. At similar kappa numbers the split sulfidity pulps had viscosities 5 to 10 cps greater than those of the MCC pulps. The high initial alkali pulps produced higher tensile and burst index values relative the MCC pulps at a similar tear index. The MCC pulps were slightly easier to refine relative to the split sulfidity pulps.

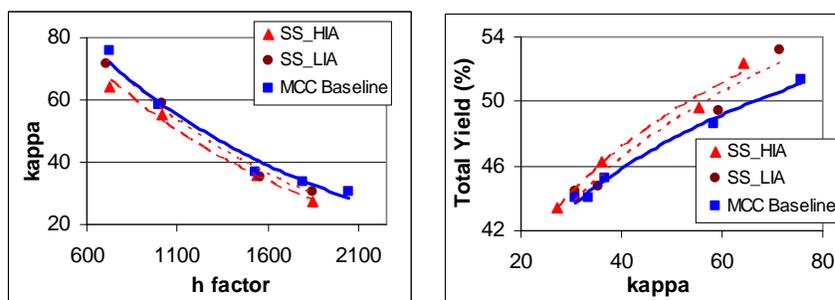


Figure 3.2 Delignification and yield results for split sulfidity pulping

The co-absorption of H_2S and CO_2 during the scrubbing in sulfur recovery, results in the production of $NaHCO_3$. During recausticization all sodium exiting the gasifier will be converted to $NaOH$. The conversion of $NaHCO_3$ to $NaOH$ requires twice as much lime compared to the conversion of $NaCO_3$ to $NaOH$. Thus, there is a two-fold increase in the amount of lime required to produce an equivalent amount of $NaOH$, and as a result, BLG will increase the overall causticization load.

The potential for in-situ causticization within the gasifier could dramatically affect the load on the recaust cycle and lime kiln. In current recovery operations, the sodium carbonate obtained from the slaking of the boiler smelt is converted to sodium hydroxide using calcium oxide. The byproduct calcium carbonate is then calcined in large rotating kilns to regenerate the calcium oxide. A 1000 ton per day pulp mill will use about 100,000 barrels of fuel oil per year to fire its lime kiln. Through novel chemistries it may be possible to carry out the causticization reactions directly within a black liquor gasifier. This could potentially eliminate the need for the lime cycle and the associated fuel costs (44).

3.1.3 Polysulfide-anthraquinone pulping

The effects of pulping southern pine with higher PS charges and alkali profiling have been evaluated (section 6.3 and 6.4). Table 3.1 shows a summary of the yield increases that were measured at various PS charges and sulfidities. At 40% sulfidity the impact of alkali profiling in the initial stage was also evaluated. Three different levels of alkali were investigated. In the low initial alkali (LIA) cook, 56% of the alkali was charged to the impregnation stage. The corresponding values for the medium initial alkali (MIA) was 65% and for the high initial alkali (HIA) 75%. The flexibility to optimize the alkali profile and PS use would only be possible in combination with BLG (67).

Table 3.1 Total yield improvement from PS procedures compared to 25% S MCC pulp

Cook ID	Estimated Yield at 30 kappa	Yield Improvement (% pts.)	Average Viscosity (cps)
MCC 25% S	45.2	n.a.	39.1
1% PS 25% S	47.7	2.4	38.6
2% PS 25% S	48.1	2.9	38.0
1% PS 40% S LIA	46.7	1.5	49.5
2% PS 40% S LIA	47.3	2.1	51.6
3% PS 40% S LIA	47.4	2.2	55.7
3% PS 40% S MIA	48.9	3.7	47.7
3% PS 40% S HIA	45.8	0.6	46.7

At 25% sulfidity the kappa numbers with PSAQ were comparable to the MCC reference. The yield benefit was about 2% for a 1% PS charge, and about 3% for a 2% PS charge. At 40% sulfidity the kappa number decreased with increasing PS charge, and increasing levels initial alkali. The level of initial alkali had a significant effect on the yield. There is indication of an optimum condition for initial alkali charge, where too great or too low of an initial hydroxide concentration negatively affects the pulp yield. The work exploring MIA and HIA indicates that there exists a maximum in yield benefit as a function of initial alkali concentration. Comparing these results to the ZAP process using PSAQ a yield benefit of about 6% at 30 kappa was reported, where the initial alkali charge in the PS pretreatment stage was zero (64). Olm et al. also described a minimum yield condition which was shown to exist at a hydroxide concentration of about 0.3 mol/l. At hydroxide concentrations lower or greater than 0.3 mol/l, higher yields could be achieved. The results indicate that there also may exist a maximum yield benefit at higher levels of initial alkali. The LIA condition in our procedure corresponds to an initial hydroxide concentration of about 0.6 mol/l, which is greater than the concentration reported for the yield minimum in the ZAP process. The maximum yield benefit was found around an initial hydroxide concentration of 0.9 mol/l. The effect of initial alkali on pulp yield should be further investigated to optimize the benefits of PS pulping.

3.2 Process simulation

Computer process simulation is a commonly used engineering tool with a wide range of applications in the solution of problems. In the area of chemical and manufacture process engineering, it is frequently utilized to evaluate the feasibility of new technologies or to determine operating parameters for process improvement and optimization. WinGEMS is a software simulation tool designed specifically for applications in the pulp and paper industry. The computer software is built on a modular design, where different unit operations specific to pulp and paper processes can be linked to represent process segments or whole plants. The overall model is then solved in a sequential order through multiple iterations until the specified convergence criteria are met.

The software was originally developed at the University of Idaho in the early 1970's and is now marketed and supported by MetsoAutomation (68,69).

Despite continuous evolution, WinGEMS does not have a block model for the BLG process. Initial simulation work around BLG integration into the kraft process was completed using preexisting WinGEMS blocks, achieving estimates of what effects could be expected in process variable operating costs. This work is described in the manuscripts (section 5). In order to better simulate the integration of BLG into kraft pulping operations and the effects of BLG enabled modified pulping technologies on process parameters, it was necessary to develop such a model. The following discussion briefly describes the development of the WinGEMS BLG block, and then its application in full mill simulations of modified kraft pulping operations.

3.2.1 Development of BLG model for WinGEMS

The purpose of constructing the BLG model was the desire to incorporate a BLG block into a full mill WinGEMS simulation, where its interaction with other mill unit operations could be evaluated in terms of process variables of interest to the user. The model developed for this application bases the material and energy balances around the steam reformer on empirical relationships rather than first principles. This approach allows for the prediction of model output streams based on the given BL input stream and process parameters, as well as the back-calculation of the required amounts of bed fluidizing steam and energy supplied through the pulsed heaters to sustain the endothermic steam reforming reactions. An outline of the unit operation input and output streams is shown in Figure 3.1.

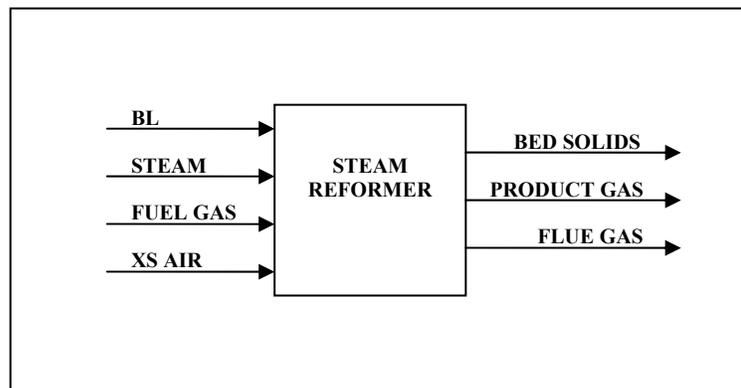


Figure 3.1 Input and output stream structure for BLG model

To simplify the BLG model and its control a number of parameters were identified and utilized for user input and reaction constraints internal to the model. These parameters were based on process data provided by MTCI. As a result, the range of operating conditions that can be used with the model in process simulations is limited by the original data. The development and validation of the WinGEMS BLG block model has been described in the manuscripts (section 9).

3.2.2 Simulation of the effects of BLG integration on kraft mill operations

Case studies were performed in WinGEMS comparing full mill simulations of a kraft process using modified continuous cooking to BLG processes with split sulfidity and polysulfide-anthraquinone pulping. A detailed discussion of the findings has been included in the manuscripts (section 10). Input assumptions for the different simulations were based on available literature, industry contacts and laboratory results generated throughout this dissertation project. Process unit operations were comparatively analyzed among the different cases. Noteworthy results include the increased load on the lime kiln cycle due largely to the much greater generation of carbonate salts in BLG as compared to conventional recovery boiler smelt production. Combined with this fact is the amount of carbonate created from carbon dioxide which is co-absorbed with H₂S during syngas scrubbing with amine systems and green liquor. In addition, the BLG cases also generated less steam from the processed black liquor than conventional recovery boiler operations. To make up the steam demand difference additional hog fuel was combusted in a power boiler, resulting in increased costs. The unit operation variables predicted through the simulation were used to calculate cost factors for variable process cost items. The net variable operating costs for each case were determined from these cost factors. The obtained results indicate that implementing BLG with the investigated modified pulping technologies would lead to increases in the net variable operating cost per oven dry ton pulp produced ranging from 1.8 to 3.9% compared to the kraft-MCC base case. It was also found that the cost of kiln fuel and the price of power sales to the grid drive the relative cost performance of the evaluated cases. When comparing the BLG cases to the MCC reference, the net variable operating cost break even point based on lime kiln fuel cost ranges from \$47 to \$38 per barrel of kiln fuel depending on the BLG process, which is much lower than currently available prices. When performing similar comparisons of net variable operating costs based on variable power sales price, significant cost savings could be realized in all BLG processes at prices for power sold to the grid above 5 ¢/KWh.

3.3 Conclusions

The following section outlines the overall conclusions drawn from the project.

3.3.1 Conclusions from split sulfidity pulping

Compared to the kraft MCC reference cooks, the investigated split sulfidity pulping procedure returned pulps with one to two percent greater yield at a higher rate of delignification. The SS pulps were found to have greater viscosity and improved tensile and burst strength.

3.3.2 Conclusions from green liquor pretreatment pulping

Compared to the kraft MCC reference cooks, the investigated green liquor pretreatment pulping procedure generated pulps of comparable yield and viscosity. The resulting pulp strength was also somewhat improved. However, the rate of delignification was lower than in the MCC reference procedure, and this could not be overcome by increasing the levels of charged TTA. The greatest benefit from GL pretreatment would be

realized through the possibility of decreasing the load on the lime kiln, creating an opportunity for de-bottlenecking or cost savings from a decrease in lime kiln fuel demand.

3.3.3 Conclusions from polysulfide pulping with anthraquinone

The investigated PSAQ procedure resulted in increased levels of delignification compared to the MCC reference. This benefit increased with increasing levels of initial alkali charge. The obtained pulp yields suggest possible yield improvements of up to 3%, with an approximate yield benefit of 1% total yield per % PS charged on OD wood. This result is in line with literature data. The performed work has suggested that there exists an optimum condition for PSAQ pulping with alkali profiling. The best results obtained in this work with respect to delignification rate, yield benefit and even alkali profile was achieved using 3% PS on wood at 40% sulfidity and an alkali profile where the total available alkali was added to the cook in three separate stages as fractions 45/31/24 (Stage1/Stage2/Stage3) of the total.

3.3.4 Conclusions from WinGEMS simulation work

Initial simulation work around the integration of BLG into the kraft process combined with modified pulping technologies showed that the net variable process operating cost would increase due to increased load on the lime kiln. This cost could be offset through implementation of modified pulping technologies that allowed for greater pulp yield, lower the overall process demand for wood, chemicals and fuel. The work also indicated the desirability of having a BLG WinGEMS module available for further simulation. Further simulation work has resulted in the generation of such a WinGEMS module for the MTCI low temperature steam reformer, or black liquor gasifier. The module has been utilized in simulation case studies exploring SS and PSAQ pulping using BLG as the central unit operation in chemical recovery. The obtained results indicated that the net process variable operating cost was driven by two major factors, lime kiln fuel and power sales price. Under the initial assumptions, where lime kiln fuel was set to \$50/barrel and power sales price at \$0.35/kWhr, the net variable operating costs for the BLG cases showed a cost increase of about 3% compared to the MCC reference case. The overall conclusion from this simulation case study is that BLG integration into the kraft process is highly dependent on the price of lime kiln fuel and the price and amount of power produced from BLGCC conversion of syngas. Under the initial assumptions made in this case study, the significantly increased load on the lime kiln is not overcome by the benefits realized in pulping operations through the introduction of modified pulping technologies, nor by the additional revenue generated from the generation and sale of green power. However, if modifications could be made to the recausticizing unit operations, such as high sulfidity green liquor pretreatment, offloading the slaker and resulting load on the lime cycle, this would change. Another such approach would be auto-causticization in the white liquor stream. Also, as indicated in figures 10.3 and 10.4, if the lime kiln fuel cost is decreased or the power sale price increased, the BLGCC kraft process with split sulfidity or PSAQ pulping becomes a more economically favorable alternative than the conventional reference kraft process, based on variable operating costs. When comparing the BLG cases to the MCC reference, the net variable operating cost break even point based on lime kiln fuel cost is about \$47/barrel

for the SS and PS2% processes, and about \$38/barrel for the PS2% process. This is significantly lower than assumed kiln fuel price of \$60/barrel used in this work. If the sales price for power to the grid was increased from 3.5 to 6 ¢/KWh cost savings of about \$40/ODtP could be realized in all BLG processes.

3.4 Future work

Future work in the area of pulping integrated with BLG should be focused on technologies or processes with BLG that allow for decreased load on the lime kiln, such as auto-causticizing or alkaline-sulfite pulping. Of these, mini-sulfide sulfite pulping with anthraquinone, MSSAQ, may be the most intriguing, as it would likely permit the elimination of the lime kiln cycle entirely. Pulping work to investigate and optimize MSSAQ pulping and simulation work showing the overall process effects of BLG implementation integrated with MSSAQ pulping should be performed.

Future work in the area of simulation should be focused on the processes and process modifications suggested for future pulping work. Of special interest would be MSS-AQ simulation based on a BLG recovery system. In addition, a continuous effort for improvement of the BLG block module as more data become available, to increase the robustness and predictive capability of the model with regards to varying inputs and operational parameters, is desirable. Finally, the development of a validated combined cycle power plant within the WinGEMS software package would be most valuable.

4 REFERENCES

- 1) Nilsson, L.J.; Larson, E.D.; Gilbreath, K.R.; Gupta, A. *Energy Efficiency and the Pulp and Paper Industry*; ACEEE: Washington D.C./Berkeley, CA, 1995.
- 2) Jahne, F. "Commercial Success of Gasification Technology", *Tappi J.* **1999**, 82(10): 49.
- 3) Whitty, K.; Verrill, C.L. "A Historical Look at The Development of Alternative Black Liquor Recovery Technologies and The Evolution of Black Liquor Gasifier Designs", *Proc. 2004 TAPPI Int. Chem. Rec. Conf.*; TAPPI Press: Atlanta, GA, 2004; p 13-33.
- 4) Stigsson, L., "ChemrecTM [Kvaerner Chemrec AB's] Black-Liquor Gasification", *Proc. 1998 TAPPI Int. Chem. Rec. Conf.*; TAPPI Press: Atlanta, GA, 1998; p 663-674.
- 5) Grace, T.M.; Timmer, W.M. "A Comparison of Alternative Black Liquor Recovery Technologies", *Proc. 1995 TAPPI Int. Chem. Rec. Conf.*; TAPPI Press: Atlanta, GA, 1995.
- 6) Rowbottom, B.; Newport, D.; Connor, E. "Black Liquor Gasification at Norampac", *Proc. 2005 TAPPI Engineering Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
- 7) Chemrec ; URL <http://www.chemrec.se>; 2005.
- 8) Whitty, K.; Ekblom, T.; Stigsson, L. "Chemrec Gasification of Black Liquor"; published on website URL <http://www.chemrec.se/forsta.htm>; 2000.
- 9) Lindblom, M. "An Overview of Chemrec Process Concepts"; Presentation at the Colloquium on Black Liquor Combustion and Gasification; Park City, Utah, May, 2003.
- 10) Erickson, D.; Brown, C. "Operating Experience with Gasification Pilot Project"; *Tappi J.* **1999**, 82(9).
- 11) Kleppe, P.J., *TAPPI* 53:1 35-47 (1970)
- 12) McDonough, T.J., "Kraft Pulp Yield Basics", *Proc. Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998, Vol. 1, p1.
- 13) Sixta, H. ed., Handbook of Pulp and Paper Vol 1 and 2. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2006** Ch. 4
- 14) Aurell, R., Hartler, N., *Svensk Papperstidning* 68(4):59-68 (1965)
- 15) Kondo, R., Sarkanen, K.,V., *Holzforshung* 38:31 (1984)
- 16) Gellerstedt, G. *Pulping Chemistry*. In: Wood and Cellulosic Chemistry, 2nd ed., Hon, D.N.S., Shiraishi, N., Eds., M. Dekker, New York, Basel, **2001** p.859
- 17) Adler, E., *Wood Sci. Technol.* 11:169 (1977)
- 18) Gierrer, J., *Holzforshung*, 36:43 (1982)
- 19) Gellerstedt, G., Lindfors, E-L., *Nordic Pulp Paper Res. J.*, 2(2):71 (1987)
- 20) Gustavsson, C., Sjostrom, K., Wafa Al-Dajani, W., *Nordic Pulp Paper Res. J.*, 14(1):71 (1999)
- 21) Nimz, H., H., *Holzforshung*, 335 16-26 (1981)
- 22) Gierrer, J., *Svensk Papperstidning* 73:571 (1970)
- 23) Gierrer, J., *Wood Sci. Technol.* 19:1289 (1985)
- 24) Dimmel,;D.R., Bovee, L.F., Brogdon, B.N., *Wood Chem. Technol.*, 14:1 (1994)
- 25) Gierrer, J., Wannstrom, S., *Holzforshung*, 40(6):347 (1986)
- 26) Ishii, T., Shimizu, K., *Chemistry of Cell Wall Polysaccharides*. In: Wood and Cellulosic Chemistry, 2nd ed., Hon, D.N.S., Shiraishi, N., Eds., M. Dekker, New York, Basel, **2001** p.859

-
- 27) Meller, A., *Holzforschung*, 19(4):118 (1965)
 - 28) Johansson, B.; Mjoberg, J.; Sandstrom, P.; Teder, A. "Modified Continuous Kraft Pulping - Now a Reality"; *Svensk Papperstidning--Nordisk Cellulosa*. **1984**, 87(10): 30-35.
 - 29) Andrews, E.K. Ph.D. thesis, North Carolina State University, Raleigh, NC, 1982.
 - 30) Andrews, E.K.; Chang, H-m.; Kirkman, A.G.; Eckert, R.C. "Extending Delignification in Kraft and Kraft/Oxygen Pulping of Softwood by Treatment with Sodium Sulfur Liquors"; *Proc. Japan Tappi Symposium on Wood pulp chemistry*; TAPPI Press: Atlanta, GA, 1982.
 - 31) Lopez, I.; Chang, H-m.; Jameel H.; Wizani, W. "Effect of Sodium Sulfide Pretreatment on Kraft Pulping"; *Proc. 1999 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1999; pp135.
 - 32) Herschmiller, D.W. "Kraft Cooking with Split Sulfidity- A Way to Break the Yield Barrier"; *Proc. Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998; Vol. 1 pp 59.
 - 33) Olm, L.; Tisdat, G. "Kinetics of the Initial Stage of Kraft Pulping"; *Svensk Papperstidning--Nordisk Cellulosa*. **1979**, 82(15): 458-464.
 - 34) LeMon, S.; Teder, A. "Kinetics of Delignification in Kraft Pulping (1). Bulk Delignification of Pine"; *Svensk Papperstidning--Nordisk Cellulosa*, **1973**, 76(11): 407.
 - 35) Olm, L.; Tormund, D.; Jensen, A. "Kraft Pulping with Sulfide Pretreatment-Part-1 Delignification and Carbohydrate Degradation"; *Nord. Pulp Pap. Res. J.* **2000**, 15, 62.
 - 36) Jiang, J.E; Herschmiller, D.W. "Sulfide Profiling for Increased Kraft Pulping Selectivity"; *Proc. 1996 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1996, p. 311-318.
 - 37) Lownertz, P.P.H.; Herschmiller, D.W. "Kraft Cooking with Split White Liquors and High Initial Sulfide Concentration: Impact on Pulping and Recovery"; *Proc. 1994 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1994, p. 1217-1224.
 - 38) Mao, B.; Hartler, N. "Improved Modified Kraft Cooking. (1). Pretreatment with a Sodium Sulfide Solution"; *Paperi ja Puu*. **1992**, 74(6): 491-494.
 - 39) Mao, B.; Hartler, N. "Improved Modified Kraft Cooking. (2). Modified Cooking Using High Initial Sulfide Concentration"; *Nordic Pulp and Paper Research J.*, **1992**, 7(4): 168-173.
 - 40) Mao, B.; Hartler, N. "Improved Modified Kraft Cooking,4: Modified Cooking with Improved Sulfide and Lignin Profiles"; *Paperi ja Puu*. **1995**, 77(6/7): 419-422.
 - 41) Olm, L.; Backstrom, M.; Tormund, D. "Pretreatment of Softwood with Sulfide Containing Liquor Prior to Kraft Cook"; *Proc. 1994 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1994; 29.
 - 42) Jiang, J.E.; Greenwood, B.F.; Phillips, J.R.; Stromberg, C.B. "Improved Kraft Pulping by Controlled Sulfide Additions"; *Proc. 7th ISWPC Conference*; CICCST: Beijing, China, 1993.
 - 43) Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H.; "Effects on Pulp Yield and Properties Using Modified Pulping Procedures Involving Sulfur Profiling and Green Liquor Pretreatment"; Presented at 2004 Tappi Fall Technical Conference, Atlanta, GA, 2004.
 - 44) Van Heiningen, A.; Schwiderke, E.; Chen, X. "Kinetics of the Direct Causticizing Reaction Between Black Liquor and Titanates During Low Temperature Gasification"; *Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
 - 45) Li, Z.; Li, J.; Kubes, G.J. "Kinetics of Delignification and Cellulose Degradation During Kraft Pulping with Polysulfide and Anthraquinone"; *JPPS*. **2002**, 28(7): 234-239.
 - 46) Griffin, C.W.; Kumar, K.R.; Gratzl, J.; Jameel, H. "Effects of Adding Anthraquinone and Polysulfide to the Modified Continuous Cooking (MCC) Process"; *Proc. 1995 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1995; 19-30.

-
- 47) Jiang, J.E. “*Extended Delignification of Southern Pine [Pinus spp.] with Anthraquinone and Polysulfide*”; TAPPI J. **1995**, 78(2): 126-132.
- 48) Jiang, J.E. “*Extended Modified Cooking of Southern Pine [Pinus] with Polysulfide: Effects on Pulp Yield and Physical Properties*”; TAPPI J. **1994**, 77(2): 120-124.
- 49) Landmark, P.A.; Kleppe, P.J.; Johnsen, K. “*Pulp Yield Increasing Process in Polysulfide Kraft Cooks*”; Tappi J. **1965**, 58(8): 56.
- 50) Vennemark, E. “*Some Ideas on Polysulfide Cooking*”; Svensk Papperstidning. **1964**, 67(5): 157.
- 51) Kleppe, P.J.; Minja, R.J.A. “*The Possibilities to Apply Polysulfide-AQ in Kraft Mills*”; Proc. *Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998, Vol. 1, pp 113.
- 52) Sanyer, N.; Laundrie, J.F. “*Factor Affecting Yield Increase and Fiber Quality in Polysulfide Pulping of Loblolly Pine, Other Softwoods, and Red Oak*”; Tappi J. **1964**, 47(10): 640.
- 53) Luthe, C.; Berry, R. “*Polysulphide Pulping of Western Softwoods: Yield Benefits and Effects on Pulp Properties*”; Pulp. Pap. Can. **2005**, 106(3): 27-33.
- 54) Munro, F.; Uloth, V.; Tench, L.; MacLeod, M.; Dorris, G. “*Mill-Scale Implementation of Paprican's Process for Polysulphide Liquor Production in Kraft Mill Causticizers - Part 2: Results of Pulp Mill Production Trials*”; Pulp. Pap. Can. **2002**, 103(1): 57-61.
- 55) Tench, L.; Uloth, V.; Dorris, G.; Hornsey, D.; Munro, F. “*Mill Scale Implementation of Paprican's Process for Polysulfide Liquor Production in Kraft Mill Causticizers. Part-1 Batch Trials and Optimization*”; TAPPI J. **1999**, 82(10): 120.
- 56) Yamaguchi, A. “*Operating Experiences with the MOXY Process and Quinoid Compounds*”; In *Anthraquinone Pulping: Anthology of Published Papers 1977-1996*; Goyal, G.C., Ed.; TAPPI Press: Atlanta, GA, 1997; pp 287-291.
- 57) Nishijima, H.; et al., “*Review of PS/AQ Pulping to Date in Japanese Kraft Mills and the Impact on Productivity*”; Proc. *1995 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1995; 31-40.
- 58) MacLeod, M.; Radiotis, T.; Uloth, V.; Munro, F.; Tench, L. “*Basket Cases IV: Higher Yield with Papriox™ Polysulfide-AQ Pulping of Hardwoods*”; TAPPI J. **2002**, 1(10): 3-8.
- 59) Olm, L.; Tormund, D.; Bernor Gidert E. “*Possibilities to Increase the Pulp Yield in a Kraft Cook of [the] ITC-Type*”; Proc. *Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998; Vol. 1, 69-78.
- 60) Hakanen, A.; Teder, A. “*Modified Kraft Cooking with Polysulfide: Yield, Viscosity, and Physical Properties*”; TAPPI J. **1997**, 80(7): pp 86,93,100, 189-196.
- 61) Jiang, J.E.; Crofut, K.R.; Jones, D.B. “*Polysulfide Pulping of Southern Hardwood Employing the MOXYRG and Green-Liquor Crystallization Processes*”; Proc. *1994 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1994; pp 799-806.
- 62) Gustafsson, R.; Ek, M.; Teder, A. “*Polysulphide Pretreatment of Softwood for Increased Delignification and Higher Pulp Viscosity*”; JPPS. **2004**, 30(5): 129-135.
- 63) Mao, B. F.; Hartler, N. “*Improved Modified Kraft Cooking,3: Modified Vapor-Phase Polysulfide Cooking*”; TAPPI J. **1994**, 77(11): 149-153.
- 64) Lindstrom, M.; Teder, A. “*Effect of Polysulfide Pretreatment When Kraft Pulping to Very Low Kappa Number*”; Nordic Pulp Paper Res. J. **1995**, 10(1): 8-11.
- 65) Olm, L.; Tormund, D. “*ZAP Cooking- Increase Yield in PS and PS-AQ Cooking with Zero Effective Alkali in the Pretreatment Stage*”; Nordic Pulp Paper Res. J. **2004**, 19(1): 6.
- 66) Brannvall, E.; Gustafsson, R.; Teder, A.; “*Properties of Hyperalkaline Polysulphide Pulps*”; Nordic Pulp Paper Res. J. **2003**, 18(4): 436-440.

-
- 67) Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H. *"The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Properties"*; Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference; TAPPI Press: Atlanta, GA, 2005.
- 68) Edwards, L.L., et al. GEMS User's Manual, University of Idaho, Moscow, ID, 1972, 1977, 1983, 1989.
- 69) Metsoautomation website:
[http://www.metsoautomation.com/automation/index.nsf/FR?ReadForm&ATL=/Automation/pp_prod.nsf/](http://www.metsoautomation.com/automation/index.nsf/FR?ReadForm&ATL=/Automation/pp_prod.nsf/WebWID/WTB-061205-2256F-8ECE6)
WebWID/WTB-061205-2256F-8ECE6

**5 ECONOMICS OF INTEGRATING BLACK LIQUOR GASIFICATION WITH PULPING: PART I
– EFFECT OF SULFUR PROFILING**

Lindstrom, M.E., Kirkman, A., Jameel, H. et al. “*Economics of Integrating Black Liquor Gasification With Pulping: Part I – Effect Of Sulfur Profiling.*” Proceedings Tappi Fall Technical Conference, Tappi Press, Atlanta, GA, (2002)

ECONOMICS OF INTEGRATING BLACK LIQUOR GASIFICATION WITH PULPING: PART I – EFFECT OF SULFUR PROFILING

Mathias Lindstrom, Adrianna Kirkman, Hasan Jameel

Julie Cheng, Christy Huggins, Brandon Bray

Department of Wood and Paper Science

North Carolina State University

Raleigh, NC 27695-8005

USA

ABSTRACT

Using black liquor gasification (BLG) the recovered sodium and sulfur can be split into two separate fractions with varying degrees of separation dependent on the operating conditions and the technology used. This separation creates some opportunities in the pulping process, due to its potential to increase the yield or to extend delignification. There may be an increase in the causticizing load. Of the various pulping options with black liquor gasification, sulfur profiling would be the lowest capital cost process to implement especially for mills with a modified continuous or batch process. In this paper, the process changes that are necessary to implement sulfur profiling are examined along with the economics. The results show that BLG increases the pulp production cost from \$140.23/ODtP to \$143.31/ODtP at H₂S/CO₂ co-absorption ratio of 10:1. Most of the cost increase is due to the increase in the lime kiln fuel and the lime makeup. An increase in yield of 1% changes the pulp production cost from \$140.23/ODtP to \$140.45/ODtP for the Tomlinson vs. BLG with split sulfidity pulping. If the yield increase is 2%, the cost decreases to \$138.91. It may also be possible to use the NaHS and Na₂CO₃ stream in the impregnation phase without affecting the overall alkali usage, since sulfur absorption is more effective at the lower pH. At the same EA charge of 19%, the cost increased from \$140.23/ODtP for the Tomlinson case versus \$141.15/ODtP for the BLG case with Na₂CO₃ pretreatment. But at the same TTA usage the %EA is 15% and the cost is decreased to \$136.09/ODtP.

INTRODUCTION

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 sulfur can be split into two separate fractions. This separation creates some opportunities in the pulping process, which can lead to production cost savings or improved operations.

The implementation of black liquor gasification can increase the efficiency of combined heat and power generation in the pulp mill. It may be possible to produce twice as much electricity per ton of black liquor solid as compared to a modern Tomlinson recovery boiler.

The Tomlinson Recovery Boiler has the disadvantages of low thermal efficiency, low power to heat ratio and the risk of smelt/water explosions. Gasification technology addresses some of these concerns. Black liquor gasification technologies can be classified by the operating temperature (1). High temperature gasifiers operate at about 1000°C (Chemrec) and low temperature gasifiers operate at less than 700°C (MTCI). In the high temperature gasifier the smelt leaves in the molten form and in the low temperature system the inorganics leave as solids.

A schematic of the Chemrec black liquor gasification system is shown in Figure 1. The fuel gas stream contains most of the sulfur as hydrogen sulfide and carbonyl sulfide. A solvent-based regenerative system is used to clean up the raw fuel gas and form a sulfur rich solvent stream. The solvent is then regenerated to liberate the sulfur rich gas stream.

A simplified schematic of the MTCI 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 (2). Feedstock such as spent liquor is fed to the reactor, which is fluidized with superheated steam from a waste heat recovery boiler.

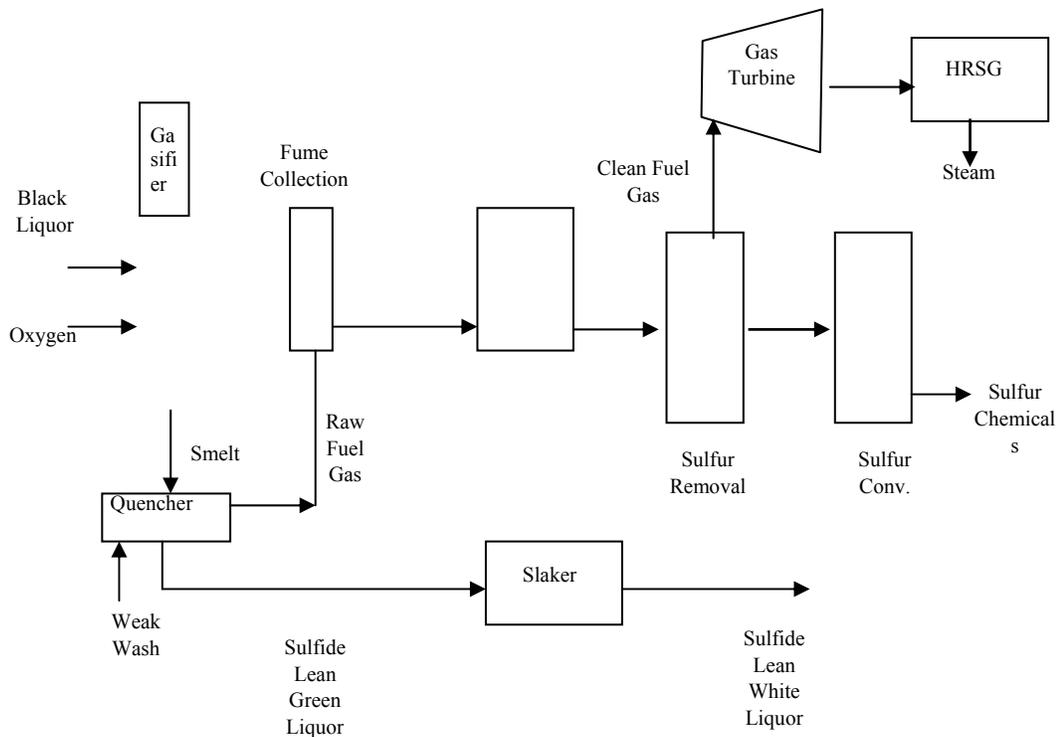


Figure 5.1 Schematic of a High Pressure Black Liquor Gasification System

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 leaves mostly with the gas stream and the sodium stays in solid form. Product gases are routed through a cyclone to remove the bulk of the entrained particulate matter and then 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, 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.

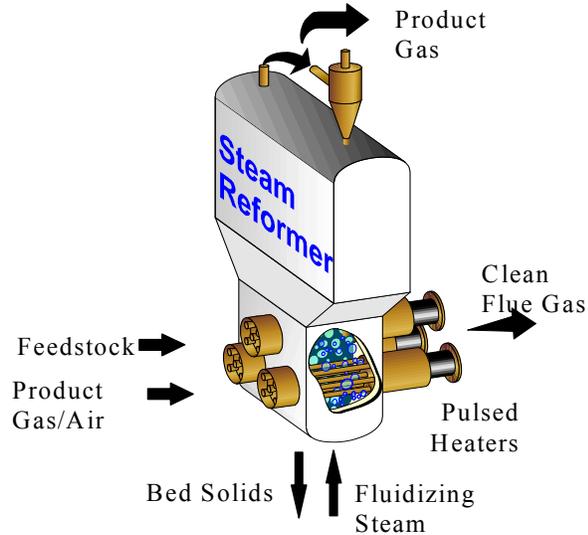


Figure 5.2 Schematic of a MTCI Steam Reformer

INTEGRATION OF BLG INTO PULPING

One of the advantages of the black liquor gasification over the Tomlinson boiler is that the sodium and the sulfur are split into separate streams which can then be utilized in the pulping process as desired. The splitting of the sodium and the sulfur can be taken advantages of with the following pulping technologies:

- Split Sulfidity Pulping
- Polysulfide Pulping
- Alkaline Sulfite Pulping : Alkaline Sulfite- AQ (AS-AQ) or Mini-Sulfite Sulfide AQ Process (MSSAQ)

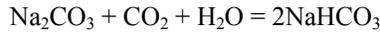
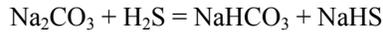
In split sulfidity pulping, it would be necessary to generate two streams of white liquor – one that is sulfide rich and another that is sulfide lean. In polysulfide pulping, a portion of the sulfur stream would be oxidized to elemental sulfur, which would be used mixed with the sulfur lean white liquor to produce polysulfide liquor. In the ASAQ or MSSAQ process, the sulfur gas stream would be burnt to produce SO_2 , which would then be absorbed into the Na_2CO_3 stream from the gasifier. The decision between AS-AQ and MSS-AQ, will depend on the amount of Na_2S in the liquor from the gasifier.

Sulfur profiling would be the lowest capital cost process to implement especially for mills with a modified continuous or batch pulping process. It may also be possible to get some of the benefits of split sulfidity pulping in conventional indirect-heated batch digesters. In this paper, the process changes necessary to implement sulfur profiling will be examined along with the economics. Previously, a cost benefit analysis for polysulfide pulping has been done for low polysulfide charges (3).

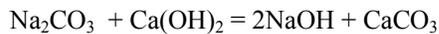
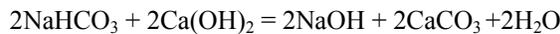
Black liquor gasification will potentially increase the causticizing load due to the release of H_2S . In conventional recovery the sulfur ends up as Na_2S in the green liquor stream, while in gasification for each mole of H_2S the sodium now becomes available as Na_2CO_3 . A higher amount of Na_2CO_3 will have to be converted to NaOH . In addition, the concurrent capture of CO_2 in a downstream H_2S scrubbing process will also increase the causticizing load.

CASE 1: Production of Conventional White Liquor

The first case studied was for the production of conventional white liquor as shown in Figure 3. All the sulfur chemicals along with some CO₂ is absorbed in the sulfide lean green liquor (Na₂CO₃) and then combined before the slaker.



In this case the white liquor produced will be similar to that from a conventional boiler and split sulfidity pulping cannot be implemented. The absorption of H₂S and CO₂ in Na₂CO₃ results in the production of NaHCO₃, which will result in an increase in the causticization load. The equations below show that it takes twice as much lime to produce an equivalent amount of NaOH from NaHCO₃.



The economic impact of this process was evaluated by simulating the system using WinGEMS. The base case consisted of a Tomlinson boiler with a continuous digester. The gasifier was simulated using a combustor block with appropriate reaction blocks to represent the absorption steps and the handling of sodium. From the blocks representing the combustor, the following streams were predicted:

Gas stream containing Carbon Dioxide, Hydrogen Sulfide, Oxygen, Nitrogen and Water Vapor

Chemical stream containing Na₂CO₃

Loss streams containing sodium and sulfur

The Na₂CO₃ solution was formed using weak wash from the lime cycle. The H₂S absorption with the Na₂CO₃ liquor and the subsequent causticizing of the carbonate and bicarbonate components was performed with a series of Reaction and Slaking/Causticizing blocks. These reactions were based on the stoichiometry represented by the equations above.

The results for the base case and for the production of conventional white liquor are shown in Tables 1 and 2. The effect of a change in the amount of CO₂ that is co-absorbed along with the H₂S is also shown. The expected mole ratio of H₂S to CO₂ that will be co-absorbed is 10:1. The economics of the power cycle was not accounted for in this simulation. The energy generated from the combustion of black liquor in the black liquor gasifier case (BLG) was significantly higher than that for the Tomlinson boiler because a combustor was used to simulate the gasifier. For our cost calculations, it was assumed that the BTU from the Tomlinson and the BLG are the same (this assumption will have to be need to be adjusted in a further study). Any changes in the amount of energy available was valued as an incremental change in BTU from the Tomlinson case.

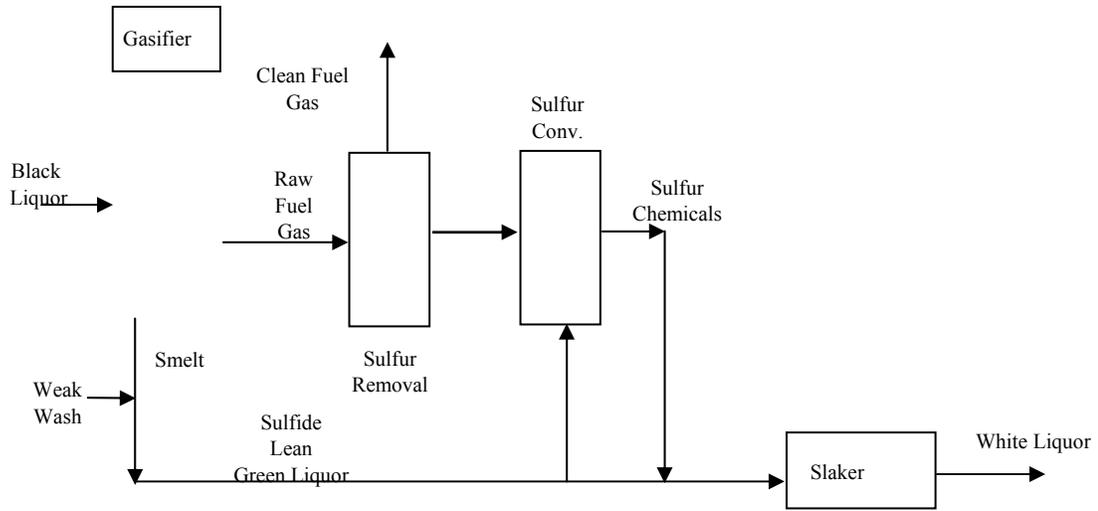


Figure 5.3 Schematic for the Production of Conventional White Liquor with BLG

The results show that BLG increases the pulp production cost from \$140.23/ODtP to \$143.31/ODtP at a co-absorption ratio of 10:1. Most of the cost increase is due to the increase in the lime kiln fuel and the lime makeup. The impact of CO₂ co-absorption was quite low. The increase in causticizing cost and lime kiln production bottlenecks demonstrates the need to evaluate other technologies such as auto-causticizing.

CASE 2: Production of Split Sulfidity Liquor

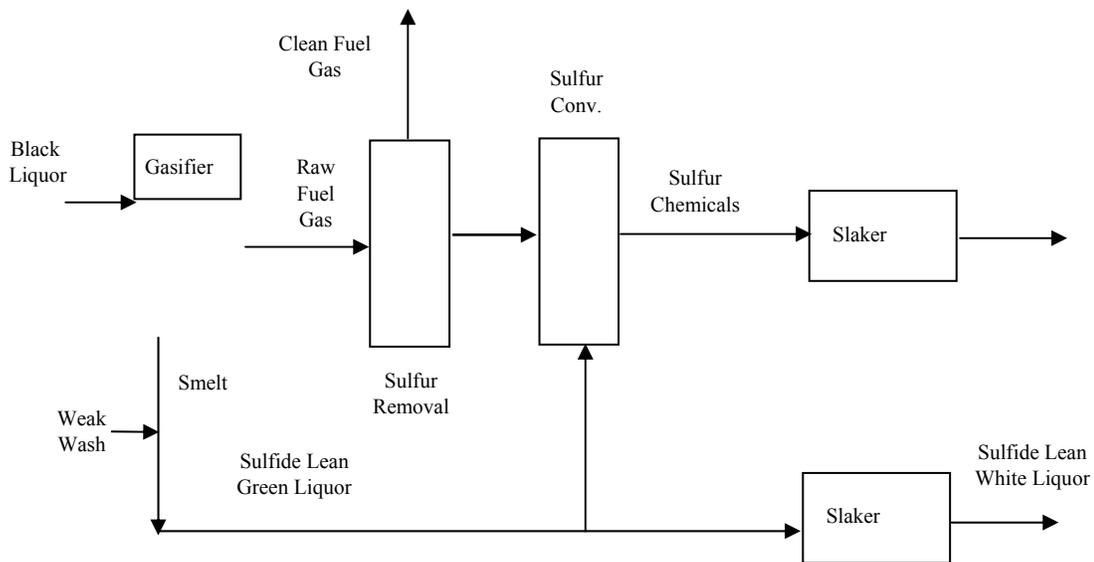


Figure 5.4 Schematic for the Production of Sulfide Lean and Sulfide Rich White Liquor with BLG

The schematic for the production of split sulfidity liquor is shown in Figure 4. In this scheme a second slaker was necessary to keep the sulfide lean and rich liquors separate. It should be noted that the sulfur gases were absorbed into Na_2CO_3 instead of NaOH to minimize the co-absorption of CO_2 in the liquor. The production of two different white liquor streams will enable one to take advantage of split sulfidity pulping.

The application of modified delignification in the kraft process has been investigated with respect to selectivity, pulp yield and strength properties. The basic principles of modified extended delignification consist of level alkali concentration throughout the cook, a high initial sulfide concentration, low concentrations of lignin and Na^+ in the final stage of the cook, and lower temperature in the initial and final stages of the cook (4). The concept of sulfur profiling, or split sulfidity pulping, employing a sulfur rich stream in the rapid initial phase, followed by a sulfur lean stream in the bulk and residual phase, has been investigated (5-9). Compared to conventional kraft cooks of similar H-factor, split sulfidity pulping has been shown to enhance selectivity of the pulping reactions resulting in higher lignin removal and pulp viscosity. Split sulfidity pulping, has been shown to increase pulp yield and strength properties (9-16). The basic approaches consist of an initial presteaming or pretreatment stage, followed by one or two cooking stages. A sulfur rich stream was charged in the pretreatment or first cooking stage followed by a sulfur lean stream in the second stage. Compared to conventional reference cooks the results indicate a yield increase of about 1-2 % and higher viscosity pulp for cooks to kappa less than 20.

In the modified batch systems commercially available the requirement for initial high sulfide concentration is accomplished by using the spent cooking liquor containing high sulfide for pre-treatment (17). Pre-treatment of the chips using black liquor before digesting with the white liquor allows a significant reduction of H-factor or alkali charge to reach the same kappa level as conventional batch system (18). The implementation of the modified batch system into an existing batch mill is very capital intensive. It may be possible to get some of the benefits of a modified batch pulping system by using the liquors with different sulfidities during the heat up phase of an indirect-heated batch digester, thereby decreasing the capital required to attain some of the benefits of extended delignification. In the modified continuous cooking system, the white liquor is added in multiple steps to level out the alkali concentration and there are multiple extractions to keep the dissolved lignin low towards the end of the cook. However, there is no good method to take advantage of the high sulfidity that is beneficial during the initial phase of the cook. Black liquor gasification with its ability to split the sodium and the sulfur will enable us to charge a higher amount of sulfur in the initial phase of the cook.

The benefit of split sulfidity pulping can be taken advantage of either be taken in a yield increase or by lowering of the kappa number to the bleach plant at the same yield. The results of a yield increase on the overall pulping and causticizing economics are shown in Tables 3 and 4 for three different yield increases. An increase in yield of 1% changes the pulp production cost from \$140.23/ODtP to \$140.45/ODtP for the Tomlinson vs. BLG with split sulfidity pulping. At this yield increase, the cost for Tomlinson and the BLG are comparable. If the yield increase is 2%, the cost decreases to \$138.91ODtP.

CASE 3: Use of Na_2CO_3 in the Pretreatment Stage

Previous work (9-10) has demonstrated the feasibility of using green liquor in the impregnation stage, without increasing overall chemical usage. It has also been shown (19) that the amount of sulfur adsorbed during the pretreatment decreases with higher $[\text{OH}^-]$. By impregnating chips with high sulfidity, low pH liquor, a mill may enhance yield and further decrease the causticizing load. Since the black liquor process increases the causticizing load, it would be of interest to evaluate the option where the pretreatment is done using a mixture of NaOH , Na_2CO_3 and NaHS . This option is shown in Figure 5. The need for another slaking operation is not necessary in this process.

The results are shown in Tables 5 and 6 for different cases of effective alkali charge. It is expected that the EA requirement will decrease because of the pretreatment with the sulfide rich liquor. Assuming a yield increase of 1.5% at the same EA charge of 19%, the use of Na_2CO_3 and NaHS in the pretreatment stage changes the cost from \$140.23/ODtP for the Tomlinson case versus \$141.15/ODtP for the BLG case with Na_2CO_3 pretreatment. It has been shown in previous work (9) that pretreating with this liquor will decrease the %EA charge. It has been speculated that the total amount of TTA used may not change significantly.

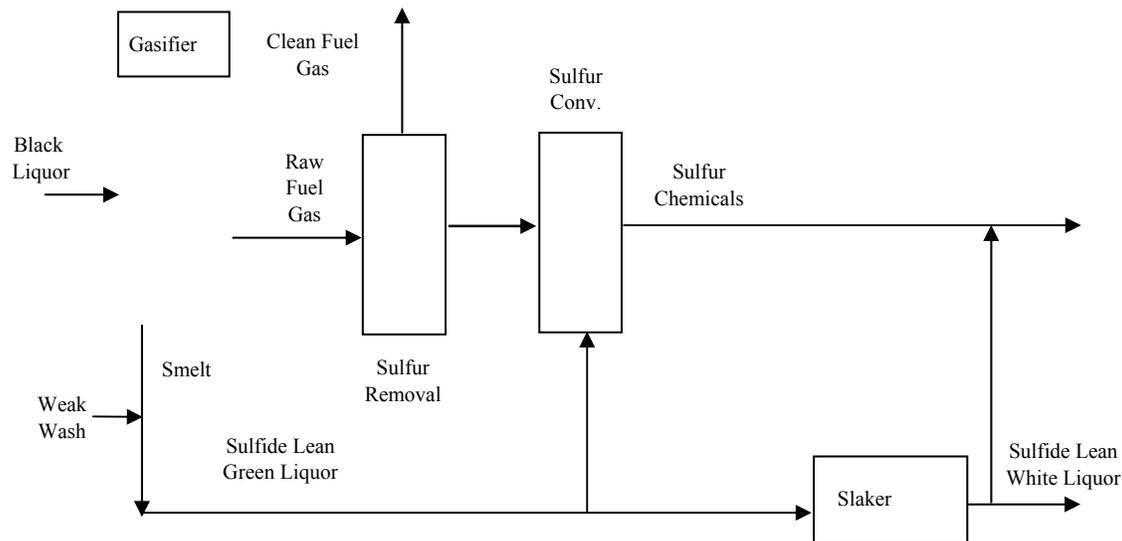


Figure 5.5 Schematic for using NaHS and Na₂CO₃ in Pretreatment with BLG

But at the same TTA usage the %EA is 15% and the cost is decreased to \$136.09/ODtP. It is expected that we may be able to operate at the same TTA usage.

CONCLUSIONS

Using black liquor gasification (BLG) the sodium and the sulfur can be split into two separate fractions with varying degrees of separation dependent on the operating conditions and the technology used. The low temperature process (MTCI Steam Reformer) is capable of splitting the sulfur and the sodium completely. This separation of the sodium and the sulfur creates some opportunities in the pulping process, which can lead to production cost savings or lower environmental impact. As a result, integration of the gasification process into the overall mill will affect the economics of gasification. The splitting of the sulfur and caustic has the potential to increase the pulping yield, but the negative aspects of the increase in the causticizing load also needs to be taken into account. The splitting of the sodium and the sulfur can be taken advantages of with the following technologies:

- Sulfur Profiling
- Polysulfide Pulping
- Mini-Sulfite Sulfide AQ Process (MSSAQ)

Sulfur profiling would be the lowest capital cost process to implement especially for mill with a modified continuous or batch process. The use of liquors with varying sulfidity will be of greatest interest to bleached mills that have a continuous digester with capability for MCC. After black liquor gasification it is possible to generate streams of NaHS and Na₂CO₃ and a stream of NaOH. The relative amounts of these streams will depend on the sulfidity of the liquor and the causticizing load. High sulfidity in the initial phase is very important to improve the yield and that a shortage of sulfide ions in the transition phase of delignification can lower the yield by approximately 1.5%. Black liquor gasification enables us to charge a higher amount of sulfur in the initial phase of the cook. This increased the yield by about 1-2%, or it decreased the kappa number by 4 units without a change in the yield. It is also possible to use the NaHS and Na₂CO₃ stream in the impregnation phase without affecting the overall alkali usage, since sulfur absorption is more effective at the lower pH. The use of the NaHS and Na₂CO₃ stream for impregnation minimizes the impact of gasification on causticizing.

The above processes were simulated using WinGEMS to quantify the impacts on the various mill unit operations. The results show that BLG increases the pulp production cost from \$140.23/ODtP to \$143.31/ODtP at H₂S/CO₂ co-absorption ratio of 10:1. Most of the cost increase is due to the increase in the lime kiln fuel and the lime makeup. The co-absorption ratio did not have a big impact on the cost. An increase in yield of 1% changes the pulp production cost from \$140.23/ODtP to \$140.45/ODtP for the Tomlinson vs. BLG with split

sulfidity pulping. If the yield increase is 2%, the cost decreases to \$138.91. It may also possible to use the NaHS and Na₂CO₃ stream before slaking in the impregnation phase without affecting the overall alkali usage, since sulfur absorption is more effective at the lower pH. At the same EA charge of 19%, the cost increased from \$140.23/ODtP for the Tomlinson case versus \$141.15/ODtP for the BLG case with Na₂CO₃ pretreatment. But at the same TTA usage the %EA is 15% and the cost is decreased to \$136.09/ODtP.

In Part II and III, of this work the integration of black liquor gasification into a mill with polysulfide use especially at high charges and sulfite pulping will be discussed.

REFERENCES

1. Stigsson, L., Proceedings 1998 International Chemical Recovery Conference, p663 (1998)
2. Rockvam, L.N., Thermochem Recovery International, Personal communications (2001)
3. Larson, E.D, Yang, W., Iisa, I., Malcolm, E., McDonald, G., Fredrick, J., Kreutz, T., Brown, C., International Chemical Recovery Conference Proceedings, p 1.(1998)
4. Johansson, B., Mjoberg, J., Sandstrom, P., Teder, A., Svensk Papperstid. 87(10):30 (1984).
5. Herschmiller, D.W., "Breaking the yield barrier", p. 59 TAPPI PRESS, 1998
6. LeMon, S. and Teder, A., Svensk Papperstidning, 79(11):407 (1973)
7. Olm, L. and Tisdat, G., Svensk Papperstidning, 82(15):458 (1979)
8. Olm, L. and Teder, A., Paperi ja Puu, 63(4a):315 (1981)
9. Andrews, E.K., dissertation, North Carolina State University, 1982
10. Andrews, E.K., Chang, H-m., Kirkman, A.G., Eckert, R.C., "Extending delignification in kraft and kraft/oxygen pulping of softwood by treatment with sodium sulfur liquors, Japan Tappi Symposium on Wood pulp chemistry, 1982.
11. Jiang, J.E., Crofut, K.R., Jones, D.B., *Proceedings of the TAPPI pulping conference*, p. 799, TAPPI Press, Atlanta, GA (1993)
12. Lownertz, P.P.H. and Herschmiller, D.W., *Proceedings of the TAPPI pulping conference*, p. 1217, TAPPI Press, Atlanta, GA (1994)
13. Jiang, J.E. and Herschmiller, D.W., *Proceedings of the TAPPI pulping conference*, p. 317, TAPPI Press, Atlanta, GA (1996)
14. Mao, B. and Hartler, N., Paperi ja Puu, 74(6):491 (1992)
15. Mao, B. and Hartler, N., Nordic Pulp and Paper Research J., 7(4):168 (1992)
16. Mao, B. and Hartler, N., Paperi ja Puu, 77(6-7):419 (1995)
17. Tormund, D., Teder, A., "A new finding on sulfide chemistry in kraft pulping," Tappi pulping conference p 247 (1989).
18. Abuhasan, J., PhD thesis North Carolina State University, p 82 (1994).
19. I. Lopez, H-m Chang, H. Jameel and W. Wizani, Tappi Pulping Conference Proceedings, p135 Orlando, Florida October 1999

AUTHORS

Hasan Jameel and Adrianna Kirkman are Professors in the Department of Wood and Paper Science Mathias Lindstrom is a graduate student working on integrating black liquor gasification and pulping Julie Cheng, Christy Huggins and Brandon Bray are undergraduate students who worked on modifying WinGEMS to simulate the gasifier and slaking reactions as part of a senior project.

Table 5.1 Effect of Black Liquor Gasification and the H₂S to CO₂ Co-absorption on the Process

Fiber Line					
	Unit	Kraft Base	BLG (5:1)	BLG (10:1)	BLG (20:1)
Chips	ODtC/day	2409.24	2409.24	2409.24	2409.24
Brown Pulp Produced	ODtP/day	993.77	993.77	993.77	993.77
Digester Steam	kg/ODtP	1720.29	1739.69	1734.35	1731.68
Yield					
Brown Pulp	%	41.25	41.25	41.25	41.25
White Liquor (synthetic)					
Flow	mt/hr	178.51	186.16	184.00	182.92
TTA as NaOH	g/L	151.28	151.27	151.26	151.25
Sulfidity	%	24.97	24.36	24.66	24.81
Recovery					
Evaporator					
Flow to evaporator	mt/hr	476.98	483.85	481.91	480.93
Solids to evaporator	%	15.99	15.81	15.85	15.88
Dissolved solids to evaporator	kg/ODtP	1360.49	1847.19	1844.98	1841.25
Steam used (evaporated)	kg/ODtP	1581.26	1613.59	1604.82	1600.41
Steam used (concentrated)	kg/ODtP	553.60	555.10	554.43	554.11
Boiler / Gasifier					
Flow to unit	mt/hr	118.20	100.28	100.17	100.12
Solids fired	%	66.26	60.12	60.13	60.13
Dissolved solids to unit	kg/ODtP	1314.80	1456.15	1844.98	1841.25
Amount Inorganic	kg/ODtP	4.88	1.40	1.39	1.39
Amount Organic	kg/ODtP	1314.80	1316.17	1315.51	1315.20
Energy available for Steam	Mcal/day	4.71*10 ⁶	5.66*10 ⁶	5.65*10 ⁶	5.65*10 ⁶
Gas to Turbines, mt/hr	mt/hr	x	541.84	541.58	541.45
Slaker					
Flow	mt/hr	231.38	265.18	261.13	259.10
Reburned lime	kg/ODtP	322.84	473.65	462.18	456.45
Fresh lime	kg/ODtP	8.70	13.66	13.32	13.15
Make-up lime	mt/day	8.65	12.49	12.18	12.02
White Liquor make-up					
NaOH (make-up)	kg/ODtP	22.05	18.94	18.93	18.91
Na ₂ SO ₄	kg/ODtP	8.64	19.82	19.72	19.64
Elemental Sulfur	kg/ODtP	0.00	0.00	0.00	0.00

Table 5.1 continued**Kiln**

Throughput	ODt/day	571.59	847.87	827.16	816.82
Fuel consumed	kg/day	56542	72668	70874	69978

Water Usage

Scrubber Mill Water	mt/hr	143.41	141.73	139.56	138.47
Brownstock Washer Shwr Make-up	mt/hr	117.24	110.82	112.56	113.44
Mud Filter Mill Water	mt/hr	22.55	22.55	22.55	22.55
Mud Tank Cons. Reg. Mill Water	mt/hr	283.69	283.69	283.69	283.69
Total	mt/hr	566.90	558.79	558.36	558.15
Green Liqour Heater Steam	kg/ODtP	55.50	83.68	83.93	84.04

Table 5.2 Effect of Black Liquor Gasification and the H₂S to CO₂ Co-absorption on Cost**Cost analysis \$/ODtP**

	Cost, USD	Kraft Basecase	BLG(5:1) DELTA	% BLG(10:1) DELTA	% BLG(20:1) DELTA
Chips/kg	0.062	150.31	150.31	0.00	150.31
NaOH/lb	0.141	6.84	5.87	-16.42	5.87
Na2SO4/lb	0.05	0.95	2.18	56.42	2.17
Fresh Lime/lb	0.032	0.61	0.96	36.30	0.94
Steam used/kg	0.006	23.46	23.95	2.04	23.87
Kiln fuel/barrel	20	8.35	10.73	22.19	10.47
Water/1000 gal	0.072	0.99	0.97	-1.45	0.97
Total	x	191.51	194.98	1.78	194.59
Energy available/ODTP	6	51.28	61.63	16.79	61.56
Net Cost	x	140.23	133.35	-5.15	133.03

Table 5.3 Effect of Split Sulfidity and Yield Increase on the Process

Fiber Line

	Unit	Kraft Base	BLG 1% Yield	BLG 1.5% Yield	BLG 2% Yield
Chips	ODtC/day	2409.24	2353.18	2331.67	2306.38
Brown Pulp Produced	ODtP/day	993.77	993.77	993.77	993.77
Digester Steam	kg/ODtP	1720.29	1659.61	1653.06	1645.24

Yield

Brown Pulp	%	41.25	42.23	42.62	43.09
------------	---	-------	-------	-------	-------

White Liquor (synthetic)

Flow	mt/hr	178.51	179.87	178.21	176.27
TTA as NaOH	g/L	151.28	151.26	151.27	151.25
Sulfidity	%	24.97	24.66	24.66	24.66

Recovery

Evaporator

Flow to evaporator	mt/hr	476.98	473.69	470.48	466.70
Solids to evaporator	%	15.99	15.49	15.36	15.21
Dissolved solids to evaporator	kg/ODtP	1360.49	1772.00	1745.70	1731.69
Steam used (evaporated)	kg/ODtP	1581.26	1595.87	1591.37	1586.20
Steam used (concentrated)	kg/ODtP	553.60	532.52	524.62	515.27

Boiler / Gasifier

Flow to unit	mt/hr	118.20	95.99	94.49	92.72
Solids fired	%	66.26	60.04	60.00	59.96
Dissolved solids to unit	kg/ODtP	1314.80	1391.77	1745.70	1731.69
Amount Inorganic	kg/ODtP	4.88	1.42	1.43	1.44
Amount Organic	kg/ODtP	1314.80	1255.35	1234.21	1209.23
Energy available for Steam	Mcal/day	4.71*10 ⁶	5.42*10 ⁶	5.33*10 ⁶	5.23*10 ⁶
Gas to Turbines, mt/hr	mt/hr	x	519.08	510.99	501.43

Slaker

Flow	mt/hr	231.38	200.03	198.15	195.94
Reburned lime	kg/ODtP	322.84	451.52	447.23	442.17
Fresh lime	kg/ODtP	8.70	13.01	12.90	12.74
Make-up lime	mt/day	8.65	11.90	11.79	11.65

White Liquor make-up

NaOH (make-up)	kg/ODtP	22.05	18.70	18.40	18.11
Na ₂ SO ₄	kg/ODtP	8.64	19.44	19.40	19.40
Elemental Sulfur	kg/ODtP	0.00	0.00	0.00	0.00

Table 5.3 continued**Kiln**

Throughput	ODt/day	571.59	807.94	800.28	791.24
Fuel consumed	kg/day	56542	69209	68555	67780

Water Usage

Scrubber Mill Water	mt/hr	143.41	135.92	134.47	132.78
Brownstock Washer Shwr Make-up	mt/hr	117.24	114.34	115.23	116.26
Mud Filter Mill Water	mt/hr	22.55	22.55	22.55	22.55
Mud Tank Cons. Reg. Mill Water	mt/hr	283.69	283.69	283.69	283.69
Total	mt/hr	566.90	556.50	555.95	555.28
Green Liqour Heater Steam	kg/ODtP	55.50	67.78	67.15	66.43

Table 5.4 Effect of Split Sulfidity and Yield Increase on Cost**Cost analysis \$/ODtP**

	Cost, USD	Kraft Basecase	BLG 1%Yield	% DELTA	BLG 1.5%Yield	% DELTA	BLG 2%Yield	% DELTA
Chips/kg	0.062	150.31	146.81	-2.38	145.47	-3.33	143.89	-4.46
NaOH/lb	0.141	6.84	5.80	-17.92	5.71	-19.84	5.62	-21.75
Na2SO4/lb	0.05	0.95	2.14	55.56	2.13	55.47	2.13	55.48
Fresh Lime/lb	0.032	0.61	0.92	33.15	0.91	32.56	0.90	31.74
Steam used/kg	0.006	23.46	23.13	-1.42	23.02	-1.94	22.88	-2.56
Kiln fuel/barrel	20	8.35	10.22	18.30	10.13	17.52	10.01	16.58
Water/1000 gal	0.072	0.99	0.97	-1.87	0.97	-1.97	0.97	-2.09
Total	x	191.51	189.99	-0.80	188.33	-1.69	186.40	-2.74
Energy available/ODTP	6	51.28	48.71	-5.28	47.79	-7.32	46.70	-9.83
Net Cost	x	140.23	141.28	0.74	140.54	0.22	139.70	-0.38

Table 5.5 Effect of using Na₂CO₃ for Pretreatment and %EA Use on the Process

Fiber Line

	Unit	Kraft Base	BLG 15%EA	BLG 17%EA	BLG 19%EA
Chips	ODtC/day	2409.24	2331.77	2331.78	2331.76
Brown Pulp Produced	ODtP/day	993.77	993.77	993.77	993.77
Digester Steam	kg/ODtP	1720.29	1697.14	1753.06	1809.05
			13.00	15.00	19.00
Yield					
Brown Pulp	%	41.25	42.62	42.62	42.62
White Liquor (synthetic)					
Flow	mt/hr	178.51	175.82	199.30	222.82
TTA as NaOH	g/L	151.28	151.35	151.34	151.31
Sulfidity	%	24.97	24.66	24.66	24.66
Recovery					
Evaporator					
Flow to evaporator	mt/hr	476.98	468.51	489.80	511.12
Solids to evaporator	%	15.99	15.87	15.82	15.77
Dissolved solids to evaporator	kg/ODtP	1360.49	1796.09	1871.76	1953.22
Steam used (evaporated)	kg/ODtP	1581.26	1558.43	1631.54	1704.89
Steam used (concentrated)	kg/ODtP	553.60	539.99	562.86	585.66
Boiler / Gasifier					
Flow to unit	mt/hr	118.20	97.74	100.61	103.45
Solids fired	%	66.26	60.18	59.66	59.17
Dissolved solids to unit	kg/ODtP	1314.79	1420.48	1871.76	1953.22
Amount Inorganic	kg/ODtP	4.88	1.95	2.14	2.31
Amount Organic	kg/ODtP	1314.80	1229.70	1234.41	1238.98
Energy available for Steam	Mcal/day	4,71*10 ⁶	5.35*10 ⁶ est.	5.33*10 ⁶ est.	5.30*10 ⁶ est.
Gas to Turbines, mt/hr	mt/hr	x	523.87	539.07	554.15
Slaker					
Flow	mt/hr	231.38	195.43	221.61	247.85
Reburned lime	kg/ODtP	322.84	347.61	394.18	440.53
Fresh lime	kg/ODtP	8.70	10.04	11.37	12.71
Make-up lime	mt/day	8.65	9.18	10.40	11.62
White Liquor make-up					
NaOH (make-up)	kg/ODtP	22.05	11.13	10.71	9.93
Na ₂ SO ₄	kg/ODtP	8.64	20.82	23.50	26.42
Elemental Sulfur	kg/ODtP	0.00	0.00	0.00	0.00

Table 5.5 continued**Kiln**

Throughput	ODt/day	571.59	622.16	705.52	788.50
Fuel consumed	kg/day	56542	53530	60655	67766

Water Usage

Scrubber Mill Water	mt/hr	143.41	131.45	151.94	172.55
Brownstock Washer Shwr Make-up	mt/hr	117.24	121.77	107.24	92.67
Mud Filter Mill Water	mt/hr	22.55	22.55	22.55	22.55
Mud Tank Cons. Reg. Mill Water	mt/hr	283.69	283.69	283.69	283.69
Total	mt/hr	566.90	559.46	565.42	571.46
Green Liqour Heater Steam	kg/ODtP	55.50	83.70	95.22	106.90

Table 5.6 Effect of using Na₂CO₃ for Pretreatment and %EA Use on Cost**Cost analysis \$/ODtP**

	Cost, USD	Kraft Basecase	BLG 15%EA	% DELTA	BLG 17%EA	% DELTA	BLG 19%EA	% DELTA
Chips/kg	0.062	150.31	145.48	-3.32	145.48	-3.32	145.48	-3.32
NaOH/lb	0.141	6.84	3.45	-98.01	3.32	-105.91	3.08	-122.10
Na₂SO₄/lb	0.05	0.95	2.29	58.51	2.59	63.25	2.91	67.30
Fresh Lime/lb	0.032	0.61	0.71	13.37	0.80	23.52	0.89	31.55
Steam used/kg	0.006	23.46	23.28	-0.81	24.26	3.27	25.24	7.03
Kiln fuel/barrel	20	8.35	7.91	-5.63	8.96	6.78	10.01	16.56
Water/1000 gal	0.072	0.99	0.97	-1.33	0.98	-0.26	0.99	0.80
Total	x	191.51	184.08	-4.04	186.38	-2.75	188.60	-1.55
Energy available/ODTP	6	51.28	47.99	-6.87	47.77	-7.36	47.44	-8.10
Net Cost	x	140.23	136.09	-3.04	138.61	-1.17	141.15	0.66

6 EFFECTS ON PULP YIELD AND PROPERTIES USING MODIFIED PULPING PROCEDURES INVOLVING SULFUR PROFILING AND GREEN LIQUOR PRETREATMENT

Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H.; *“Effects on Pulp Yield and Properties Using Modified Pulping Procedures Involving Sulfur Profiling and Green Liquor Pretreatment”*; Presented at 2004 Tappi Fall Technical Conference, Atlanta, GA, 2004

EFFECTS ON PULP YIELD AND PROPERTIES USING MODIFIED PULPING PROCEDURES INVOLVING SULFUR PROFILING AND GREEN LIQUOR PRETREATMENT

Mathias Lindstrom, Ved Naithani, Adrianna Kirkman, Hasan Jameel

Department of Wood and Paper Science

North Carolina State University

Raleigh, NC 27695-8005

USA

ABSTRACT

Using black liquor gasification (BLG), the recovered entities of sodium and sulfur can be split into two separate fractions with varying degrees of separation dependent on the operating conditions and the technology used. The separation of these chemicals creates some opportunities in the pulping process where chemical profiling may be employed to increase the pulp yield or to extend delignification. This benefit may be offset by an increase in the causticizing load. Of the various pulping options with black liquor gasification, sulfur profiling would be the lowest capital cost process to implement, especially for mills with a modified continuous or batch process. Previous process simulation work showed that BLG implementation alone would likely increase the cost of pulping operations due to the higher costs associated with limekiln operation. However, it was also found that by combining BLG implementation with pulping process modifications like split sulfidity pulping or green liquor pretreatment, the overall operational costs associated with pulping and chemical recovery could be substantially decreased. The work described here explores the possibilities made available for modified continuous cooking through the implementation of black liquor gasification. Laboratory pulping protocols were developed for modified continuous cooking, split sulfidity and green liquor pretreatment pulping. The obtained results indicate that the split sulfidity protocol can potentially be used to produce kraft pulps with higher yield, viscosity and strength properties relative the simulated MCC protocol; whereas the green liquor pretreatment protocol can be used to produce pulps with yields similar to the MCC protocol, but with higher viscosity and strength properties. Moreover, significant cost savings can be realized by using the green liquor pretreatment approach in place of the MCC protocol, as the load on the recaust system and particularly the limekiln would be reduced.

INTRODUCTION

The implementation of black liquor gasification, BLG, into a pulp mill chemical recovery system will allow for the splitting of sodium and sulfur into separate streams which can then be utilized in the pulping process as desired. This separation creates some opportunities in the pulping process, which can lead to production cost savings or improved operations. The following modified pulping technologies can advantageously be used in combination with black liquor gasification to realize these potential benefits.

- Split Sulfidity Pulping
- Polysulfide Pulping
- Alkaline Sulfite Pulping: Alkaline Sulfite- AQ (AS-AQ)
or Mini-Sulfite Sulfide AQ Process (MSSAQ)

The basic principles of modified extended delignification consist of level alkali concentration throughout the cook, a high initial sulfide concentration, low concentrations of lignin and Na^+ in the final stage of the cook, and lower temperature in the initial and final stages of the cook (1). Two technologies that can accommodate these principles, split sulfidity pulping and green liquor pretreatment, will be considered in this paper.

The concept of sulfur profiling, or split sulfidity pulping, employing a sulfur rich stream in the rapid initial phase, followed by a sulfur lean stream in the bulk and residual phase, has been investigated (2-6). Compared to conventional kraft cooks of similar H-factor, split sulfidity pulping has been shown to enhance selectivity of the pulping reactions resulting in higher lignin removal and pulp viscosity. Moreover, split sulfidity pulping, has been shown to increase pulp yield and strength properties (6-14). The basic approaches consist of an initial presteaming or pretreatment stage, followed by one or two cooking stages. A sulfur rich stream was charged in

the pretreatment or first cooking stage followed by a sulfur lean stream in the second stage. Compared to conventional reference cooks the results indicate a yield increase of about 1-2 % and higher viscosity pulp for cooks to kappa less than 20.

In the modified batch systems commercially available the requirement for initial high sulfide concentration is accomplished by using the spent cooking liquor containing high sulfide for pre-treatment (15). Pre-treatment of the chips using black liquor before digesting with the white liquor allows a significant reduction of H-factor or alkali charge to reach the same kappa level as conventional batch system (16). Modifications to enable these methods in an existing batch mill are very capital intensive. A different alternative would be to use liquors with different sulfidities during the heat-up phase of an indirect-heated batch digester, thereby decreasing the capital required to attain some of the benefits of extended delignification. In the modified continuous cooking system, white liquor is added in multiple steps to level out the alkali concentration and there are multiple extractions to keep the dissolved lignin low towards the end of the cook. However, there is no good method to take advantage of the high sulfidity that is beneficial during the initial phase of the cook. The implementation of black liquor gasification would overcome these issues, allowing for the generation of separate sulfide and sodium streams that could be applied in either batch or continuous pulping systems to take full advantage of the modified extended delignification.

Black liquor gasification will potentially increase the causticizing load due to the release of H_2S . In conventional recovery the sulfur ends up as Na_2S in the green liquor stream, while in gasification for each mole of H_2S the sodium now becomes available as Na_2CO_3 . A higher amount of Na_2CO_3 will have to be converted to $NaOH$. In addition, the concurrent capture of CO_2 in a downstream H_2S scrubbing process will also increase the causticizing load. One pulping technology that could potentially offset the increased demands on the recaust cycle is green liquor pretreatment. Using green liquor to pretreat the pulp in a first cooking stage would decrease the amount of Na_2CO_3 that requires conversion to $NaOH$ for the production of traditional white liquor.

Previous work (6,7) has demonstrated the feasibility of using green liquor in the impregnation stage, without increasing overall chemical usage. It has also been shown (17) that the amount of sulfur adsorbed during the pretreatment decreases with higher $[OH^-]$. The chemical sorption profiles and effect of green liquor pretreatment in kraft pulping have been demonstrated (18,19). By impregnating chips with high sulfidity, low pH liquor, a mill may enhance yield and further decrease the causticizing load.

Split sulfidity and green liquor pretreatment pulping processes have previously been simulated using WinGEMS™ to quantify the impacts on the various mill unit operations. The results showed that BLG implementation might increase the pulp production operational cost by \$3 per oven dry ton pulp. Most of the cost increase is due to the increase in the limekiln fuel and the lime makeup. However, the cost increase could be overcome and turned into a cost savings of \$2 per oven dry ton pulp, by a 2 % increase in pulp yield. Further cost reduction may be realized by reducing the load on the limekiln. Increasing the pulp yield or lowering of the kappa number to the bleach plant at the same yield could potentially be achieved by employing split sulfidity and/or green liquor pretreatment pulping; the latter would also reduce the load on the limekiln (20).

The following experimental program explores the pulping opportunities that were demonstrated in WinGEMS regarding pulping using split sulfidity and green liquor pretreatment. The developed cooking protocols for these two modified pulping technologies utilize the very high initial sulfide liquor concentrations that would be enabled by the implementation of black liquor gasification and the option of not converting all of the Na_2CO_3 to $NaOH$ in the recaust cycle. Process diagrams outlining how these liquors could be generated have been presented in previous work (20).

EXPERIMENTAL

Wood

Screened mixed southern softwood chips were used throughout the laboratory cooking. For each cook, 800 oven dry grams of chips were soaked in water over night. The chips were drained for 30 minutes and placed in the M&K batch digester prior to chemical addition.

Development of Modified Continuous Cooking procedure (21)

A laboratory cooking procedure was developed to simulate modified continuous cooking, MCC™. The cooking protocol was divided into three stages with addition of active chemical at the end of the first and second stage. The total cooking time from “time 0” (time = 0 at T = 100 °C) was fixed at 240 minutes, while the cooking temperature was varied to produce the desired h factor (153-166 °C). The active alkali, AA was set to 19.5 % on OD pulp and the sulfidity to 25 %. In addition, Na₂CO₃ was added as 15 % of the total chemical on wood, simulating a system dead load. The resulting total titratable alkali, TTA was divided for addition between the three stages. In the first stage, the chips were placed in the digester with 65 % of the TTA and water, to bring the liquor to wood ratio, L/W, to 3.5. The cook was then brought to 120 °C and held at temperature for 15 minutes. For the second stage white liquor heated to 125 °C was added equaling 20 % of the TTA, bringing the cumulative added TTA to 85 %. The cook was then brought to the desired temperature and held there until 105 minutes had elapsed from “time 0”. For the third stage, white liquor heated to 125 °C equaling the final 15 % of the TTA was added, bringing the L/W to about 4.5. The cook was then held at temperature until complete. The M&K batch digester system used in the experimental work was fitted with valves to enable liquor addition and extraction. An American LEWA Inc. type EK2 pump was used to feed heated liquor under pressure into the lab digester. The parameters for the MCC procedure are outlined in Table 1.

Table 6.1 Parameters for MCC protocol

	Cumulative % TTA	L/W	Stage Temperature (°C)	Time at Temperature (min)
Stage I	65	3.5	120	15
Stage II	85	4.1	153-166	~ 70
Stage III	100	4.5	153-166	120

Digester liquor samples were collected at predetermined intervals throughout the cook and titrated for residual effective alkali, using a procedure modified from SCAN-N 33:94. The sample collection scheme is outlined in Table 2. The developed MCC procedure was employed to generate kraft baseline data for comparison to later cooks, exploring split sulfidity and green liquor pretreatment.

Table 6.2 Outline of collection scheme for digester liquor samples

Sample	Time elapsed from “Time 0”	Comments
1	~ 25 minutes	At the completion of stage I, prior to liquor addition
2	60 minutes	After the first liquor addition, having reached final T and sufficient mixing
3	105 minutes	At the completion of stage II, prior to liquor addition
4	120 minutes	After the second liquor addition and sufficient mixing
5	240 minutes	At the completion of stage III, during the blow of the cook

Development of Split Sulfidity and Green Liquor Pretreatment procedure

The split sulfidity cooking protocols, displayed in Table 3, closely resembled that of the MCC baseline. The main difference is the liquor profile used. The total titratable alkali was kept constant throughout both the MCC baseline and split sulfidity cooks, but the addition scheme of the Na₂S and NaOH was altered. To maximize the sulfidity effect on the pulp, the total amount of Na₂S used was added in Stage 1. The NaOH was then split between the three different stages using two different approaches: Split Sulfidity – High Initial Alkali and Split Sulfidity – Low Initial Alkali (SS_HIA and SS_LIA). The Na₂CO₃ was evenly added to each stage to simulate system dead load. In the first approach (SS_HIA) the NaOH was added evenly, one third to each stage, resulting in a high initial alkali concentration followed by uniform increases in alkali through the liquor additions. In the second approach (SS_LIA), the amount of NaOH added to stage I was limited to a small amount (about 11 % of the total NaOH added), resulting in a low initial alkali concentration, but adequate to promote a sufficiently high level of pH during the first stage.

Table 6.3 Parameters for Split Sulfidity protocols, high initial and low initial alkali (SS_HIA/SS_LIA)

SS_HIA		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	47.6	100	33.3	33.3	3.5	120	15
Stage II	73.9	0	33.3	33.3	4.1	153-166	~70
Stage III	100	0	33.3	33.3	4.5	153-166	120
SS_LIA		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	33.28	100	10.9	33.3	3.5	120	15
Stage II	66.76	0	44.5	33.3	4.1	153-166	~70
Stage III	100	0	44.5	33.3	4.5	153-166	120

The green liquor pretreatment protocol is analogous to the one described for split sulfidity. To generate a high concentration Na₂CO₃ green liquor, simulating a decreased level of recaustization in the recovery loop, 25 % of the NaOH used previously was replaced by 25 % Na₂CO₃ maintaining a constant system TTA. The concept of high and low initial alkali was again employed and the resulting parameters for the green liquor pretreatment cooks are shown in Table 4. In order to produce pulps of lower kappa a series of cooks was additionally performed where the system TTA was increased by 10 %, using the same TTA component breakdown as the high initial alkali protocol. The modified green liquor pretreatment procedure was labeled “High TTA”.

Table 6.4 Parameters for Green Liquor Pretreatment protocols, high initial and low initial alkali (GLPT_HIA/GLPT_LIA)

GLPT_HIA		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	57.33	100	33.3	65.0	3.5	120	15
Stage II	78.7	0	33.3	17.5	4.1	153-166	~70
Stage III	100	0	33.3	17.5	4.5	153-166	120
GLPT_LIA		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	46.6	100	10.9	65.0	3.5	120	15
Stage II	73.3	0	44.5	17.5	4.1	153-166	~70
Stage III	100	0	44.5	17.5	4.5	153-166	120

All obtained pulps were thoroughly washed with water, disintegrated using an impeller mixer and screened. The screen accepts were fluffed prior to yield determination and refrigerated for storage. The total yield is given as the sum of the oven dry accepts and rejects. Pulp kappa numbers and viscosities were determined for all screen accept samples. Samples with kappa number exceeding 50 were treated with standard chlorite delignification to remove undissolved lignin. A total of six screened pulp samples, representing each procedure in the low and high kappa range, were refined using a PFI mill according to CPPA Standard C.7. Handsheets were made according to TAPPI T 205, and tested following T 220. The resulting sheet caliper, tear, tensile and burst, were determined according to TAPPI T 411, T 414, T 494, and T 403 respectively.

RESULTS AND DISCUSSION

MCC, Split Sulfidity and Green Liquor Pretreatment cooks

The significant difference between the cooking protocols can be found in their respective residual effective alkali (REA) profiles. The profiles were generated from cooking liquor samples collected according to the outline in Table 2. The points were selected at intervals from “time 0”, representing the end of the different stages and points following a liquor addition having allowed for temperature adjustment and mixing. The results, shown in Figures 1 through 4, illustrate how the liquor profiling results in significantly different levels of cooking liquor REA between the different protocols and how they vary for each stage within each cook. As shown, the MCC baseline cooks have a high initial REA, which then decreases over time as the cook progresses. There is a slight increase in REA after the second liquor addition, but the goal of the procedure, a smooth REA profile is achieved.

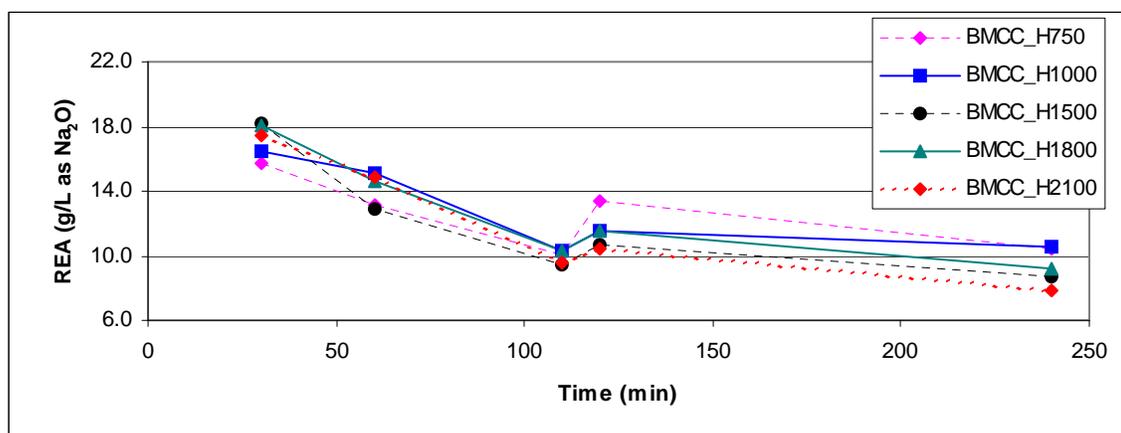


Figure 6.1 Residual Effective Alkali (REA) profiles for MCC procedure

When looking at the split sulfidity protocols the situation is very different. Here, the goal is to minimize the initial REA (Stage I) to then increase the level and maintain a high REA throughout the second and third stages. The initial REA level for the SS_HIA (High Initial Alkali) cooks are as expected higher than those of the SS_LIA (Low Initial Alkali) cooks, but reach similar levels during the second and third stage. Noteworthy is that the final REA is very similar among all three protocols. The initial data points at $t = 30$ minutes for the cooks MCCSS_H1500 and H1800, are higher than expected. However, when looking at the subsequent REA data points there is good agreement between all four cooks.

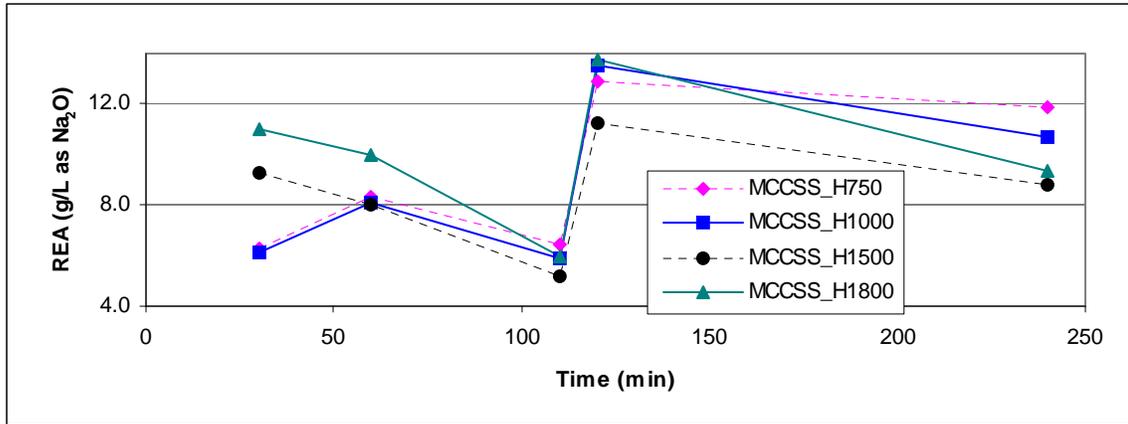


Figure 6.2 Residual Effective Alkali (REA) profiles for SS_HIA procedure

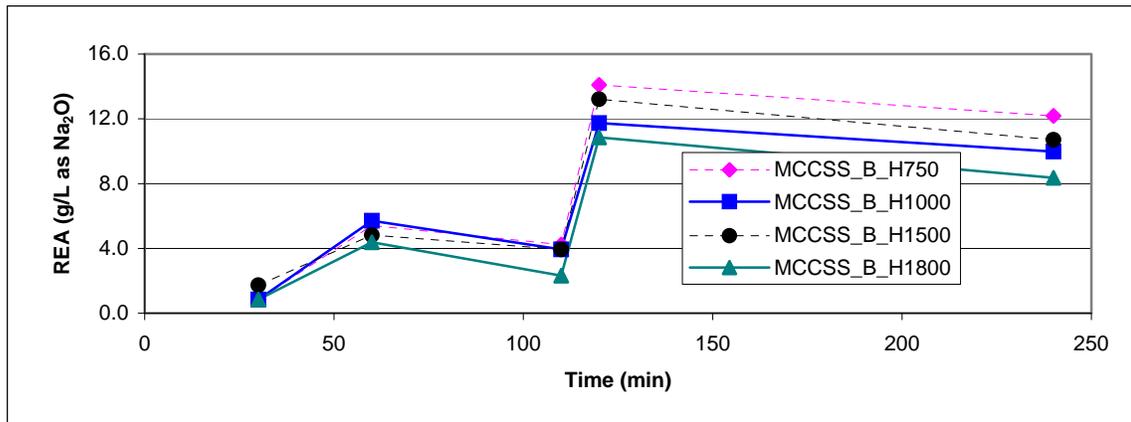


Figure 6.3 Residual Effective Alkali (REA) profiles for SS_LIA procedure

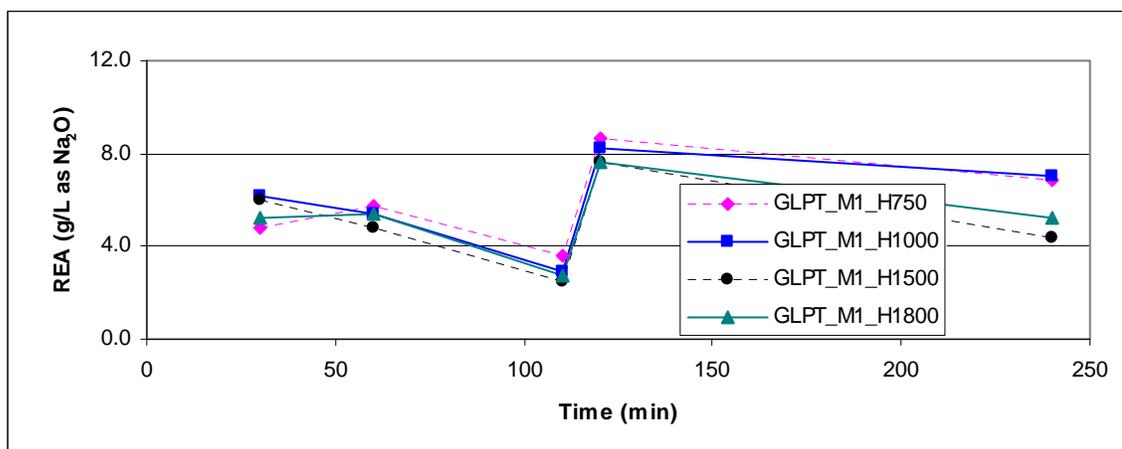


Figure 6.4 Residual Effective Alkali (REA) profiles for GLPT modified procedure

Pulp yield, kappa and viscosity for MCC and Split Sulfidity cooks

Three series of baseline cooks were performed according to the given MCC protocol. The average values for yield, kappa, and viscosities are reported in Table 5. Two series of cooks were performed using the split sulfidity high initial alkali (SS_HIA) and low initial alkali (SS_LIA). The obtained average values for the split sulfidity cook yield, kappa, and viscosity are displayed in Table 6. From these data the following relationships were explored: kappa versus h factor, total yield versus kappa, and viscosity versus kappa.

Table 6.5 MCC baseline pulp yield, kappa and viscosity

		MCC Baseline average values		
target	actual	Total Yield (%)	kappa	Viscosity (cps)
750	726	51.4	75.9	67.6
1000	1001	48.6	58.5	41.9
1500	1527	45.3	36.8	37.0
1800	1794	44.0	33.4	32.8
2100	2044	44.0	30.8	27.8

Table 6.6 Split Sulfidity baseline pulp yield, kappa and viscosity

		SS_HIA average values		
target	actual	Total Yield (%)	kappa	Viscosity (cps)
750	729	52.4	64.4	63.2
1000	1015	49.6	55.4	55.2
1500	1542	46.2	36.0	42.2
1800	1844	43.4	27.4	30.4
		SS_LIA average values		
target	actual	Total Yield (%)	kappa	Viscosity (cps)
750	711	53.2	71.5	72.3
1000	1019	49.4	59.2	58.4
1500	1553	44.7	35.5	40.9
1800	1843	44.5	30.8	34.9

Figure 5 shows how the split sulfidity procedures compare to the MCC procedure in regards of lignin removal as a function of h factor. As shown, the split sulfidity procedures produce lower kappa pulps at similar h factors relative the MCC procedure. Also, for the split sulfidity cooks, the high initial alkali approach produced pulps of lower kappa than the low initial alkali approach.

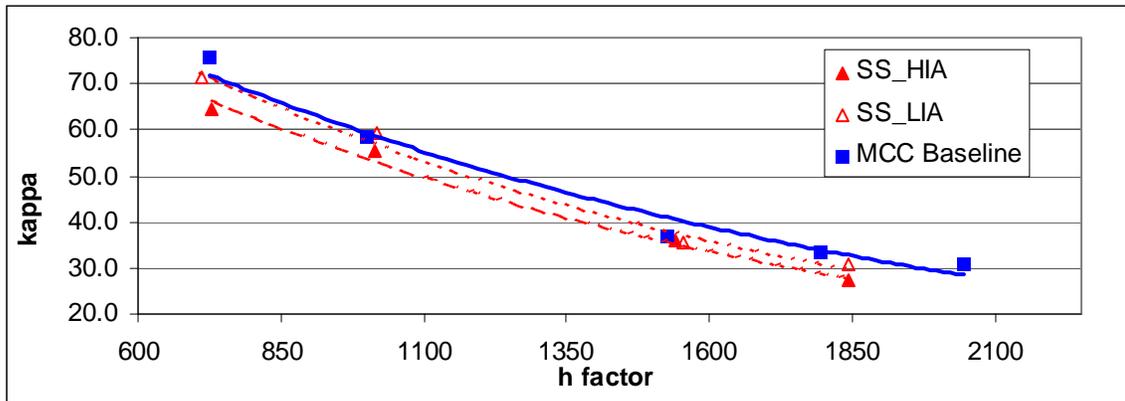


Figure 6.5 Kappa number versus final h factor for the MCC baseline, SS_HIA and SS_LIA cooks

The total pulp yield as a function of kappa was compared for the split sulfidity and MCC procedures. The resulting graph shown in Figure 6, indicates that the split sulfidity procedures produce pulp yields one to two percent greater than the MCC procedures. The difference is more pronounced at higher kappa. Also, the split sulfidity high initial alkali approach produced higher yields than the low initial alkali approach.

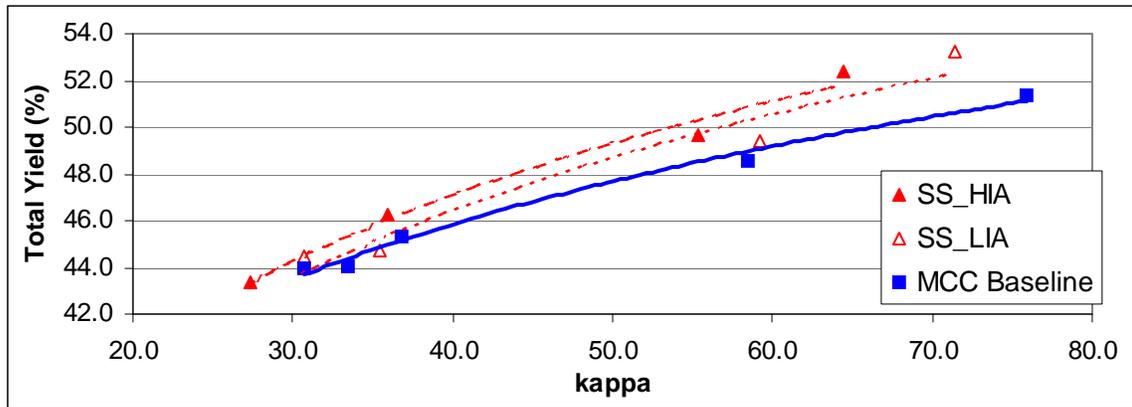


Figure 6.6 Total yield versus kappa for the MCC baseline, SS_HIA and SS_LIA cooks

The pulp viscosity as a function of kappa was similarly compared for the different procedures. The resulting graph is shown in Figure 7. As shown in the figure, the split sulfidity procedures produce pulps of viscosities in the range of 5 to 10 cps greater than those of the MCC pulps at similar kappa.

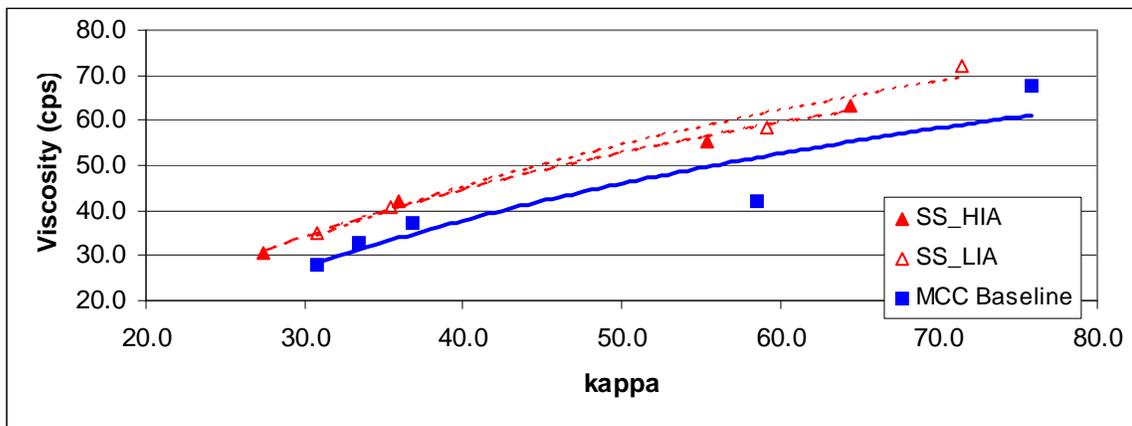


Figure 6.7 Viscosity versus kappa for the MCC baseline, SS_HIA and SS_LIA cooks

Pulp yield, kappa and viscosity for MCC and Green Liquor Pretreatment cooks

The obtained yield, kappa and viscosity values for the green liquor pretreatment procedures are displayed in Table 7. The high and low initial alkali procedures did not produce pulps of sufficiently low kappa number. To overcome this, the system TTA was increased by 10 % and employed in a modified procedure based on the high initial alkali approach. The obtained data is also shown in Table 7.

The obtained values for the green liquor pretreatment cooks were compared to the MCC data in a similar manner to that for the split sulfidity cooks. Figure 8 shows the resulting pulp kappa as a function of h factor. As seen in the figure, all of the green liquor pretreatment procedures produce pulps of kappa higher than those of the MCC procedure. The modified green liquor pretreatment (High TTA) generated the lowest kappa pulp. The total yields as a function of kappa, were compared and the resulting graph is shown in Figure 9. The figure indicates that the green liquor pretreatment procedures do not produce an appreciable yield increase, producing pulp yields similar to those of the MCC procedure at comparable levels of kappa.

Table 6.7

Green liquor pretreatment baseline pulp yield, kappa and viscosity

		GLPT_HIA values		
target	actual	Total Yield (%)	kappa	Viscosity (cps)
750	726	56.0	97.5	x
1000	1001	53.2	86.4	67.5
1500	1527	49.2	65.6	59.9
1800	1794	47.9	54.2	56.7
		GLPT_LIA values		
target	actual	Total Yield (%)	kappa	Viscosity (cps)
750	726	55.3	98.6	53.4
1000	1001	x	x	x
1500	1527	x	x	x
1800	1794	51.1	70.7	50.6
		GLPT_HIA Modified values		
target	actual	Total Yield (%)	kappa	Viscosity (cps)
750	719	53.7	93.7	67.1
1000	1002	50.4	71.8	67.3
1500	1424	48.5	60.6	53.9
1800	1807	46.1	39.5	49.5

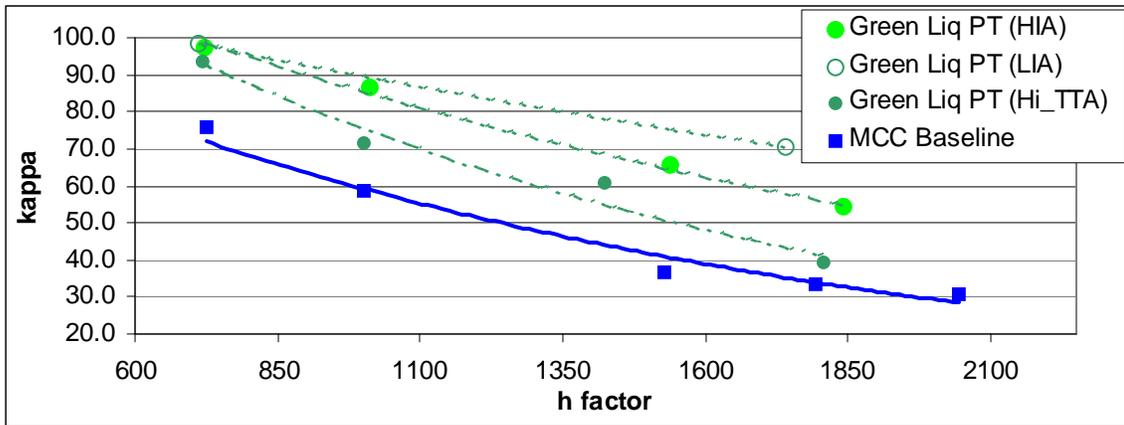


Figure 6.8. Kappa number versus final h factor for the MCC baseline, GLPT_HIA, GLPT_LIA and GLPT modified cooks

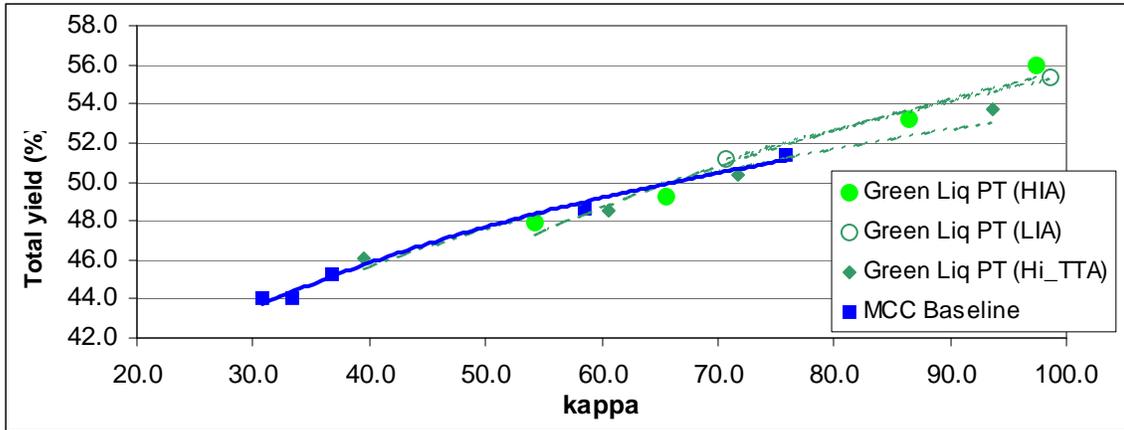


Figure 6.9 Total yield versus kappa for the MCC baseline, GLPT_HIA, GLPT_LIA and GLPT modified cooks

Figure 10 displays the obtained viscosity values as a function of kappa. As seen in the figure, the modified green liquor pretreatment procedure produced pulps of similar viscosity to those of the MCC procedure.

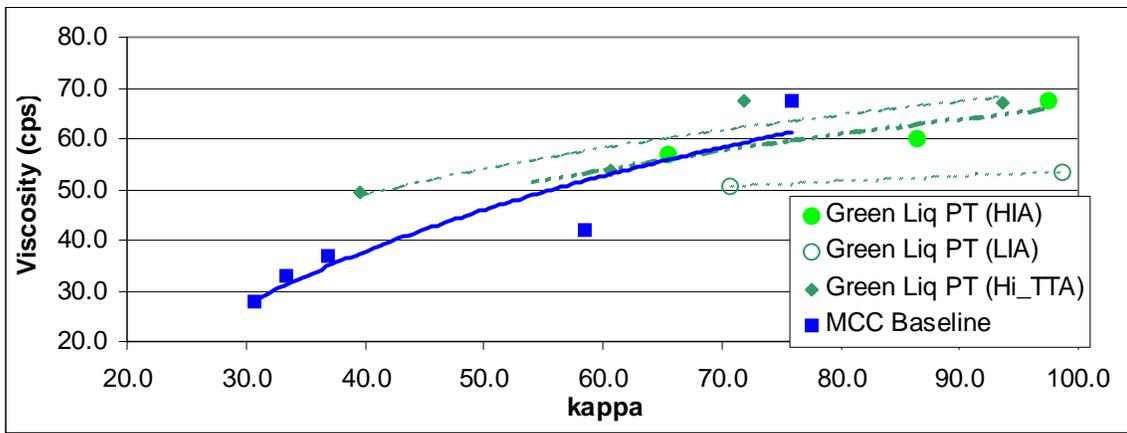


Figure 6.10 Viscosity versus kappa for the MCC baseline, GLPT_HIA, GLPT_LIA and GLPT modified cooks

Pulp strength properties for low and high kappa

As previously described, pulp samples representing each of the three procedures in the low and high kappa range, target h factor 1800 and 750, respectively, were used in the strength study. For the green liquor pretreatment cooks, both pulps were from the modified high TTA procedure. For the MCC baseline the high kappa pulp was selected from the second series, and the low kappa pulp from the third. For the split sulfidity cooks, both pulps were selected from the high initial alkali procedure; the low kappa pulp from the first series and the high kappa pulp from the second series. All pulps were refined using a PFI mill to four different points of revolutions. The freeness responses to refining of low and high kappa pulps representing the different cooking procedures are displayed in Figures 11 and 12. As shown in the figures, the MCC pulps refine to a lower freeness at similar levels of refining compared to the split sulfidity and green liquor pretreatment pulps. Also, the high kappa pulps have a significantly slower refining response than the low kappa pulps.

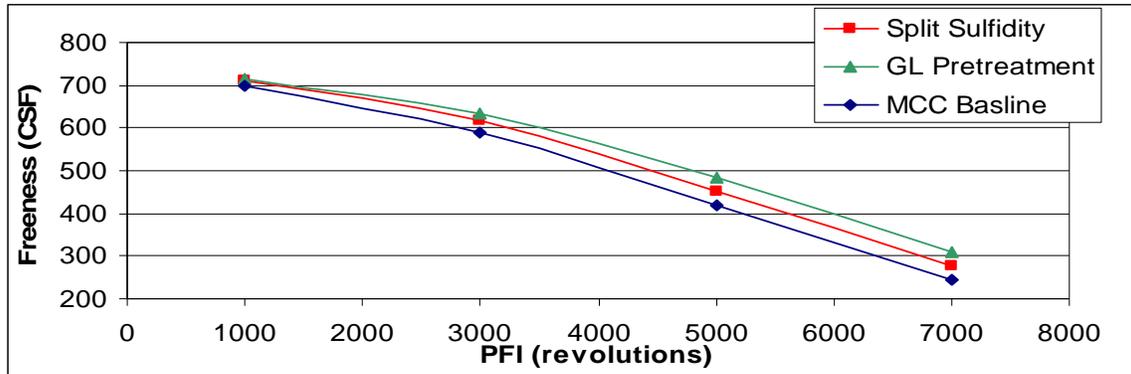


Figure 6.11 Refining response for low kappa pulps

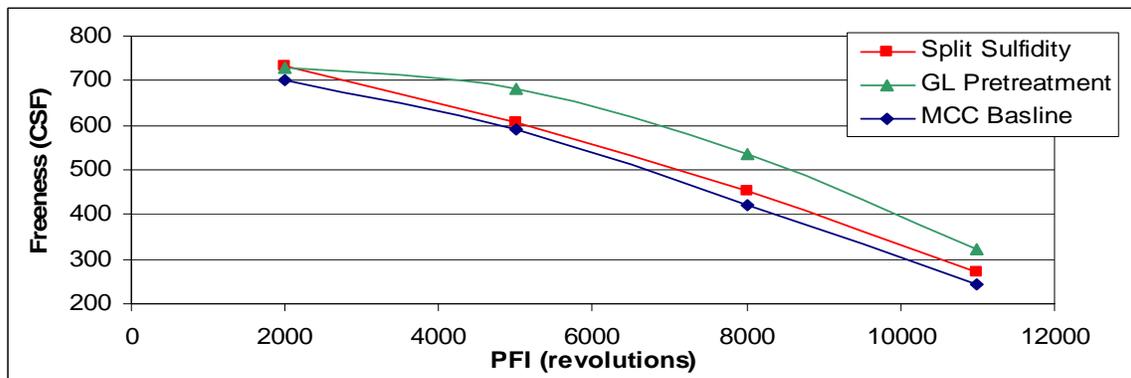


Figure 6.12 Refining response for high kappa pulps

The values obtained through the hand sheet study are displayed in Tables 8 and 9. The low (Table 8) and high (Table 9) kappa pulps have been treated and analyzed separately.

Table 6.8 Pulp strength properties for low kappa range cooks

Pulp ID	BMCC2_H1800	Average Values			
		Apparent density (kg/m ³)	Tear Index (mN*m ² /g)	Tensile Index (N*m/g)	Burst Index ((kPa*m ² /g)
PFI (revolutions)	Basis Wt. (g/m ²)				
1000	65.0	132.2	19.5	66.5	4.96
3000	65.1	143.1	12.3	74.5	5.80
5000	63.2	152.8	11.4	77.8	6.62
7000	62.7	157.3	11.1	85.7	6.98
Pulp ID	SS1_H1800				
1000	64.9	131.8	16.8	65.6	5.53
3000	63.3	144.7	14.8	76.0	6.78
5000	63.2	150.3	14.1	78.0	6.91
7000	62.7	156.4	13.4	77.6	7.14
Pulp ID	GLPT_M1_H1800				
1000	66.2	126.7	19.0	64.4	5.69
3000	64.6	140.9	17.2	74.7	6.64
5000	65.0	146.6	13.9	79.8	7.02
7000	64.1	153.9	13.0	82.7	7.61

Table 6.9 Pulp strength properties for high kappa range cooks

Pulp ID	BMCC3_H750	Average Values			
		Apparent density (kg/m ³)	Tear Index (mN*m ² /g)	Tensile Index (N*m/g)	Burst Index ((kPa*m ² /g)
PFI (revolutions)	Basis Wt. (g/m ²)				
2000	67.2	119.9	19.9	61.3	4.38
5000	64.8	134.3	12.8	69.6	5.50
8000	65.2	142.2	10.9	69.9	6.15
11000	64.3	151.2	11.2	68.3	6.71
Pulp ID	SS2_H750				
2000	64.5	128.0	22.9	62.8	4.98
5000	66.9	135.9	14.5	70.8	6.65
8000	64.1	148.6	13.8	79.6	7.19
11000	64.0	153.9	13.1	85.6	7.00
Pulp ID	GLPT_M1_H750				
2000	66.2	131.0	19.0	62.7	5.69
5000	64.6	145.7	17.2	67.4	6.64
8000	65.0	151.6	13.9	70.0	7.02
11000	64.1	159.1	13.0	72.0	7.61

The relationship between the sheet tear, tensile and burst values were investigated by plotting the tensile index versus the tear index and the burst index versus the tear index. Figures 13 and 14 show these relationships for the low kappa pulps, Figures 15 and 16 for the high kappa pulps.

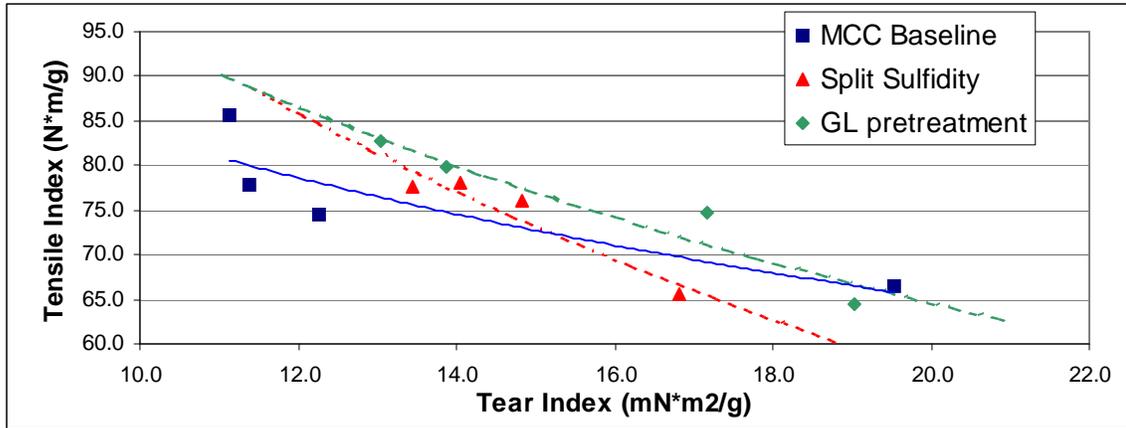


Figure 6.13 Tensile index versus tear index for low kappa pulps

As shown in Figure 13, in the case of the more highly refined low kappa pulps the tensile index is greater for the split sulfidity and green liquor pretreatment pulps compared to the MCC pulps. This difference is less pronounced at higher levels of tear index. Also, as shown in Figure 14, the burst index is higher for both the split sulfidity and green liquor pretreatment pulps relative the MCC pulps. These observations indicate that the split sulfidity and green liquor pretreatment procedures generated low kappa pulps that are stronger than those obtained through the MCC procedure. At a tear index of 14 mN*m²/g the split sulfidity and the green liquor pretreatment pulps respectively held a tensile index of 2.5 and 5 units greater than the MCC pulp. Similarly, at the same tear index their burst index values were about 1 unit greater than that of the MCC pulp.

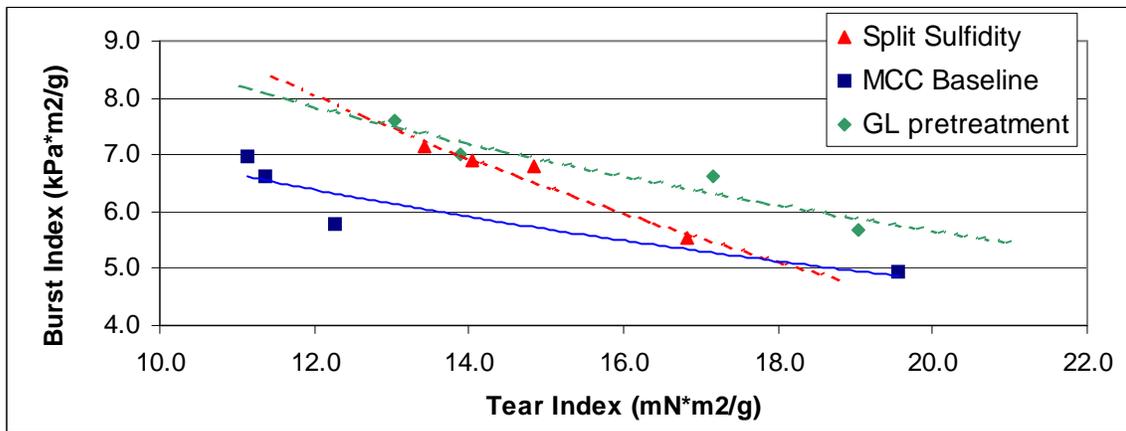


Figure 6.14 Burst index versus tear index for low kappa pulps

The same holds true for the high kappa pulps, as displayed in Figures 15 and 16. Also, at a tear index of 14 mN*m²/g the split sulfidity the green liquor pretreatment pulps respectively held a tensile index of 12 and 2.5 units greater than the MCC pulp. Here, at the same tear index their burst index values were about 1.5 units greater than that of the MCC pulp. Overall, the split sulfidity produced the highest tensile index values, while its values for tear index and burst index were similar to those of the green liquor pretreatment pulps. The MCC pulps produced the lowest values in all three indexes. However, the green liquor pretreatment pulps were of a kappa slightly higher than those of obtained using the MCC procedure.

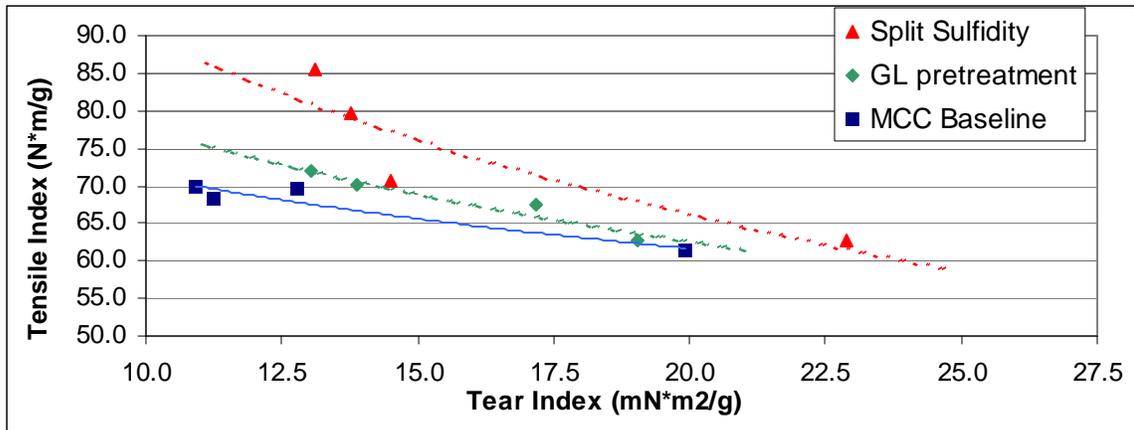


Figure 6.15 Tensile index versus tear index for high kappa pulps

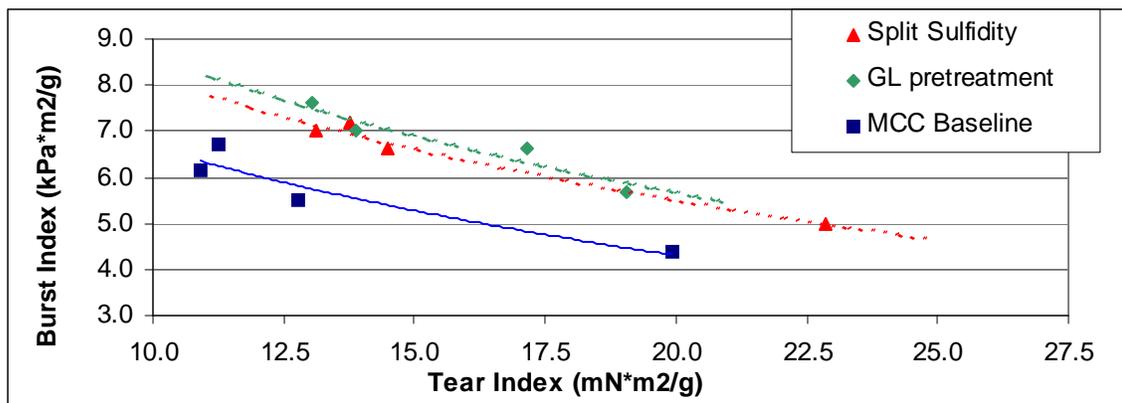


Figure 6.16 Burst index versus tear index for high kappa pulps

CONCLUSIONS

The split sulfidity procedures generated pulps of lower kappa than the MCC procedure at similar h factors. At similar kappa, the split sulfidity cooks produced total pulp yields one to two percent greater than those achieved through the MCC procedure, with significantly higher pulp viscosities. The split sulfidity high initial alkali approach produced pulps of lower kappa and higher yields than the low initial alkali approach. The high initial alkali pulps produced higher tensile and burst index values relative the MCC pulps at similar tear index.

The green liquor pretreatment procedures generated pulps of higher kappa than the MCC procedure at similar h factors. Increasing the green liquor pretreatment system TTA by 10 % lowered the pulp kappa, but it still remained higher than those of the MCC pulps. The pulp yields and viscosities were similar to those of the MCC procedure. The high TTA green liquor pretreatment pulps produced higher tensile and burst index values relative the MCC pulps at similar tear index.

The MCC pulps were slightly easier to refine relative to the split sulfidity and green liquor pretreatment pulps.

The obtained results indicate that the split sulfidity protocol can potentially be used to produce pulps with higher yield, viscosity and strength properties relative the simulated MCC protocol; whereas the green liquor

pretreatment protocol produced pulps with yields and viscosities similar to the MCC protocol, but with higher strength properties. Moreover, significant cost savings can be realized by using the green liquor pretreatment approach in place of the MCC protocol, as the load on the recaust system and particularly the limekiln would be reduced.

FUTURE WORK

The area of green liquor pretreatment will be further explored to determine the required level of system TTA to generate pulps of similar kappa to those produced using the MCC protocol. Further studies will explore the application of polysulfide in the first stage of the cooking sequence.

REFERENCES

1. Johansson, B., Mjoberg, J., Sandstrom, P., Teder, A., Svensk Papperstid. 87(10):30 (1984).
2. Herschmiller, D.W., "Breaking the yield barrier", p. 59 TAPPI PRESS, 1998
3. LeMon, S. and Teder, A., Svensk Papperstidning, 79(11):407 (1973)
4. Olm, L. and Tisdat, G., Svensk Papperstidning, 82(15):458 (1979)
5. Olm, L. and Teder, A., Paperi ja Puu, 63(4a):315 (1981)
6. Andrews, E.K., dissertation, North Carolina State University, 1982
7. Andrews, E.K., Chang, H-m., Kirkman, A.G., Eckert, R.C., "Extending delignification in kraft and kraft/oxygen pulping of softwood by treatment with sodium sulfur liquors, Japan Tappi Symposium on Wood pulp chemistry, 1982.
8. Jiang, J.E., Crofut, K.R., Jones, D.B., *Proceedings of the TAPPI pulping conference*, p. 799, TAPPI Press, Atlanta, GA (1993)
9. Lownertz, P.P.H. and Herschmiller, D.W., *Proceedings of the TAPPI pulping conference*, p. 1217, TAPPI Press, Atlanta, GA (1994)
10. Jiang, J.E. and Herschmiller, D.W., *Proceedings of the TAPPI pulping conference*, p. 317, TAPPI Press, Atlanta, GA (1996)
11. Mao, B. and Hartler, N., Paperi ja Puu, 74(6):491 (1992)
12. Mao, B. and Hartler, N., Nordic Pulp and Paper Research J., 7(4):168 (1992)
13. Mao, B. and Hartler, N., Paperi ja Puu, 77(6-7):419 (1995)
14. Olm, L.; Tormund, D.; Jensen, *Nord. Pulp Pap. Res. J.*, 15:62 (2000)
15. Tormund, D., Teder, A., "A new finding on sulfide chemistry in kraft pulping," Tappi pulping conference p 247 (1989).
16. Abuhasan, J., PhD thesis North Carolina State University, p 82 (1994).
17. I. Lopez, H-m Chang, H. Jameel and W. Wizani, Tappi Pulping Conference Proceedings, p135 Orlando, Florida October 1999
18. Ban, W., Lucia, L. A., *Ind. Eng. Chem. Res.* 42, no. 3: 646-652 (2003)
19. Lucia, L. A., Ban, W., Ragauskas, A. J., *Pap Age* 118, no. 8: 24-26 (2003)
20. Lindstrom, M., Kirkman, A., Jameel, H. et al. "Economics of Integrating Black Liquor Gasification With Pulping: Part I – Effect of Sulfur Profiling." *Proceedings, 2002 TAPPI Fall Technical Conference*, TAPPI Press, Atlanta, GA, (2002) CD-ROM
21. Andritz Inc., Personal communication, October, 2003.

7 THE EFFECT OF INTEGRATING POLYSULFIDE PULPING AND BLACK LIQUOR GASIFICATION ON PULP YIELD AND PROPERTIES

Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H. *"The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Properties"*; Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference; TAPPI Press: Atlanta, GA, 2005.

THE EFFECT OF INTEGRATING POLYSULFIDE PULPING AND BLACK LIQUOR GASIFICATION ON PULP YIELD AND PROPERTIES

Mathias Lindström, Ved Naithani, Adrianna Kirkman, Hasan Jameel

Department of Wood and Paper Science

North Carolina State University

Raleigh, NC 27695-8005

USA

ABSTRACT

The implementation of black liquor gasification (BLG) into the Kraft recovery cycle would present several opportunities and potential benefits regarding pulp mill operation and process economics. In a mill using BLG the recovered entities of sodium and sulfur could be split into two separate fractions. The separation of these chemicals would enable the application of modified pulping technologies to increase the pulp yield or extend delignification. BLG combined with polysulfide (PS) and/or anthraquinone (AQ) addition, could substantially decrease the overall operational costs associated with Kraft pulping and chemical recovery. The effects of Kraft cooking with polysulfide and anthraquinone addition were explored through a multi-stage laboratory cooking protocol simulating modified continuous cooking (MCC). Investigated variables include the pulping liquor concentrations of polysulfide, HS^- , OH^- , and CO_3^{2-} and the resulting level of charged stage and system total titratable alkali (TTA). Results showed yield increases of 1% per % PS for the investigated range of 1 to 3% PS on wood. The PS pulps refined more quickly relative the MCC reference, and had a tear index penalty at fixed levels of tensile and burst index comparable to literature data. The effect of initial active alkali charge was found to be influential relative obtained pulp yields at higher levels of PS charge.

INTRODUCTION

The implementation of black liquor gasification, BLG, into a pulp mill chemical recovery system will allow for the splitting of sodium and sulfur into separate streams. This separation will enable several modified pulping technologies which can be used to increase pulp yield and improve pulp properties. The utilization of polysulfide (PS), often in conjunction with anthraquinone (AQ), as additives to the Kraft process, their effect on pulping chemistry and kinetics has been explored for some time (1-6). Its' effectiveness has been established, and is typically reported as increasing the pulp yield by one percent for each percent of PS added to the pulping liquor (7-8). However, efficiently generating high concentrations of PS within the Kraft chemical recovery cycle has proved a challenge. There are currently three primary competing processes available for PS generation, Chiyoda, MOXY™ and Paprilox® (9). These processes, in general terms, produce pulping liquors with PS concentrations of five to eight grams per liter and PS selectivities ranging from 60 to 90 percent (10-13). A chemical recovery system based around BLG would allow for different pathways to generate PS liquors at potentially higher concentrations and selectivities.

Research efforts in the area of PS have generally been in one of two major areas; work investigating optimum parameters for PS pulping (14-17), or PS pulping as it relates to PS utilization in Kraft process operations and/or associated PS generation technologies (10-13,18-20). A smaller area of work has been based around the potential implementation of BLG and the opportunities created by the unrestricted management of sulfur and sodium as separate entities (21). This paper is aimed at evaluating the potential of PS pulping in conjunction with gasification and novel recovery operations and their implications on the modern Kraft process.

In addition to making chemical recovery and pulping liquor regeneration feasible for several modified pulping technologies, such as Kraft split sulfidity and Kraft PSAQ pulping, as well as sulfite- AQ and mini-sulfite sulfide-AQ, the separation of sulfur and sodium can advantageously be applied in modified delignification. The basic principles of modified extended delignification consist of level alkali concentration throughout the cook, a high initial sulfide concentration, low concentrations of lignin and Na^+ in the final stage of the cook, and lower temperature in the initial and final stages of the cook (22). These principles could straightforwardly be implemented into an existing continuous Kraft or super-batch process, along with the possibility generating and applying high concentrations of PS.

Some limitations to the generation and utilization of pulping liquors with high PS concentrations exist. The most fundamental will be the amount of sulfur available in the pulping system, and how this sulfur most efficiently should be applied to the wood, as a balance between Na₂S and PS. In addition the amount of NaOH that can be added to each stage can also be modified. The work presented outlines some of the basic considerations of Kraft pulping with PSAQ as they relate to the pulping system chemical charge and the effects on pulp yield and properties.

EXPERIMENTAL

Mixed southern softwood chips were used throughout the laboratory pulping. The chips were air-dried to greater than 90 percent solids content and screened collecting the four to ten mm fraction. The chips were soaked in water over night, and then drained for 30 minutes before being placed in the M&K batch digester prior to chemical addition. 800 oven dry grams of wood were used in each cook. Polysulfide liquor was generated by dissolving elemental sulfur in Na₂S. The mixture was heated at 60 °C under an N₂ atmosphere until completely dissolved.

Reference pulps were generated using a simulated modified continuous cooking procedure (23). The cooking protocol was divided into three stages with addition of active chemical at the end of the first and second stage. The active alkali, AA, charge was varied from 17.0 to 22.5% on OD pulp to produce pulps in the 25 to 40 kappa range. Two different sulfidity conditions were explored, 25 and 40%. In addition, Na₂CO₃ was added as 15% of the total chemical on wood, simulating a system dead load. The resulting total titratable alkali, TTA was divided for addition between the three stages. In the first stage, the chips were placed in the digester with 65% of the TTA and water, to bring the liquor to wood ratio, L/W, to 3.5. The cook was then brought to 120 °C and held at temperature for 15 minutes. For the second stage white liquor heated to 125 °C was added equaling 20% of the TTA, bringing the cumulative added TTA to 85%. The cook was then brought to the desired temperature and held there until 105 minutes had elapsed from “time 0”. For the third stage, white liquor heated to 125 °C equaling the final 15% of the TTA was added, bringing the L/W to about 4.5. The cook was then held at temperature until complete. The total cooking time from “time 0” (time = 0 at T = 100 °C) was fixed at 240 minutes, while the cooking temperature was held at 164 °C. This resulted in cooks of h factor slightly above 1800. The parameters for the MCC procedure are outlined in Table 1.

Table 7.1 Parameters for MCC protocol

	Cumulative % TTA	L/W	Stage Temperature (°C)	Time at Temperature (min)
Stage I	65	3.5	120	15
Stage II	85	4.1	164	~ 70
Stage III	100	4.5	164	120

Kraft cooks employing PS were performed according to the outlined MCC procedure with some modifications. The main differences were the utilization of sulfur added as a combination of PS and Na₂S, the profile of NaOH and Na₂CO₃ addition, and the addition of anthraquinone, AQ. AQ was added to each PS cook at a charge of 0.1% on oven dry wood to enhance the delignification rate. Furthermore, to maximize the effect of PS and system sulfidity, according to the principles of extended delignification, the total amount of Na₂S used was added in Stage 1. The original procedure employed a chemical charge of 19.5% AA and 25% sulfidity. As this chemical charge was converted for the PSAQ procedure, the total amount of available sulfur was determined. Based on 800 oven dry grams of wood, this equates a total of 20.13 grams sulfur. For a one percent PS charge on oven dry wood, 8 grams of sulfur was required as PS. The remainder was used as Na₂S in the generation of the PS liquor. Any remaining sulfur was added as Na₂S. As the desired PS charge on wood is increased, more sulfur is required in the system. This can be achieved by either increasing the active alkali charge or system sulfidity, or a combination thereof. Table 2 illustrates this balance displaying two examples of the partitioning of the total sulfur available in the system at 25 and 40% sulfidity. The sulfur division between PS and Na₂S is dictated by the amount required for PS, the balance being Na₂S. As seen in the table, PS charges slightly exceeding 2 % is possible at 19.5% AA with 25% sulfidity. The corresponding value at 40% sulfidity is about 4% PS. To enable higher PS charges either the system AA charge or the sulfidity must be increased.

Table 7.2 Demonstration of sulfur utilization and system availability for PS generation

Cook Procedure	25% Sulfidity			40% Sulfidity		
	Total S available (g)	S required for PS (g)	S available as Na ₂ S (g)	Total S available (g)	S required for PS (g)	S available as Na ₂ S (g)
MCC	20.13	0	20.13	32.21	0	32.21
1% PS	20.13	8.0	12.13	32.21	8.0	24.21
2% PS	20.13	16.0	4.13	32.21	16.0	16.21
3% PS	20.13	24.0	- 3.87	32.21	24.0	8.21
4% PS	20.13	32.0	- 11.87	32.21	32.0	0.21

To offset the loss of TTA added to Stage 2 and 3 resulting from the addition of the entire amount of sulfur species in Stage 1, the profile for alkali addition was altered accordingly. The lost balance of TTA in Stage 2 and 3 was made up by decreasing the addition of NaOH and Na₂CO₃ to Stage 1 in amounts equal to that of the added sulfur species, and charging the alkali to Stage 2 and 3 maintaining the 65/20/15 ratio employed in the MCC baseline cooks. The values for the 40% sulfidity system are given in parenthesis. The resulting splits for chemical addition in the PSAQ cooks are showed in Table 3.

Table 7.3 Parameters for Polysulfide-Anthraquinone (PSAQ) cooks

PSAQ		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	65	100	56 (47)	56 (47)	3.5	120	15
Stage II	85	0	25 (30)	25 (30)	4.1	164	~70
Stage III	100	0	19 (23)	19 (23)	4.5	164	120

In addition to the PSAQ liquor parameters outlined in Table 3, two more cooking protocols were investigated at 3% PS charge, where the alkali charge in Stage 1 was increased. These conditions were aimed at exploring the effect of higher initial alkali charge on the effectiveness of PS relative the delignification rate and pulp properties. The initial PSAQ protocol employed at 3% PS charged was labeled low initial alkali (LIA), which was then followed by a medium initial alkali charge (MIA) and a high initial alkali charge (HIA). The liquor parameters for the PSAQ-MIA and HIA protocols are displayed in Table 4.

Table 7.4 Parameters for medium (MIA) and high (HIA) initial alkali PSAQ cooks

PSAQ-MIA		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	77	100	65	65	3.5	120	15
Stage II	90	0	20	20	4.1	164	~70
Stage III	100	0	15	15	4.5	164	120
PSAQ-HIA		% of Total for each chemical added					
	Cum. % TTA	Na ₂ S	NaOH	Na ₂ CO ₃	L/W	Stage Temp. (°C)	Time at Temp. (min)
Stage I	84	100	75	75	3.5	120	15
Stage II	94	0	15	15	4.1	164	~70
Stage III	100	0	10	10	4.5	164	120

All obtained pulps were thoroughly washed with water, disintegrated using an impeller mixer and screened. The screen accepts were fluffed prior to yield determination and refrigerated for storage. The total yield is given as the sum of the oven dry accepts and rejects. Pulp kappa numbers and viscosities were determined for all screen accept samples. Viscosities for samples with kappa number exceeding 50 were treated not

determined. A total of nine screened pulp samples representing each procedure, were refined using a PFI mill according to CPPA Standard C.7. Handsheets were made according to TAPPI T 205, and tested following T 220. The resulting sheet caliper, tear, tensile and burst, were determined according to TAPPI T 411, T 414, T 494, and T 403 respectively.

RESULTS AND DISCUSSION

The obtained results will be discussed in two separate parts. The first segment addresses the pulping results generated using 25% and 40% sulfidity respectively, followed by a second segment describing the pulp strengths.

Pulp yield, kappa and viscosity for 25% sulfidity pulps

The laboratory cooking parameters and the yield, kappa, and viscosities obtained for the 25% sulfidity cooks are shown in Table 5. The first three cooks in the table represent the reference MCC pulps, followed by the 1 and 2% PS pulps. As seen in the table, the system AA charge was varied to generate circa kappa 30 pulps. The 2% PS procedure required a higher AA charge to accomplish this. From these data the following relationships were explored: kappa versus AA charge, total yield versus kappa, and viscosity versus kappa. The resulting graphs are shown in Figures 1 through 3.

Table 7.5 Summary of cooks performed using 25% sulfidity

COOK	h factor	% AA on OD wood	Sulfidity (%)	TTA (gpl as Na ₂ O)	% PS on OD wood	% AQ on OD wood	kappa	Tot. Yield (%)	Viscosity (cps)
25-MCC1	1842	19.5	25	183.5	0	0.01	37.7	46.4	47.8
25-MCC2	1849	20.5	25	192.9	0	0.01	31.7	45.7	37.2
25-MCC3	1849	21.5	25	202.4	0	0.01	26.0	44.5	32.4
							0	0	0
25-PSAQ1	1843	19.5	25	220.6	1	0.01	32.5	48.4	41.8
25-PSAQ2	1841	20.5	25	192.9	1	0.01	29.8	47.4	38.5
25-PSAQ3	1847	21.5	25	202.4	1	0.01	25.5	46.7	35.5
25-PSAQ4	1847	20.5	25	192.9	2	0.01	38.6	49.1	41.9
25-PSAQ5*	1845	20.5	25	163.9	2	0.01	41.5	50.5	49.1
25-PSAQ6	1847	21.5	25	202.4	2	0.01	32.3	48.4	36.9
25-PSAQ7*	1842	21.5	25	172.4	2	0.01	37.2	50.4	49.1
25-PSAQ8	1852	22.5	25	211.8	2	0.01	31.7	48.3	35.1

Olm and Tormund (21) reported, in work exploring PS pretreatment at zero initial effective alkali, a strong negative effect of CO₃⁻² charged to the pretreatment stage on pulp yield at kappa 30. Based on these findings it was reasonable to investigate if this would also be the case in PS pretreatments at higher alkali charge. In addition to the previously described procedures, two cooks were performed to investigate the potential negative effect of carbonate dead load on pulp yield. Cooks 25-PSAQ5* and 25-PSAQ7* were performed without the addition of Na₂CO₃ resulting in lower system TTA. As compared to the other described 2% PS pulps, the obtained (carbonate-free) pulps were of higher kappa, accordingly having somewhat higher pulp yield and viscosity. This indicates that the presence of carbonate, when added in typical process dead load amounts, in PS pretreatments at sufficiently high alkali charge did not seem to have a negative impact on pulp yield at similar kappa. No further investigation of this topic was made in this work.

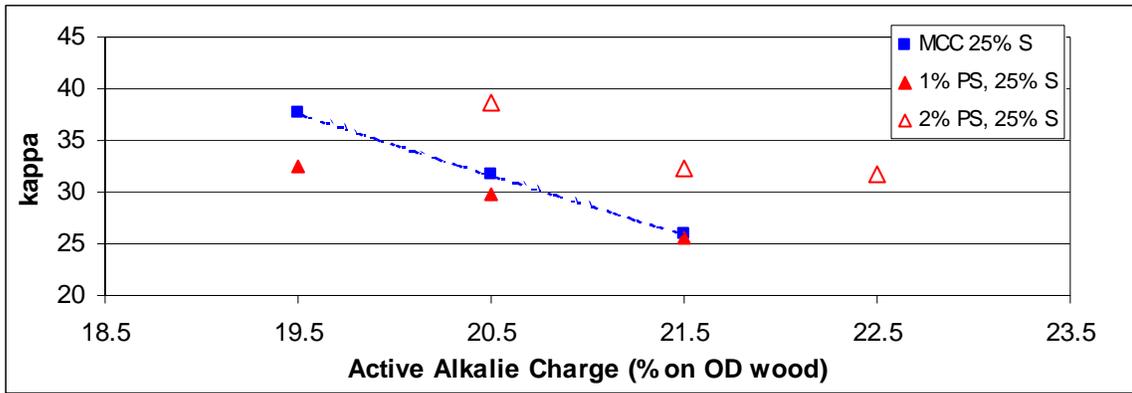


Figure 7.1 Kappa number versus AA charge for the MCC baseline and PS cooks at 25% sulfidity

Figure 1 shows how the 1 and 2% PS procedures compare to the MCC procedure at 25% sulfidity, in regards of lignin removal as a function of AA charge. As shown, the 1% PS procedure produced lower kappa pulps at similar AA charge relative the MCC procedure, whereas the 2% PS procedure produced pulps of somewhat higher kappa.

The total pulp yield as a function of kappa was compared for the 1 and 2% PS and MCC procedures. The resulting graph shown in Figure 2, indicates that the PS procedures produced pulp yields about two percent greater than the MCC procedure.

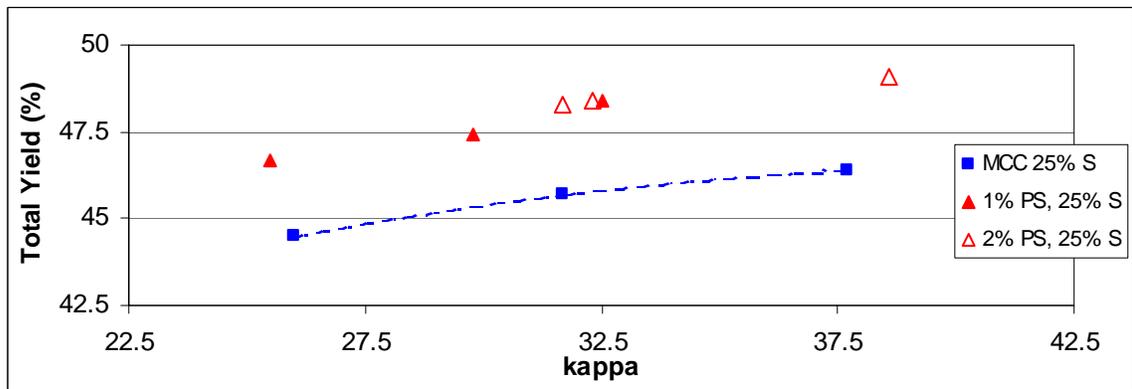


Figure 7.2 Total yield versus kappa for the MCC baseline and PS cooks at 25% sulfidity

The pulp viscosity as a function of kappa was similarly compared for the different procedures. The resulting graph is shown in Figure 3. As shown in the figure, the 1% PS procedure produced pulps of slightly greater viscosities than the MCC reference, whereas the 2 % PS procedure resulted in slightly lower viscosities at similar kappa.

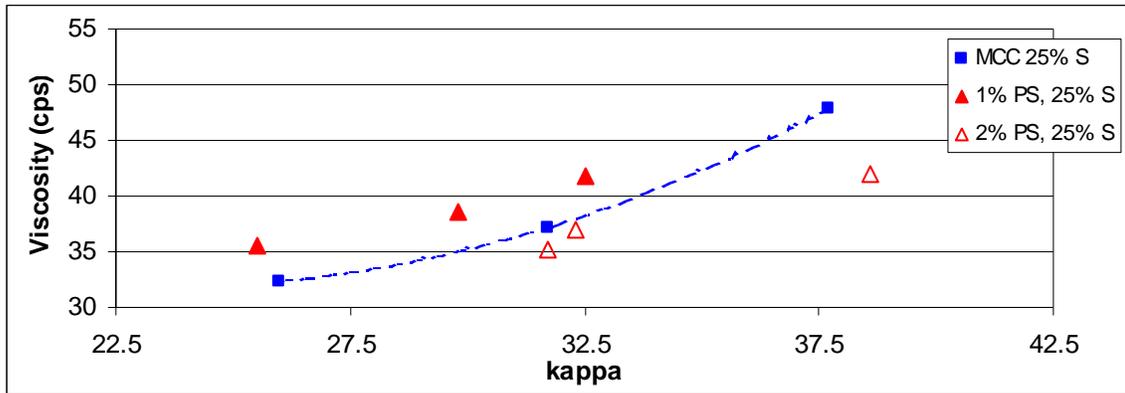


Figure 7.3 Viscosity versus kappa for the MCC baseline and PS cooks at 25% sulfidity

Pulp yield, kappa and viscosity for 40% sulfidity pulps

The laboratory cooking parameters and the yield, kappa, and viscosities obtained for the 40% sulfidity cooks are reported in Table 6. The first four cooks in the table represent the reference MCC pulps, followed by the 1, 2 and 3% PS pulps. The system AA charge was again varied to generate circa 30 kappa pulps. As seen in the

Table 7.6 Summary of cooks performed using 40% sulfidity

COOK	h factor	% AA on OD wood	Sulfidity (%)	TTA (gpl as Na ₂ O)	% PS on OD wood	% AQ on OD wood	kappa	Tot. Yield (%)	Viscosity (cps)
40-MCC1	1845	19.5	40	183.5	0	0.01	31.1	46.6	52.1
40-MCC2	1847	20.5	40	192.9	0	0.01	27.0	46.1	46.9
40-MCC3	1844	21.5	40	202.4	0	0.01	24.0	45.6	35.8
40-MCC4	1842	17.0	40	160.0	0	0.01	43.4	48.4	56.8
40-PSAQ1	1846	20.5	40	192.4	1	0.01	36.1	49.6	54.7
40-PSAQ2	1841	21.5	40	220.6	1	0.01	27.8	47.9	50.1
40-PSAQ3	1838	22.5	40	211.8	1	0.01	24.7	46.4	43.7
40-PSAQ4	1841	20.5	40	192.9	2	0.01	42.3	51.5	57.9
40-PSAQ5	1846	22.5	40	211.8	2	0.01	36.3	49.1	47.6
40-PSAQ6	1840	23.5	40	220.6	2	0.01	31.2	47.9	49.2
40-PSAQ7	1839	20.5	40	192.4	3	0.01	66.6	56.4	x
40-PSAQ8	1845	23.5	40	220.6	3	0.01	47	51.8	62.6
40-PSAQ9	1844	25.5	40	240	3	0.01	32.4	47.9	48.8
40-PSAQ10	1843	23.5	40	220.6	3	0.01	44.3	51.7	60.7
40-PSAQ11	1836	24.5	40	230.6	3	0.01	33.7	49.2	42.2
40-PSAQ12	1841	25.5	40	240.0	3	0.01	28	48.7	40.3
40-PSAQ13	1839	22.5	40	211.8	3	0.01	42.6	48.5	53.1
40-PSAQ14	1846	23.5	40	220.6	3	0.01	32.4	46.3	42.5
40-PSAQ15	1845	24.5	40	230.6	3	0.01	29	45.6	44.4

table, in the case of the 1% PS procedure this was accomplished using AA charges similar to those of the MCC baseline pulps around 20.5%. The required AA values for 2% PS were somewhat higher at 23.5% to reach

kappa 30. In the case of the 3% PS procedure kappa 30 was not readily attainable and the AA charge was initially increased to 25.5% resulting in kappa 32.4. As a result it was decided to increase the initial charge of alkali (NaOH and Na₂CO₃) to promote delignification rates. The alkali profile for the 1 and 2% PS pulps followed the balanced TTA approach used throughout the preceding cooks. Two new different alkali profiles were devised, as outlined in Table 4, where 65% and 75% of the available alkali (NaOH and Na₂CO₃) was charged to Stage 1. The sequence using 65% of the available alkali, here called medium initial alkali (MIA), uses the same alkali profile relative NaOH and Na₂CO₃ as the MCC baseline cooks but has the entire amount of sulfur (Na₂S/PS) charged to Stage 1. In the second sequence this amount was increased to 75%, and the cooks labeled high initial alkali (HIA).

The results from the 1 and 2% PS procedures at 40% sulfidity were compared to those from the 1 and 2% PS procedures at 25% sulfidity, and are shown in Figures 4 through 6.

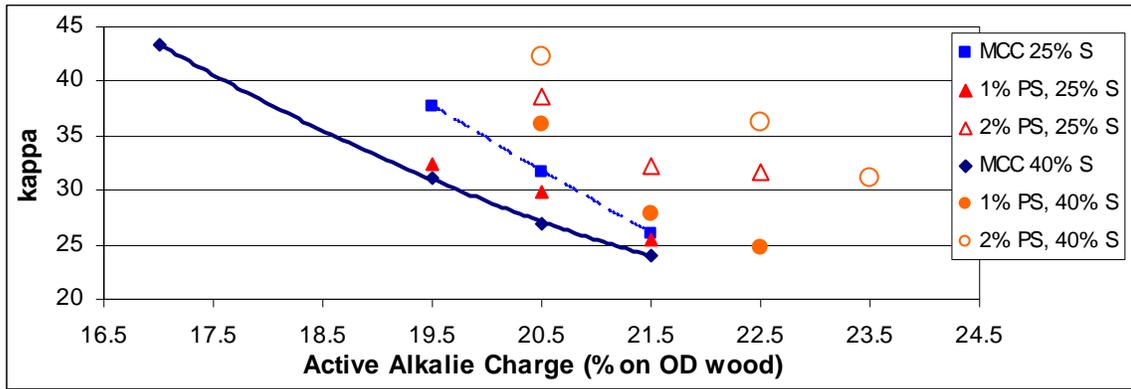


Figure 7.4 Kappa number versus AA charge for 25% and 40% sulfidity cooks

As seen in Figure 4, the resulting kappa at similar AA charge was lower for the 40% sulfidity MCC procedure relative to 25% sulfidity. The kappas obtained using the 1 and 2% PS procedures at 40% sulfidity were somewhat higher than those at 25% sulfidity and also higher than the MCC reference pulps.

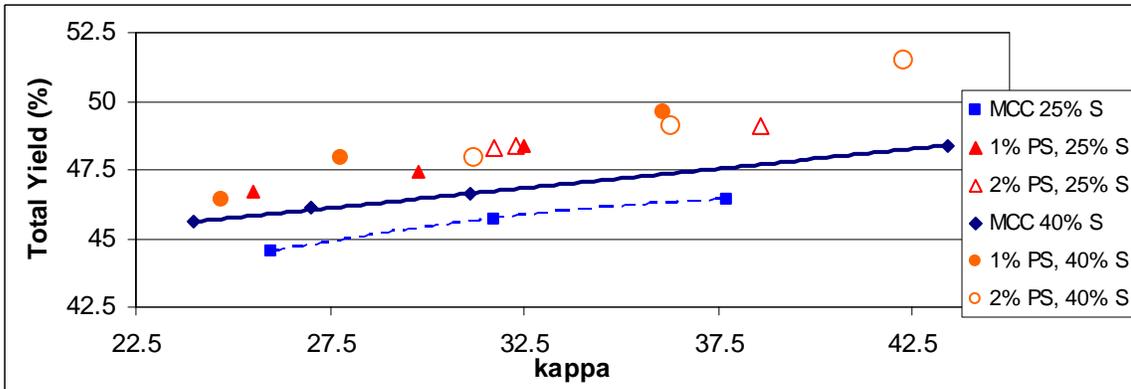


Figure 7.5 Total yield versus kappa for 25% and 40% sulfidity cooks

The total pulp yield as a function of kappa was similarly compared for the 1 and 2% PS and MCC procedures at both 25 and 40% sulfidity. As shown in Figure 5, the 40% PS procedures produced pulp yields similar to those at 25% sulfidity, but only about one percent greater than the MCC baseline pulp at 40% sulfidity.

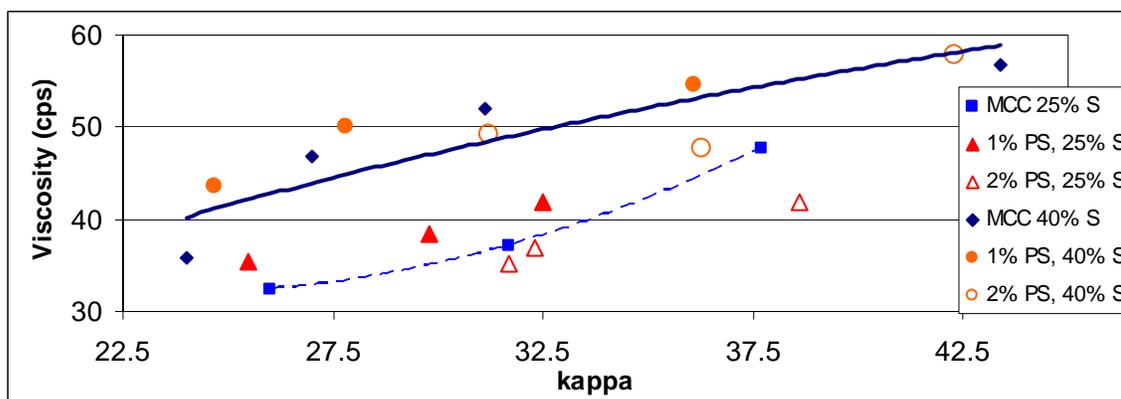


Figure 7.6 Viscosity versus kappa for 25% and 40% sulfidity cooks

The comparison of pulp viscosities is shown in Figure 6 indicates that the 40% sulfidity procedures produced higher viscosity pulp relative those at 25% sulfidity. There is no clear viscosity improvement when comparing the 1 and 2% PS and MCC procedures at 40% sulfidity.

The pulps generated using 3% PS charge at 40% sulfidity were compared to the MCC baseline at 40% sulfidity using the same relationships. As seen in Figure 7 the 3% PS procedures, low, medium and high initial alkali charge, produced pulps of similar kappa to the MCC reference, but required higher AA charges to reach kappa 30. The high initial alkali charge procedure resulted in the lowest pulp kappas, while the low initial alkali charge procedure resulted in the highest pulp kappas. It was still possible to achieve circa 30 kappa pulp using the LIA procedure, but the required AA charge was 25.5% on oven dry wood.

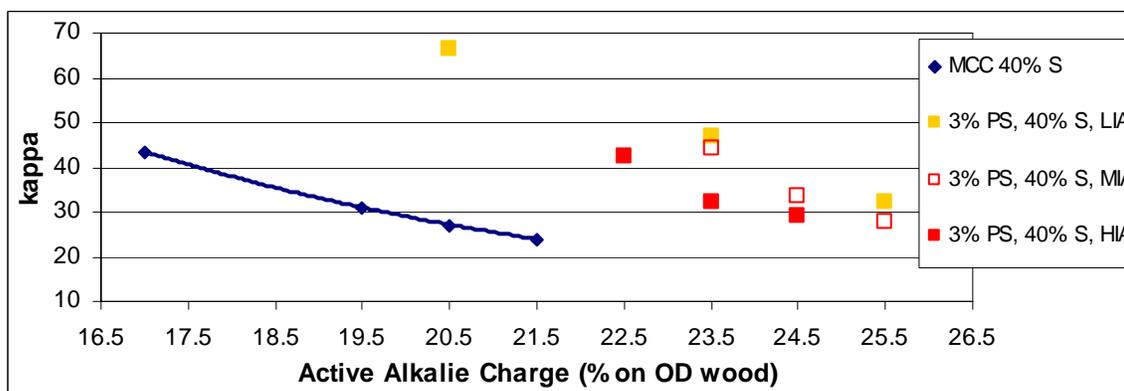


Figure 7.7 Kappa number versus AA charge for the MCC baseline and PS cooks at 40% sulfidity

The total pulp yield for the different 3 % PS procedures relative the MCC reference is shown in Figure 8. As shown, the medium initial alkali charge resulted in pulp yields about 3% greater than the MCC baseline at similar kappa. The low initial alkali charge procedure also produced greater pulp yields than the MCC baseline. These values were similar to the medium initial alkali in the higher kappa range, but slightly smaller at lower kappa. The high initial alkali charge produced pulp yields comparable to those of the MCC reference. Worth noting is that the pulp yield increased with increasing levels of initial AA charge for the low and medium initial alkali procedures, as compared to the MCC reference. This compares well to findings published by Brannvall et al., which indicated that too high or too low an alkali charge in the cooking stage following PS pretreatment will negatively affect the pulp yield (18).

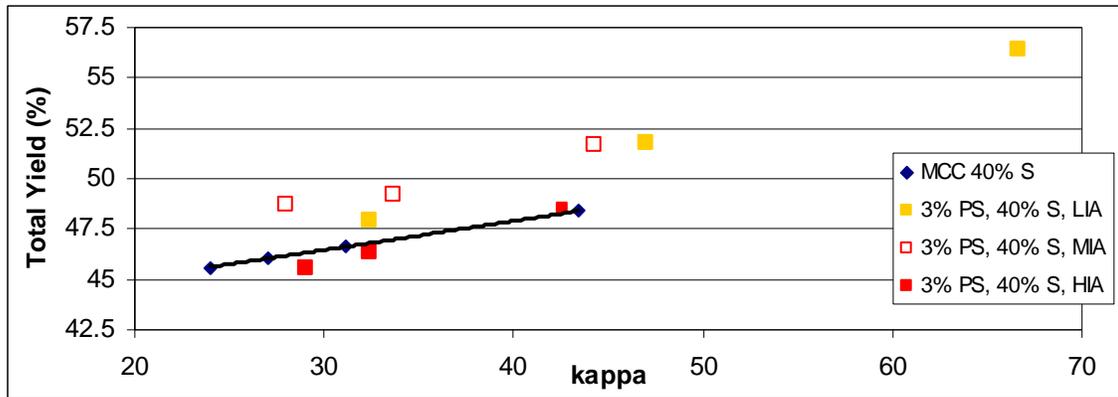


Figure 7.8 Total yield versus kappa for the MCC baseline and PS cooks at 40% sulfidity

The pulp viscosity variation with kappa for the 3% PS pulps is shown in Figure 9. As seen in the figure, there is no viscosity improvement relative the MCC baseline pulps in the lower kappa range. The low initial alkali procedure resulted in higher viscosities than the medium and high initial alkali procedures.

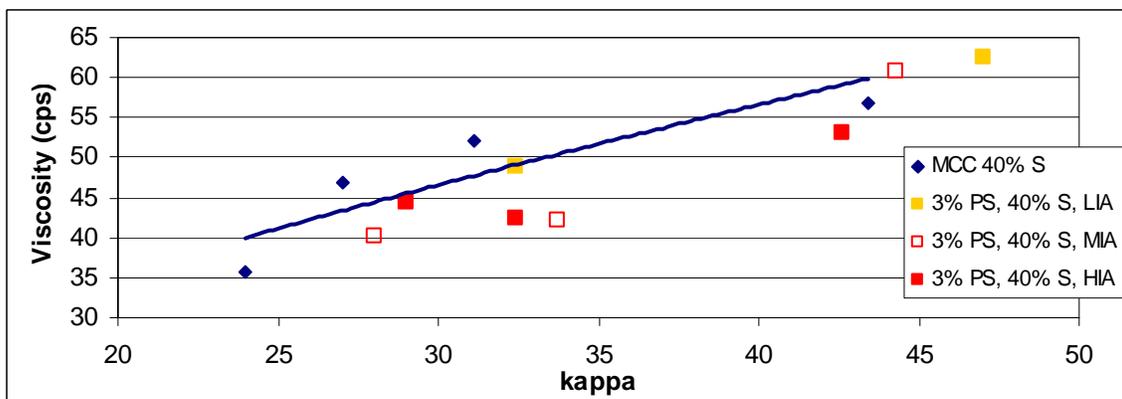


Figure 7.9 Viscosity versus kappa for the MCC baseline and PS cooks at 40% sulfidity

The results displayed in Figures 8 and 9 may be explained by the system TTA profile, as the initial alkali is increased, the alkali profile is moving away from the principles of extended delignification. In the case of the simulated MCC procedure only 65% of the system TTA is initially charged to the cook. The corresponding value for the 3% PS high initial alkali procedure is 84%. This may lead to increased carbohydrate degradation relative the MCC reference pulp. More work is required to fully optimize procedures utilizing very high PS charges and the effect of the system alkali profile on pulp yield and properties.

Pulp strength properties for 25% and 40% sulfidity pulps

As previously described, pulp samples of circa 30 kappa generated from each of the procedures were used in the strength study. All pulps were refined using a PFI mill to four different points of revolutions. The freeness responses to refining of the pulps 25% and 40% sulfidity cooking procedures are displayed in Figures 10 and 11 respectively. As shown in the figures, the PS pulps refine to a lower freeness at similar levels of refining compared to the MCC reference pulps. Also, there is not a great difference in refining response between the 25 and 40% sulfidity PS pulps.

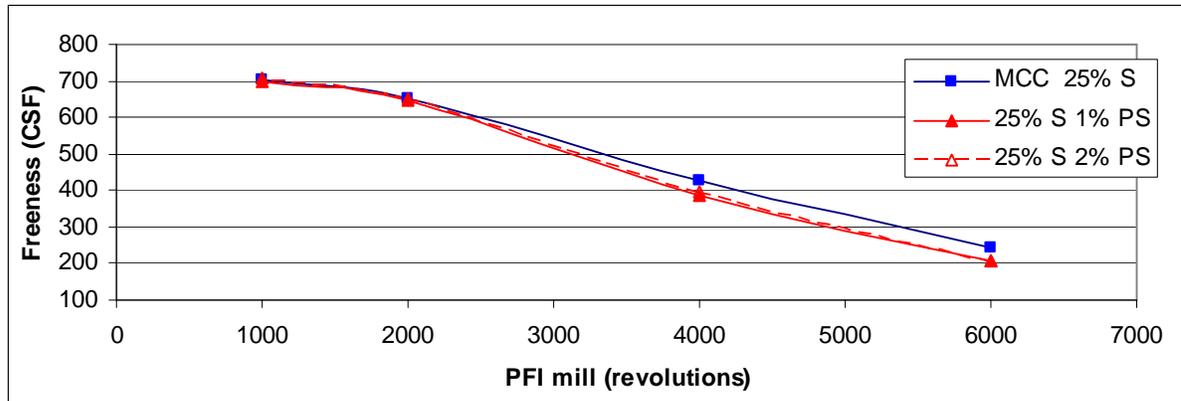


Figure 7.10 Refining response for 25% sulfidity pulps

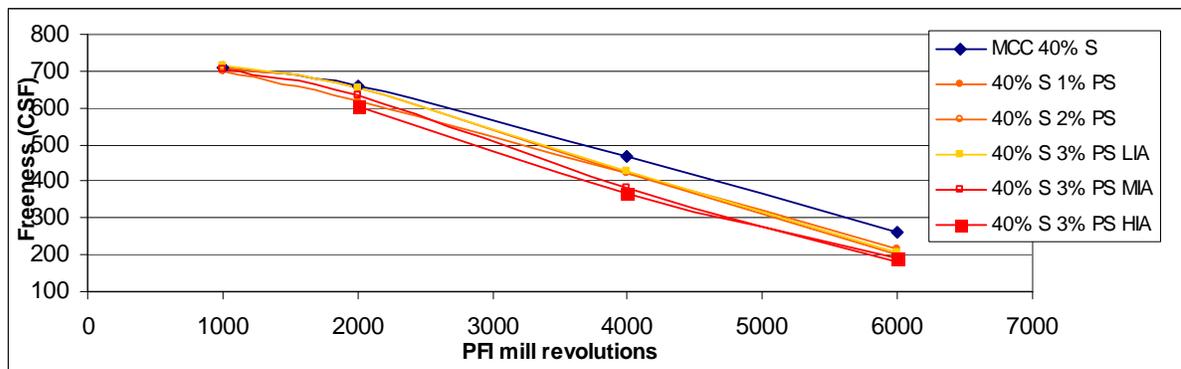


Figure 7.11 Refining response for 40% sulfidity pulps

The handsheets were tested according to TAPPI standards for caliper, tear strength, tensile strength and burst. The obtained data was used to calculate the sheet apparent density, tear, tensile and burst indices. The results are displayed in Tables 7 and 8, showing the values for each of the selected samples at four points of refining. The investigated pulp samples at 25% sulfidity were one MCC baseline pulp (25-MCC2), and one sample each for the one and two percent PS procedures (25-PSAQ2 and 25-PSAQ8).

Table 7.7 Pulp strength properties for 25% sulfidity cooks

Pulp ID	25-MCC2	Average Values			
PFI (revolutions)	Basis Wt. (g/m ²)	Apparent density (kg/m ³)	Tear Index (mN*m ² /g)	Tensile Index (N*m/g)	Burst Index (kPa*m ² /g)
1000	67.9	118.2	24.7	95.0	5.53
2000	64.3	140.4	20.3	111.5	6.95
4000	62.0	142.4	16.6	128.7	7.18
6000	61.7	139.5	16.2	133.4	7.49
(Pulp ID)	25-PSAQ2				
1000	64.5	126.3	20.7	103.4	5.14
2000	61.1	136.3	19.6	115.5	6.45
4000	66.2	145.5	17.8	117.0	7.19
6000	61.7	149.5	17.1	138.2	7.18
(Pulp ID)	25-PSAQ8				
1000	71.9	130.4	22.2	87.2	5.48
2000	63.6	134.1	18.1	113.8	6.31
4000	69.3	147.9	15.8	115.4	7.41
6000	68.3	147.8	16.1	127.9	7.40

There was a slight increase in apparent density for the PS pulps as compared to the MCC reference, but there was no significant difference between the 1% and 2% PS charges. The relationship between the sheet tear, tensile and burst index values were investigated by plotting the tensile index versus the tear index and the burst index versus the tear index. Figures 12 and 13 show these relationships for the 25% sulfidity pulps.

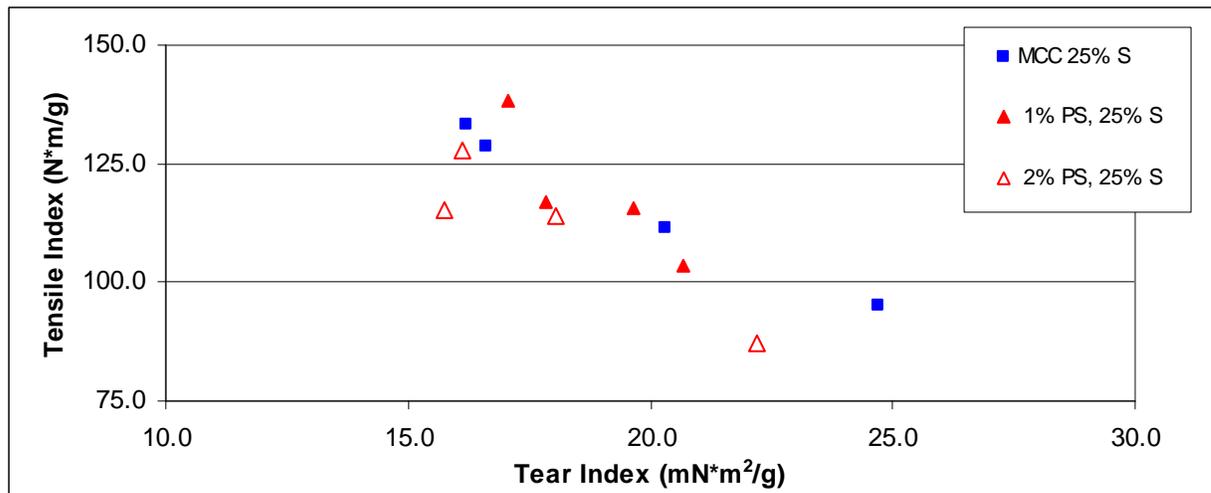


Figure 7.12 Tensile index versus tear index 25% sulfidity cooks

As shown in Figure 12, the sheet tensile index for the PS pulps is somewhat lower than that of the MCC reference pulp at similar levels of tear index. The difference is more pronounced at higher levels of tear index. When considering the relationship of sheet burst index and tear index (Figure 13), the situation is similar. The MCC reference has somewhat greater burst index at similar levels of tear index, with a more pronounced difference at higher levels of tear index. These results are in line with values reported in the literature (3,8,9).

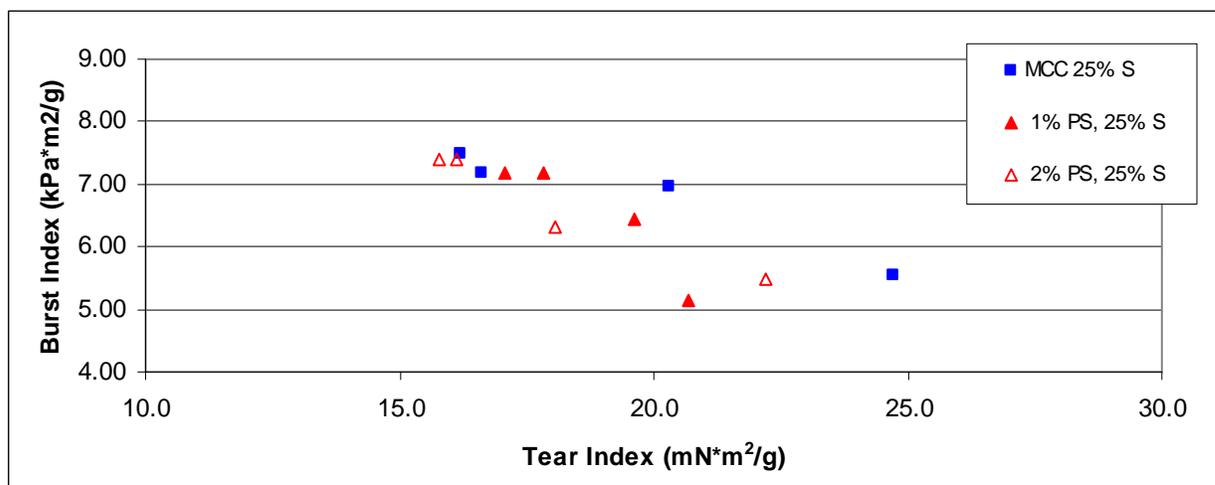


Figure 7.13 Burst index versus tear index for 25% sulfidity cooks

The strength data for the selected pulp samples from laboratory cooks performed at 40% sulfidity are shown in Table 8. One sample each from the MCC baseline (40-MCC2), and the one and two percent PS procedures (40-PSAQ2 and 40-PSAQ6), as well as one each from the three percent PS cooks at low, medium and high initial alkali charge (40-PSAQ9 (LIA), 40-PSAQ12 (MIA), 40-PSAQ15 (HIA)). The apparent density of the MCC reference pulp at 40% sulfidity is somewhat greater than that of the 25% sulfidity pulp at all levels of refining, and is comparable to the values for the one to three percent PS pulps generated at 40% sulfidity. The relationship between the sheet tear, tensile and burst values were investigated in a similar fashion. Figures 14 and 15 show these relationships for the 40% sulfidity pulps.

Table 7.8 Pulp strength properties for 40% sulfidity cooks

Pulp ID	40-MCC2	Average Values			
PFI (revolutions)	Basis Wt. (g/m ²)	Apparent density (kg/m ³)	Tear Index (mN*m ² /g)	Tensile Index (N*m/g)	Burst Index (kPa*m ² /g)
1000	66.0	128.5	22.0	99.9	5.42
2000	69.8	138.5	21.1	105.7	6.98
4000	67.8	146.0	20.0	118.0	7.51
6000	68.6	152.3	18.1	119.5	7.72
(Pulp ID)	40-PSAQ2				
1000	64.5	127.3	18.6	101.8	5.42
2000	63.2	137.1	19.5	121.3	6.17
4000	68.2	146.7	16.7	117.6	7.00
6000	63.6	151.4	14.7	128.5	7.72
(Pulp ID)	40-PSAQ6				
1000	70.2	130.3	20.2	92.7	5.57
2000	70.1	137.9	16.8	102.2	6.65
4000	62.7	143.2	16.6	111.6	7.24
6000	68.0	151.4	16.8	104.7	7.74
(Pulp ID)	40-PSAQ9 (LIA)				
1000	69.5	127.5	21.7	101.5	5.55
2000	67.9	132.5	18.6	121.5	6.36
4000	69.3	146.7	16.7	113.3	7.42
6000	70.3	152.0	16.3	117.4	8.21
(Pulp ID)	40-PSAQ12 (MIA)				
1000	67.7	131.7	18.6	97.1	5.75
2000	70.2	139.3	17.7	114.1	6.59
4000	61.4	144.7	15.5	128.2	7.39
6000	68.7	155.4	15.6	116.6	7.85
(Pulp ID)	40-PSAQ15 (HIA)				
1000	64.6	129.8	19.4	109.2	5.62
2000	68.3	140.1	16.7	122.7	6.69
4000	67.8	148.3	16.4	122.3	7.51
6000	62.3	150.4	16.0	134.5	7.60

As shown in Figure 14, the MCC reference pulp has greater values of tear index at similar levels of tensile index. Also noticeable in the figure is the scattering of the data for all five PS pulps. The intent of this graphical display is to show that there are no distinct tendencies in the investigated tensile and tear strengths among the PS pulps. The 3% PS low initial alkali pulp returned the highest tear index value, while the 3% PS high initial alkali pulp produced the greatest level of tensile index. These observations also hold true for the burst index level as displayed in Figure 15, where the MCC reference pulp again has an advantage over the PS pulps at similar levels of tear index. Overall, the results from the evaluation of pulp strength properties compared well to literature data.

The lack of clear trends within the investigated PS pulp strength properties possibly indicate that there is no great difference between Kraft pulps prepared with increasing levels of PS addition. It also makes evident the opportunities that exist to optimize this process for improved yield and physical properties.

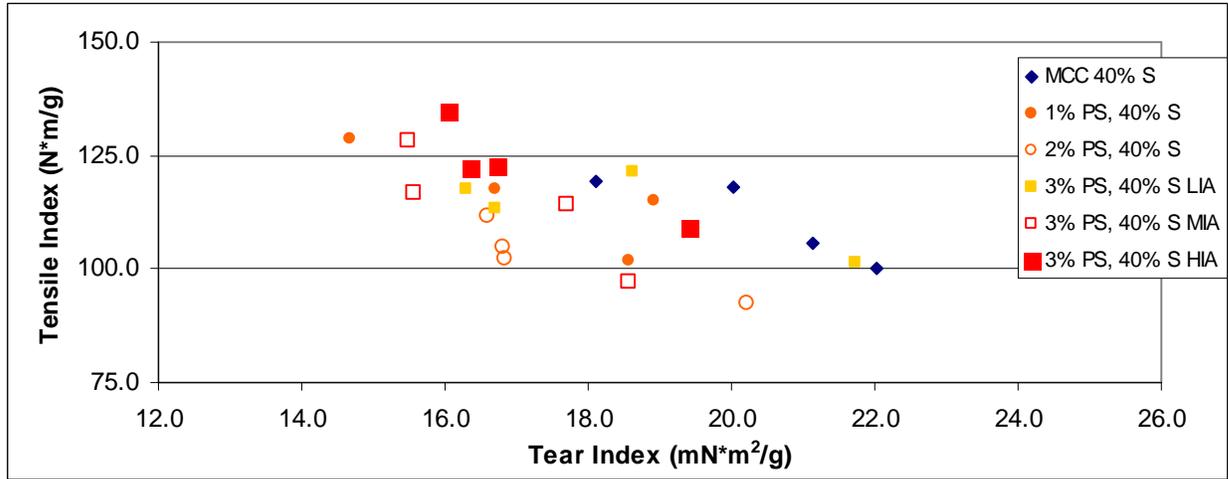


Figure 7.14 Tensile index versus tear index for 40% sulfidity cooks

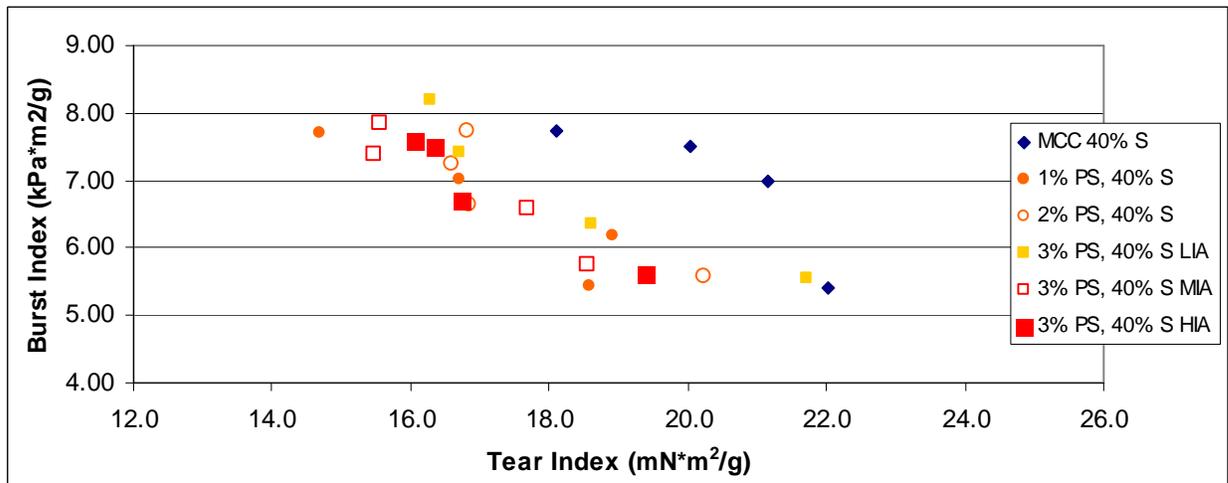


Figure 7.15 Burst index versus tear index for 40% sulfidity cooks

CONCLUSIONS

When pulping at 25% sulfidity, the 1 and 2% PS procedures produced pulps of about 2% higher total yield and comparable viscosities compared to the MCC baseline at similar kappa. Relative the MCC procedure, the 1% PS procedure returned somewhat lower kappa pulps at similar AA charge, while the 2% PS procedure resulted in somewhat higher pulp kappa. The PS pulps refined faster than the MCC reference pulp. When comparing the tensile and burst index levels at fixed levels of tear index for the 25% PS pulps to the MCC reference pulp, there is a distinct tear penalty comparable to literature data.

When pulping at 40% sulfidity, the opportunities for sulfur use, as well as the management of alkali profile, increase. With higher PS charges in the first stage of the cook, more initial alkali is required to maintain delignification rates. As a result more attention must be paid to the cook alkali profile. At 40% sulfidity, the 1

and 2% PS procedures produced pulps of about similar yield to the PS pulps generated at 25% sulfidity. At similar kappa the pulp yields were about 1% higher than the reference MCC pulp with comparable viscosities for both PS charges. Three levels of initial alkali charge were investigated when charging 3% PS, with varying results on final pulp kappa and total yield. The delignification rate increased with increasing levels of initial alkali charge (HIA > MIA > LIA). The effect on total pulp yield was also dependent on both system TTA and initial alkali charge. The LIA and MIA with 3% PS resulted in higher pulp yields relative to the MCC reference at similar kappa. Of the three investigated levels of initial alkali charge the medium initial alkali procedure returned the best results relative total pulp yield. It resulted in pulps of about 3% greater total yield with slightly lower viscosities relative the MCC baseline pulp of similar kappa. The high initial alkali procedure resulted in the lowest total yield. There clearly exists an optimum condition for initial alkali charge, where too great or too low of an initial hydroxide concentration negatively affects the pulp yield. The PS pulps refined faster than the MCC reference pulp with the 3% PS pulps producing the greatest improvement. When comparing the tensile and burst index levels at fixed levels of tear index for the 40% PS pulps to the MCC reference pulp, there is a small tear penalty, comparable to literature data.

The obtained results indicate that the investigated PS procedure can be used to increase the Kraft pulp yield by about 1 percent per percent PS added on wood, while maintaining the pulp viscosity. Although high levels of tensile and burst index are attainable, there is a distinct tear penalty comparable to literature data. The effect of the alkali profile used in a PSAQ cook will significantly affect the resulting pulp yield. More work is required to optimize the effect of alkali profile on the pulping procedure relative pulp yield and properties. The flexibility to optimize the alkali profile and PS use will only be possible in combination with BLG.

FUTURE WORK

Future work will be directed towards evaluating feasible pulping liquors as they may be envisioned through chemical recovery operations utilizing BLG. Parameters such as system active alkali charge and profile, sulfidity, and PS concentrations and their application in laboratory pulping experiments should be further optimized.

REFERENCES

1. Vennemark, E., *Svensk Papperstidning*, 67(5): 157 (1964)
2. Landmark, P.A., Kleppe, P.J., Johnsen, K., *TAPPI J.* 58(8):56 (1965)
3. Jiang, J.E., *TAPPI J.* 77(2): 120 (1994)
4. Jiang, J.E., *TAPPI J.* 78(2): 126 (1995)
5. Griffin, C.W., Kumar, K.R., Gratzl, J., Jameel, H., *TAPPI Pulping Conference Proceedings, Chicago:* 1: 19 (1995)
6. Li, Z., Li, J., Kubes, G.J., *JPPS*, 28(7): 234 (2002).
7. Sanyer, N., Landrie, J.F., *TAPPI J.* 47(10): 640 (1965)
8. Kleppe, P.J., Minja, R.J.A., *TAPPI Proc. Breaking the yield barrier symposium, Vol. 1:* 113 TAPPI PRESS, Atlanta, GA (1998)
9. Luthe, C., Berry, R., *Pulp. Pap. Can.* 106(3): 27 (2005)
10. Nishijima, H. et al. "Review of PS/AQ Pulping to Date in Japanese Kraft Mills and the Impact on Productivity," *1995 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, GA, 1995, pp. 31-40.
11. Yamaguchi, A. "Operating Experiences with the MOXY Process and Quinoid Compounds," *Anthraquinone Pulping: Anthology of Published Papers 1977-1996*, TAPPI PRESS, Atlanta, GA, 1997, pp. 287-291.
12. Tench, L., Uloth, V., Dorris, G., Hornsey, D., Munro, F., *TAPPI J.* 87(10): 120 (1999)
13. Munro, F., Uloth, V., Tench, L., MacLeod, M., Dorris, G., *Pulp. Pap. Can.* 103(1): 57 (2002)
14. Mao, B. F.; Hartler, N.; *TAPPI J.* 77(11): 149 (1994)
15. Lindstrom, M and Teder, A., *Nordic Pulp Paper Res. J.* 10(1): 8 (1995)
16. Gustafsson, R., Freysoldt, J., Teder, A., *Paperi Puu* 86(3): 169 (2004)
17. Brannvall, E., Gustafsson, R., Teder, A., *Nordic Pulp Paper Res. J.* 1(4): 436 (2003)
18. Olm, L.; Tormund, D., Bernor Gidert E., *TAPPI Proc. Breaking the yield barrier symposium, Vol 1:* 69 TAPPI PRESS, Atlanta, GA (1998)
19. MacLeod, M., Radiotis, T., Uloth, V., Munro, F., Tench, L., *TAPPI J. [New Series]* 1(8): 3 (2002)

20. Hakanen, A., Teder, A., TAPPI J. 80(7): 189 (1965)
21. Olm, L.; Tormund, D., Nordic Pulp Paper Res. J. 19(1): 6 (2004)
22. Johansson, B., Mjoberg, J., Sandstrom, P., Teder, A., Svensk Papperstid. 87(10): 30 (1984).
23. Lindstrom, M., Naithani, V., Kirkman, A., Jameel, H., "Effects on pulp yield and properties using modified pulping procedures involving sulfur profiling and green liquor pretreatment" Presented at TAPPI Fall Technical Conference, Atlanta, GA, (November, 2004)

8 THE EFFECT OF INTEGRATING POLYSULFIDE PULPING AND BLACK LIQUOR GASIFICATION ON PULP YIELD AND DELIGNIFICATION

Lindstrom, M., Naithani, V., Kirkman, A., Jameel, H., *"The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Delignification "*, Proceedings TAPPI 2006 Engineering, Pulping and Environmental Conference, Atlanta, GA, (2006).

THE EFFECT OF INTEGRATING POLYSULFIDE PULPING AND BLACK LIQUOR GASIFICATION ON PULP YIELD AND DELIGNIFICATION

Mathias Lindström, Ved Naithani, Hasan Jameel, Adrianna Kirkman

Department of Wood and Paper Science

North Carolina State University

Raleigh, NC 27695-8005

USA

ABSTRACT

Kraft recovery based around black liquor gasification would present several opportunities and benefits with regard to process operation and economics. Gasification of black liquor would split sodium and sulfur into two separate fractions. The separation of these chemicals would enable the application of modified pulping technologies to increase the pulp yield or extend delignification. The experimental objective of this work was to explore and compare MCC and polysulfide-anthraquinone cooks with different alkali profiles, to illustrate the potential effects of polysulfide and anthraquinone addition on delignification and total pulp yield. Laboratory pulps were prepared using 20.5% active alkali at sulfidity levels of 25 and 40%. When comparing the polysulfide-anthraquinone cooks to cooks using MCC with anthraquinone, yield benefits in the range of 1-2% were obtained at 25% sulfidity using a polysulfide charge of 2% on OD wood and 3-3.5% at 40% sulfidity using a 3% polysulfide charge on OD wood. By controlling active alkali profiles under the fixed pulping protocol used throughout the project, it was possible to achieve comparable or improved delignification rates using polysulfide, while maintaining higher pulp yield. Generated residual effective alkali profiles illustrate the difference between MCC and polysulfide pulping, and indicate the importance of alkali control and its effects on delignification and pulp yield. A greater benefit from PSAQ pulping can be realized at higher levels of sulfidity, where it is possible to charge a higher concentration of PS and the effects of alkali profiling can be used to optimize both delignification rate and resulting pulp yield. The most advantageous results, as compared to the MCC reference, were obtained using the PSAQ procedure at 40% sulfidity with 3% PS on wood and an alkali profile of (45/31/24). These values represent the percentages of the total available alkali charged to (stage 1 / stage 2 / stage 3) in the cook.

INTRODUCTION

The effect on pulping chemistry of polysulfide (PS), often in conjunction with anthraquinone (AQ) as additives to the Kraft process, has been explored for some time (1-6). Its effectiveness has been established, and it is typically reported that each percent of PS added increases the pulp yield by one percent (7,8). However, efficiently generating high concentrations of PS within the Kraft chemical recovery cycle is difficult. PS in combination with anthraquinone (AQ) as polysulfide-anthraquinone (PSAQ) offers a process option that can improve yield and delignification, creating opportunities for increased production or alternatively decreased operating costs at fixed output. However, the application of PS in pulping operations requires an economical method of PS generation (9). Moreover, to fully take advantage of benefits resulting from higher PS addition levels the sulfidity demand will be greater than in a conventional Kraft process (10). Black liquor gasification (BLG) offers, through the separation of sulfur and sodium, an exciting opportunity for improved PS processes, where increased PS charges and more efficient application of PS are possible.

The implementation of BLG into Kraft process chemical recovery operations will allow for more or less unrestricted management of sulfur and sodium on the pulping side. This separation of chemicals can be exploited to maximize the PS charge in the impregnation stage of the cook, while at the same time enable optimization of the alkali profile throughout the cook. The degree of sulfur/sodium separation depends on the BLG process used. Research conducted at STFI-Packforsk investigating PSAQ pulping built around the Chemrec oxygen-blown high-temperature BLG has shown the potential for significant yield improvements as compared to conventional Kraft pulping. A concept called ZAP, or Zero effective Alkali in the Pretreatment stage, has been presented, capitalizing on the optimum conditions for PS pretreatment; low or zero initial alkali, appropriate time and temperature, and a low pH at the end of the ZAP stage (11). Recent findings based on pulping liquors generated from a simulated Chemrec BLG recovery system indicated an attainable PS charge of

a 1.9% on wood with a yield improvement of about 2% pts. as compared to conventional Kraft. By a 2.6% on wood addition of sulfuric acid, to lower the final pH of the ZAP stage, a yield benefit of 4.5% pts was achieved. This value was comparable to the ideal ZAP process values (12). A different procedure combining PS pulping with alkali profiling called hyperalkaline polysulfide pulping has also been reported (13). The process utilizes two pretreatment stages followed by a cooking stage. In the first stage, alkali is charge to the wood at elevated concentrations, neutralizing the acids formed during the temperature elevation. PS is then charged in the second stage, followed by the cooking stage. The process resulted in a higher delignification rate, increased pulp viscosities and yield improvements of 1.5% as compared modified pulping without PS.

The research presented in this paper explores the possibilities of ZAP type PS pulping and the opportunities for alkali profiling enabled by a recovery system based around the MTCI low temperature BLG. The MTCI process achieves near complete separation of sulfur and sodium, i.e. allowing for ideal ZAP conditions and the possibility to optimize the alkali profile during the cook.

EXPERIMENTAL

The experimental pulping procedure used and the methods for PS liquor generation have previously been outlined in detail (10). Mixed southern softwood chips were used throughout the project. The chips were screened collecting the four to ten mm fraction and stored under refrigeration. Prior to pulping, the chips were soaked in water overnight, drained and pulped in an M&K batch digester. All cooks were performed using the simulated MCC protocol described previously, which involves three stages and two pulping liquor additions at the end of the first and second stage. The general parameters for the MCC protocol, outlined in Table 1, were designed to generate a circa 30 kappa pulp cooked to 1800 h factor. In this conventional MCC procedure 65% of the active alkali (AA) was added to the first stage, followed by liquor additions containing 20% of the AA at the end of stage 1 and the final 15% of the AA at the end of stage 2. The ratio of (65/20/15) for (stage 1/ stage 2/stage 3) is the standard liquor splits used in previous work. It was decided to maintain the same relative ratio of alkali between stage 2 and stage 3, ($20/15 = 1.3 = 57/43$), throughout the cooking sequence. A simulated carbonate dead load of 15% of the system total titratable alkali (TTA) was used throughout the cooks unless otherwise noted.

Table 8.1 Parameters for MCC protocol

	Cumulative % TTA	L/W	Stage Temperature (°C)	Time at Temperature (min)
Stage I	65	3.5	120	15
Stage II	85	4.1	164	~ 70
Stage III	100	4.5	164	120

The experimental objective was to explore MCC type Kraft cooks and PSAQ cooks with different alkali profiles, to illustrate the potential effects of PS and AQ addition on delignification and total pulp yield to an MCC process using BLG in the chemical recovery. Cooks were completed using 20.5% AA at sulfidity levels (S) of 25% and 40%. 0.1% AQ was added to both the MCC and PS cooks. The total AA available under the stipulated parameters was then split between the three stages. Table 2 outlines the performed cooks and the alkali profiles, which are given as ratios of 100 split to each stage (Stage 1/ Stage 2/ Stage 3). The PSAQ cooks at 25% sulfidity had a PS charge of 2% on OD wood; the 40% sulfidity cooks had a 3% PS charge. As shown in Table 2, the three levels of alkali charged in stage 1, initial alkali, of the MCC procedure match the middle three levels of initial alkali for the PSAQ procedure. In addition, a zero initial alkali charge (ZAP-type cook), and a very high initial alkali was explored for PSAQ.

Table 8.2 Outline of cooks performed using 25% and 40% sulfidity

COOK	% AA on OD wood	Sulfidity (%)	% PS on OD wood	% AQ on OD wood	Alkali Profile
MCC1	20.5	25 / 40	0 / 0	0.1	(20/46/34)
MCC2	20.5	25 / 40	0 / 0	0.1	(45/31/24)
MCC3	20.5	25 / 40	0 / 0	0.1	(65/20/15)
PSAQ1	20.5	25 / 40	2 / 3	0.1	(0/54/46)
PSAQ2	20.5	25 / 40	2 / 3	0.1	(20/46/34)
PSAQ3	20.5	25 / 40	2 / 3	0.1	(45/31/24)
PSAQ4	20.5	25 / 40	2 / 3	0.1	(65/20/15)
PSAQ5	20.5	25 / 40	2 / 3	0.1	(80/11/9)

Following this first sequence of cooks the effect of the alkali profile for ZAP-type cooks was also explored as outlined in Table 3. The first cook in the sequence is taken from Table 2 (PSAQ1). In the two additional cooks the amount of AA charged to stage 2 was increased to improve delignification rate.

Table 8.3 Outline of cooks performed at zero initial alkali exploring the effect of alkali profiling

COOK	% AA on OD wood	Sulfidity (%)	% PS on OD wood	% AQ on OD wood	Alkali Profile
*PSAQ1	20.5	25 / 40	2 / 3	0.1	(0/54/46)
PSAQ6	20.5	25 / 40	2 / 3	0.1	(0/65/35)
PSAQ7	20.5	25 / 40	2 / 3	0.1	(0/75/25)

RESULTS AND DISCUSSION

The obtained results from the cooks outlined in Table 2 are displayed in Figures 1 through 4. The first two figures show the data generated from the cooks performed at 25% S, the following two figures the data from the 40% S.

Figure 1 describes the pulp kappa numbers generated at 25% S using different alkali profiles. The obtained pulp kappa numbers for the MCC pulps using different alkali profiles were very similar, ranging from 27.8 to 29.3. The effect from alkali profiling was much more pronounced for the 25% S PSAQ pulps, where the zero initial alkali cook resulted in a pulp kappa of 39.0. As the alkali charge in the initial stage was increased, the pulp kappa decreased significantly. At a charge of 45% of the initial alkali the resulting kappa from PSAQ is similar to the MCC and, at higher initial alkali charge PSAQ returned lower kappa values. Thus, when comparing the kappa values from the pulping experiments performed at 25% sulfidity, the results show that relative to the MCC reference it is possible to achieve similar to lower kappa number using PSAQ.

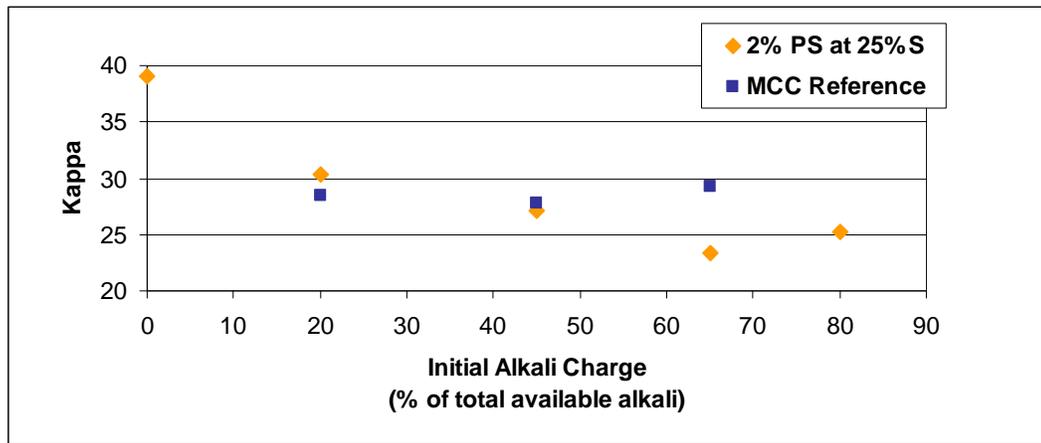


Figure 8.1 Kappa number versus initial alkali charge for 25% sulfidity pulps

The obtained total pulp yields were normalized to kappa 30 using the relationship ± 0.15 % pts. total pulp yield / kappa unit different from 30 (14). Figure 2 displays the normalized total pulp yields obtained from 25% S cooks using different levels of initial alkali. As shown the PSAQ procedure resulted in higher pulp yields than the MCC reference pulp.

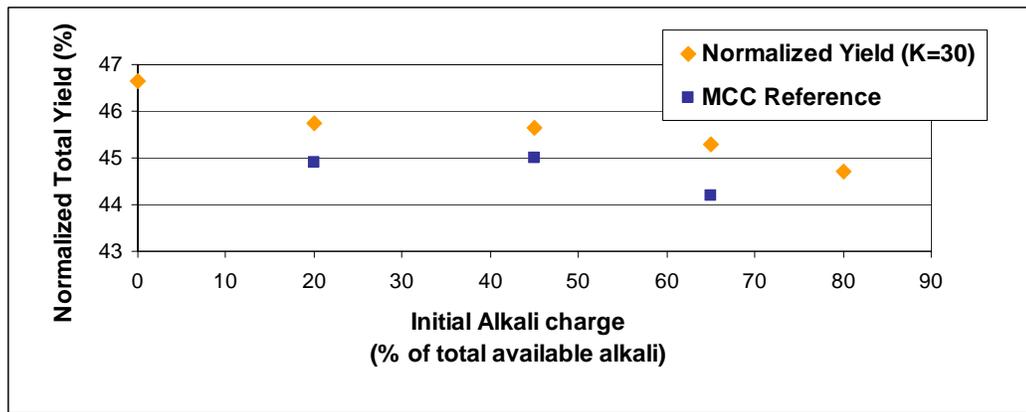


Figure 8.2 Normalized total yield versus initial alkali charge for 25% sulfidity pulps

At zero initial alkali charge the PSAQ normalized yield was 46.7% compared to 44.3% for the conventional MCC pulp using 65% of the initial alkali in the first stage, indicating a potential yield benefit of 2.4% pts. As the amount of initial alkali charged in the PSAQ procedure was increased from 0% to 80%, the obtained yield decreased by about 2% pts. while the kappa decreased by about 15. The effect from increasing levels of initial alkali on decreasing pulp yields is similar to values reported by Olm (11,12).

The pulps prepared at 40% sulfidity followed similar trends, but the differences in PSAQ delignification rates and pulp yields were more pronounced.

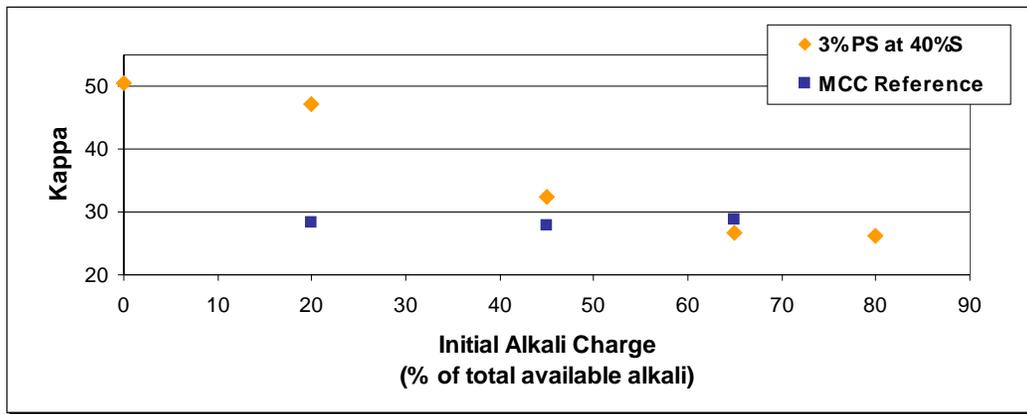


Figure 8.3 Kappa number versus initial alkali charge for 40% sulfidity pulps

As the initial alkali charge was increased from zero to 80% of the total available alkali, the obtained kappa values for the PSAQ procedure decreased from 50.4 to 26.1. Meanwhile the total yield, as above normalized to kappa 30, decreased from 48.5 to 47.7. The yield benefit from PSAQ pulping at 40% sulfidity was more pronounced across the investigated range of initial alkali and when comparing zero initial alkali PSAQ to the standard MCC reference using 65% of the available alkali in the first stage, the yield benefit is about 3% pts.

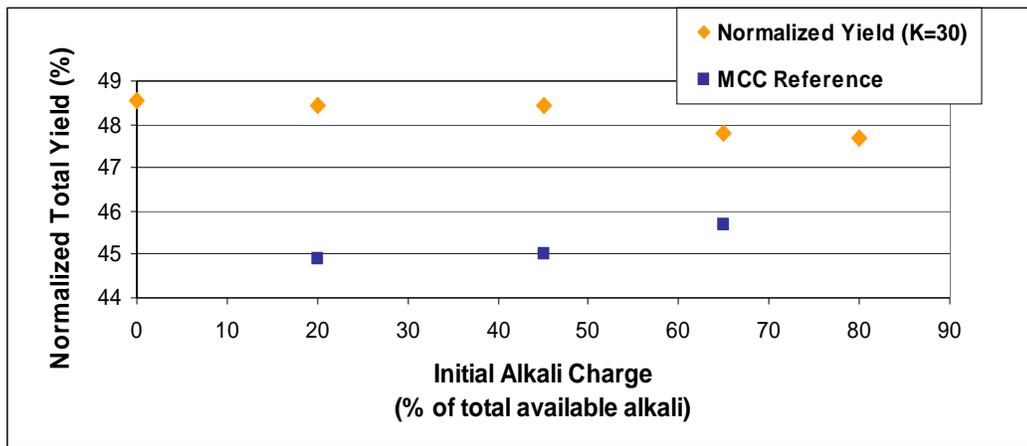


Figure 8.4 Normalized total yield versus initial alkali charge for 40% sulfidity pulps

The delignification rates for the lower initial alkali cooks (0 and 20% of TTA) were not as high as those of the MCC reference cooks. Additional cooks using zero initial alkali charge with different alkali profiles in the subsequent stages were performed to improve the overall delignification rate while maintaining the zero initial alkali condition in the first stage. Thus, the ratio of alkali added between the second and third stages was, as outlined in Table 3, varied from (0/54/46) to (0/75/25). This approach was investigated at both 25 and 40% sulfidity and the obtained results are displayed in Figure 5. As shown the 25% S PSAQ kappa numbers were decreased from about 39 to 35 accompanied by a loss in total yield of 1.3% pts. The corresponding values for the 40% sulfidity pulps were a decrease in kappa from 50 to 35 with about 2% pts. loss in yield.

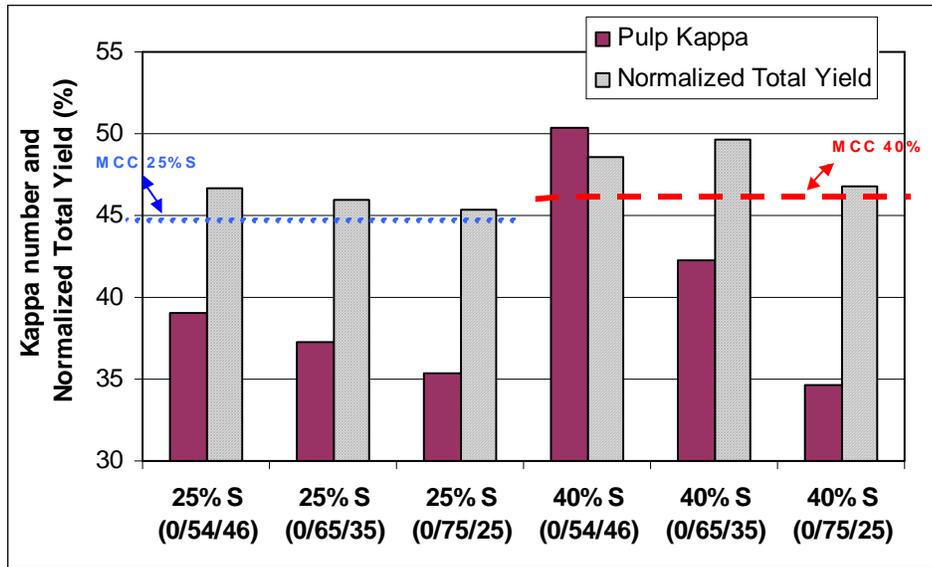


Figure 8.5 Comparing the effect of alkali profiling on delignification rate and pulp yield for zero initial alkali PSAQ cooks (25% and 40% sulfidity)

Based on these results, using ZAP type cooking it is possible to decrease the obtained pulp kappa by adding more of the available alkali to the second stage of the cook. However, as more alkali was added to the earlier parts of the cook, the obtained pulp yield decreased. The pulp yield values in Figure 5 represent the total pulp yield for each cook normalized to kappa 30. The corresponding value for the conventional MCC reference cook using an alkali profile of (65/20/15) was 44.3% using 25% sulfidity (blue line) and 45.9 using 40% sulfidity (red line). In comparison the normalized pulp yields for PSAQ at highest delignification rate (0/75/25) were 45.4 using 25% sulfidity and 46.8% using 40% sulfidity. Thus, when using zero initial alkali pulping, the delignification rate can be improved by varying the alkali profile of the cook, however, this also results in a decreasing total pulp yield.

To illustrate the effects of alkali profiling on pulping liquor residual effective alkali, samples were obtained from the digester during the course of the cook. Figures 6 through 8 compare the residual effective alkali for the cooks performed at 25% sulfidity. Figures 9 through 11 compare the residual effective alkali for the cooks performed at 40% sulfidity.

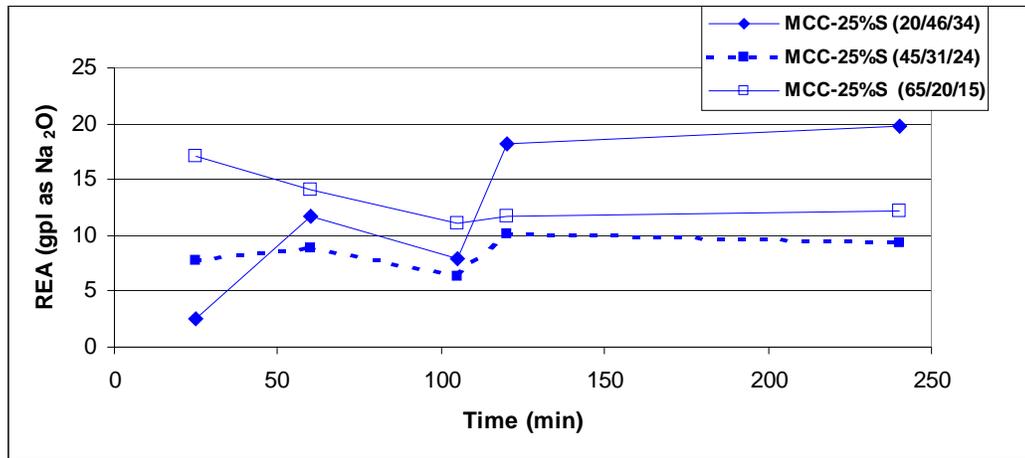


Figure 8.6 The effect of alkali profiling on residual effective alkali for MCC at 25% S

As shown in Figure 6, for MCC pulping at 25% sulfidity the alkali profile charged to the three stages as 45/31/24 gives the most level or smooth residual effective alkali profile. Although the obtained kappa and total yield are similar for the three different profiles, there is a large difference in final REA values.

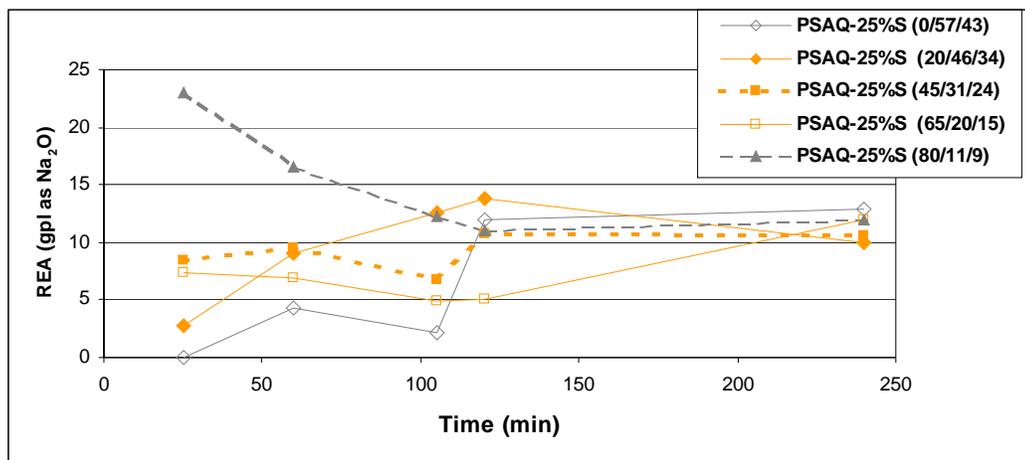


Figure 8.7 The effect of alkali profiling on residual effective alkali for PSAQ at 25% S

Similarly for the PSAQ cook REA profiles shown in Figure 7, the 45/31/24 profile gives the most level alkali profile and resulted in the median values for kappa and total yield returns. There is a small difference in final REA values between the different profiles.

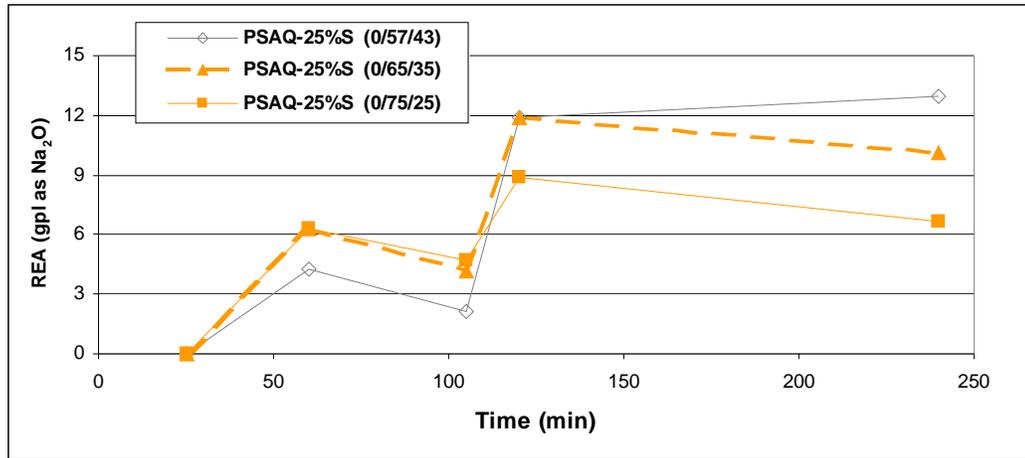


Figure 8.8 The effect of alkali profiling on REA using for PSAQ 25% S at zero initial alkali charge

As shown in Figure 8, when comparing the REA profiles for the three PSAQ cooks at 25% sulfidity using zero initial alkali the trends are similar but the final REA values vary widely, as well as the obtained kappa and total yield values.

Figure 9 outlines the REA profiles generated from MCC pulping at 40% sulfidity. The obtained values for the MCC cooks at 40% sulfidity are somewhat similar to those at 25% sulfidity, in that the 45/31/24 profile resulted in the most even curve and the lowest final REA.

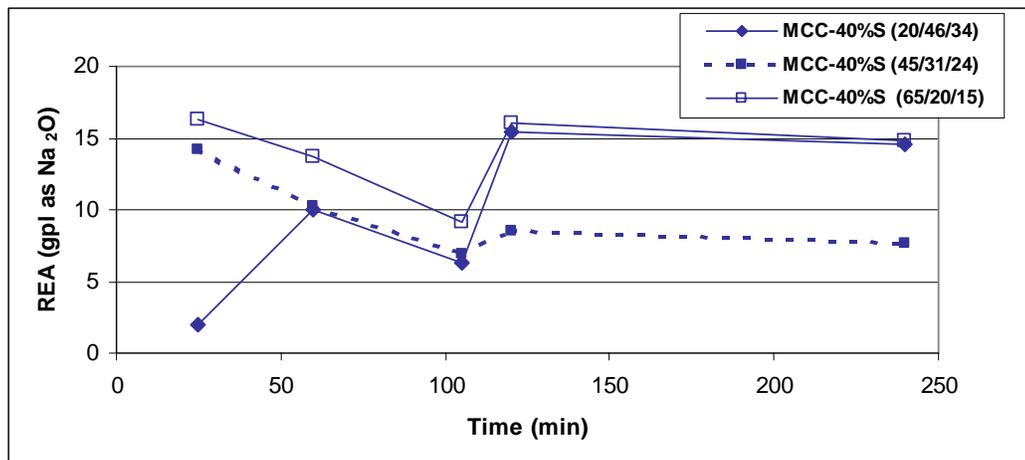


Figure 8.9 The effect of alkali profiling on residual effective alkali for MCC at 40% S

As shown in Figure 10, when pulping at 40 sulfidity using PSAQ, the 0 and 20% initial alkali charge returned very low REA values during the first part of the cook, while the final REA values were similar to those obtained through the other initial alkali profiles.

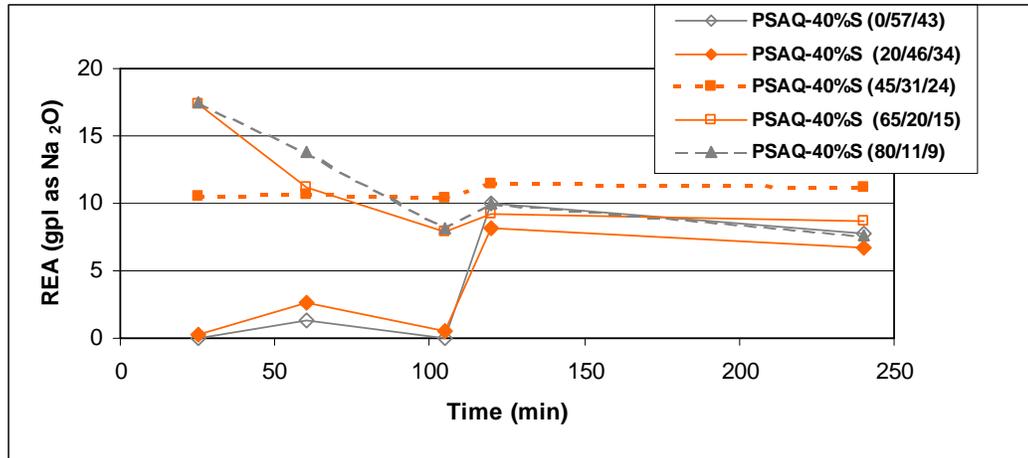


Figure 8.10 The effect of alkali profiling on residual effective alkali for PSAQ at 40% S

As shown in Figure 11, when comparing the different zero initial alkali PSAQ cooks at 40% sulfidity, the REA values during the cook follow a similar development and the final REA values are very close to one another.

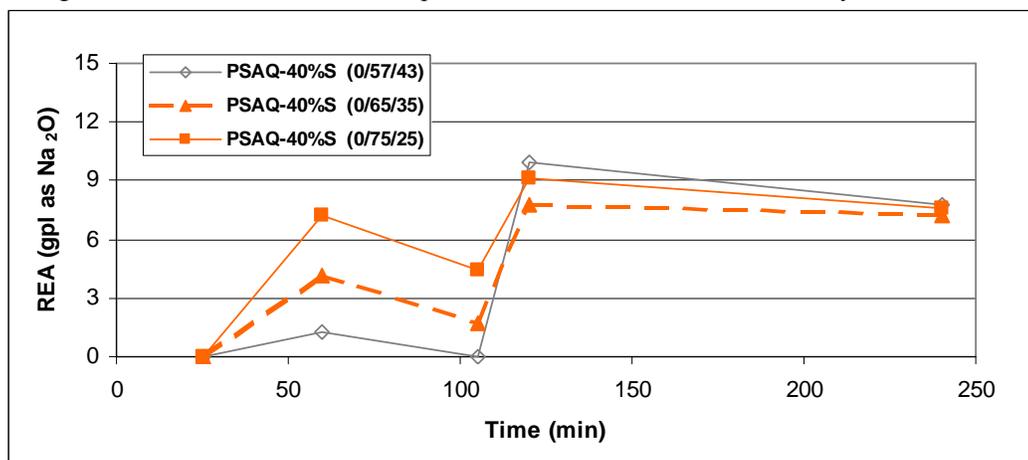


Figure 8.11 The effect of alkali profiling on REA using for PSAQ 40% S at zero initial alkali charge

As shown in the preceding figures, the effect of AA profiling has a significant impact on the REA levels in the pulping liquor during the course of the cook. When relating these findings to the effects in delignification rate and total pulp yield, the differences between MCC with AQ and PSAQ are significant. In MCC pulping, the REA profiles explored have little effect on the delignification rate, and some effect on the total pulp yield. The variation in these values is around 1 unit of measurement for both the 25% S and 40% S cooks. The effect is much greater in the PSAQ procedure, where the REA varies more greatly. In the pulping procedure used in this project OH⁻ is consumed as the PS begins to dissociate during the first stage, and the major part when the temperature is increased after the first stage. Therefore, controlling the REA profile during the cook will be very important to achieve the necessary delignification rate while maintaining the yield benefit sought from PSAQ pulping.

CONCLUSIONS

The objective of the work described in this paper was to investigate the effect of alkali profiling on yield and delignification rate using polysulfide-antraquinone (PSAQ) pulping. The possibility to implement the pulping

procedures explored in this work may require separation of sulfur and sodium in the chemical recovery cycle, as enabled by BLG.

MCC pulping at 25% and 40% sulfidity

A baseline for comparisons was generated using a simulated MCC procedure. Three different alkali profiles were explored where the initial alkali was increased from 20% to 65% of the total available alkali. The resulting alkali profiles are denoted, [20/46/34], [45/31/24] and [65/20/15]. When pulping at 25% sulfidity pulp kappa numbers varied little, from 27.8 to 29.3. The obtained total pulp yields, normalized to kappa 30, showed only a small variation from 44.3% to 45.3%. All pulp yields were for purposes of comparison normalized to kappa 30. The results were similar for the cooks at 40% sulfidity, where kappa varied from 27.8 to 28.8 and the normalized total pulp yield varied from 45.1 to 45.9. There was no apparent trend in pulp kappa or pulp yield resulting from the MCC cooks at either sulfidity level.

PSAQ pulping was explored at 25% and 40% sulfidity using five different alkali profiles. The initial alkali was varied from zero to 80% of the available alkali. The resulting alkali profiles are denoted, [0/54/46], [20/46/34], [45/31/24], [65/20/15] and [80/11/9], where three profiles were identical to those of the MCC cooks. The zero initial alkali cook is similar to the ZAP procedure and the 80% similar to the hyperalkaline procedure.

PSAQ pulping at 25% sulfidity with 2% PS charge

The ZAP-type cook had the highest normalized yield at 46.7% as well as the highest kappa, 39.0. As the initial alkali charge was increased from 0 to 80%, the kappa was lowered from 39.0 to 25.3, while the normalized pulp yield decreased from 46.7% to 44.7%. When varying the alkali profile for the zero initial alkali cooks it was possible to decrease kappa to levels comparable to the MCC pulps, but the associated decrease in yield was significant returning little overall benefits from this approach. When comparing the PSAQ results to the 25% MCC pulps, the greatest benefits with regard to both kappa and total pulp yield were obtained for the PSAQ pulps using 20 and 45% initial alkali. For these pulps the obtained kappa was similar to that of the MCC pulp while maintaining a yield benefit of about 1%.

PSAQ pulping at 40% sulfidity with 3% PS charge

When using PSAQ pulping at 40% sulfidity, the ZAP-type cook again had the highest normalized yield at 48.5, and a very high kappa, 50.4. When increasing the initial alkali charge, the delignification rate was improved significantly and the kappa decreased from 50.4 to 26.1. The normalized pulp yield also decreased, but only from 48.5 to 47.7. When varying the alkali profile for the ZAP-type cook kappa was decreased from 50.4 to 34.7 while the yield decreased from 48.5 to 46.8. When comparing PSAQ pulping at 40% sulfidity to the MCC reference, a significant improvement in yield is possible while maintaining a similar delignification rate. The yield benefit from PSAQ pulping at 40% using a PS charge of 3% on wood was 3-3.5%. The approach of varying the alkali profile for the ZAP-type cook was also more successful than at 25% sulfidity. The PSAQ procedure using initial alkali levels of 45% provided the greatest benefit in both delignification rate and pulp yield as compared to the MCC reference.

Overall, the relative benefits from PSAQ pulping in both delignification rate and yield was greater using 3% PS on wood at 40% sulfidity than 2%PS on wood at 25% sulfidity. The effects from alkali profiling were also more pronounced at 40% sulfidity. In conclusion, based on the pulping procedures used in this research, a greater benefit from PSAQ pulping can be realized at higher levels of sulfidity, where it is possible to charge a higher concentration of PS and the effects of alkali profiling can be used to optimize both delignification rate and resulting pulp yield. The most advantageous results, as compared to the MCC reference, were obtained using the PSAQ procedure at 40% sulfidity with 3% PS on wood and a (45/31/24) alkali profile.

FUTURE WORK

Future work will entail bleaching and strength property studies of selected pulps prepared in this project.

REFERENCES

1. Li, Z.; Li, J.; Kubes, G.J. “Kinetics of Delignification and Cellulose Degradation During Kraft Pulping with Polysulphide and Anthraquinone”; JPPS. **2002**, 28(7): 234-239.

2. Griffin, C.W.; Kumar, K.R.; Gratzl, J.; Jameel, H. "Effects of Adding Anthraquinone and Polysulfide to the Modified Continuous Cooking (MCC) Process"; Proc. 1995 TAPPI Pulping Conference; TAPPI Press: Atlanta, GA, 1995; 19-30.
3. Jiang, J.E. "Extended Delignification of Southern Pine [*Pinus spp.*] with Anthraquinone and Polysulfide"; TAPPI J. **1995**, 78(2): 126-132.
4. Jiang, J.E. "Extended Modified Cooking of Southern Pine [*Pinus*] with Polysulfide: Effects on Pulp Yield and Physical Properties"; TAPPI J. **1994**, 77(2): 120-124.
5. Landmark, P.A.; Kleppe, P.J.; Johnsen, K. "Pulp Yield Increasing Process in Polysulfide Kraft Cooks"; Tappi J. **1965**, 58(8): 56.
6. Vennemark, E. "Some Ideas on Polysulfide Cooking"; Svensk Papperstidning. **1964**, 67(5): 157.
7. Kleppe, P.J.; Minja, R.J.A. "The Possibilities to Apply Polysulfide-AQ in Kraft Mills"; Proc. *Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998, Vol. 1, pp 113.
8. Sanyer, N.; Landrie, J.F. "Factor Affecting Yield Increase and Fiber Quality in Polysulfide Pulping of Loblolly Pine, Other Softwoods, and Red Oak"; Tappi J. **1964**, 47(10): 640.
9. Tench, L., Wearing, J., Buchner, W. "PS/AQ Can Do More Than Just Increase Digester Yields"; Proc. *Growing yield from the ground up*, TAPPI Press: Atlanta, GA, 2006.
10. Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H. "The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Properties"; Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference; TAPPI Press: Atlanta, GA, 2005.
11. Olm, L.; Tormund, D., Nordic Pulp Paper Res. J. 19(1): 6 (2004)
12. Olm, L.; Tormund, D., "ZAP Cooking with New Liquors from a BLG Recovery System"; Proc. *Growing yield from the ground up*, TAPPI Press: Atlanta, GA, 2006.
13. Brannvall, E.; Gustafsson, R.; Teder, A.; "Properties of Hyperalkaline Polysulphide Pulps"; Nordic Pulp Paper Res. J. **2003**, 18(4): 436-440.
14. Luthe, C., Berry, R., Pulp. Pap. Can. 106(3): 27 (2005)

9 THE DEVELOPMENT AND VALIDATION OF A LOW-TEMPERATURE BLACK LIQUOR GASIFIER MODEL FOR USE IN WINGEMS©

Lindstrom, M., Naithani, V., Kirkman, A., Jameel, H., *"The Development and Validation of a Low-temperature Black Liquor Gasifier Model for Use in WinGEMS®"*, Proceedings TAPPI 2005 Engineering, Pulping and Environmental Conference, Philadelphia, PA, (2005).

Also in: TAPPI J. Vol. 5 No. 2 (2006) p.24

THE DEVELOPMENT AND VALIDATION OF A LOW-TEMPERATURE BLACK LIQUOR GASIFIER MODEL FOR USE IN WINGEMS[®]

Mathias Lindström, Ved Naithani, Adrianna Kirkman, Hasan Jameel

Department of Wood and Paper Science

North Carolina State University

Raleigh, NC 27695-8005

USA

ABSTRACT

The continuous efforts made in the area of black liquor gasification (BLG) are bringing this technology closer to commercial realization and potential wide-spread implementation. One area of research that could assist in this process is the investigation of the effects of modified pulping technologies on modern pulping operations. The separation of sodium and sulfur could be utilized in processes like polysulfide-anthraquinone, alkaline sulfite-anthraquinone or mini-sulfide sulfite-anthraquinone to dramatically improve pulp yield and overall process economics. In order to simulate low temperature black liquor gasification in conjunction with these process modifications and the resulting effects on full mill operations in WinGEMS, the development of a low temperature BLG model was required. The predictive capability of the developed BLG WinGEMS block was validated by comparison to process data. The process model generates output and back-calculated input streams with good agreement to values provided by the manufacturer. Several obstacles were overcome in the creation of the block, including requirements on user defined stream components. The BLG block is currently being used in case studies to investigate the effects of varying process carbon conversion ratios. These efforts are seen as further validation of the predictive capabilities of the model, which is envisioned to be used in full mill simulations to explore the implications of modified pulping technologies on current pulping operations.

INTRODUCTION

The implementation of black liquor gasification into conventional chemical recovery operations presents many benefits and opportunities relative to current chemical recovery technologies. The separation of sodium and sulfur into different streams will allow for the regeneration of a variety of pulping liquors that could be used to maximize pulp yield, and even design pulp properties according to market demand. In addition to the potential benefits applicable on the pulping side, BLG would also increase the efficiency of combined heat and power generation in the mill. The utilization of combined-cycle power generation will create energy management alternatives driven by the relative costs of steam production and electricity and their day to day impact on operating margins. The overall net result of BLG implementation could mean improved pulp mill operations and significant production cost savings (1-3).

With efforts focused on two different process concepts, a high-temperature, pressurized partial-oxidation process (Chemrec) and a low-temperature indirectly heated steam-reforming process (MTCI), the development of BLG technologies is approaching commercial realization. Three mill start-ups in North America are currently in operation, one utilizing the Chemrec process (Weyerhaeuser New Bern mill, NC) and two installations (G-P Big Island, Va. and Norampac, Trenton, Ont.) utilizing the MTCI process. Notwithstanding the inherent benefits of BLG relative to chemical recovery and power generation, wide-scale implementation of these processes faces industry reluctance until successful commercial operations have been proven (4).

The Tomlinson Recovery Boiler, in spite of being a mature proven technology, has the disadvantages of low thermal efficiency, low power to heat ratio and the risk of smelt/water explosions. Gasification technology addresses some of these concerns. Moreover, it allows for the separation of sodium and sulfur which in turn can be exploited to optimize pulping operations using modified pulping technologies such as those listed below.

- Split Sulfidity Pulping
- Polysulfide Pulping
- Alkaline Sulfite Pulping
 - Alkaline Sulfite- AQ (AS-AQ)

- Mini-Sulfite Sulfide AQ Process (MSSAQ)

The positive and potentially substantial impact of these technologies on the pulping process could influence decision makers to more actively pursue a paradigm shift in chemical recovery operations as exemplified by BLG.

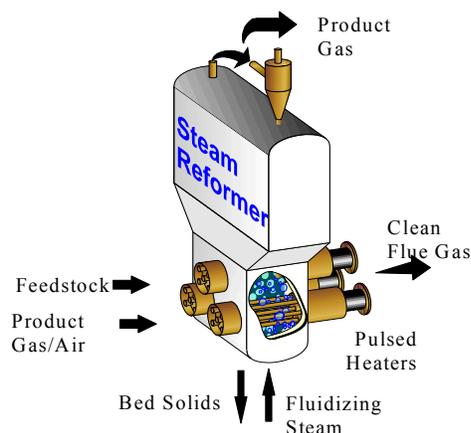
A good approach to evaluate modifications to any process is computer simulation. In order to explore the effects on the overall process operations by the implementation of BLG, alone or in conjunction with any of the above modified pulping technologies, a full mill model must be built. One of the standard simulation tools for the pulp and paper industry is WinGEMS[®]. However, there is currently no BLG block available within the WinGEMS software, thus rendering the simulation of BLG implementation complex at best (3). A black liquor gasifier model in the form of a WinGEMS block would be highly desirable. Work utilizing models of black liquor gasifiers in other software packages have been presented, focusing on the cost benefits of high- and low-temperature BLG operations in conjunction with the combined-cycle power generation (1,2), as well as fuel and energy production (5,6). The work presented here describes the development of a model for a low-temperature MTCI steam reformer in WinGEMS. This WinGEMS[®] block will be employed in subsequent work to investigate BLG operating parameters and conditions in full pulp mill simulations exploring the effects of process modifications, while predicting the BLG process output streams.

THE BLG MODEL

The MTCI low-temperature steam reformer

A simplified schematic of the MTCI system is shown in Figure 1. 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 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 as the sulfur leaves mostly with the gas output stream and the sodium stays in solid form and exits with the bed solids. Product gases are routed through a cyclone to remove the bulk of the entrained particulate matter and then quenched and scrubbed in a venturi scrubber. The sulfur species must be recovered, through scrubbing with green liquor or alternative processes, prior to other unit operations. A portion of the medium-Btu product gas can be supplied to the pulse combustion modules and combustion of this gas, or alternatively natural gas, provides the heat necessary for the endothermic reactions in the gasification process. The inorganic chemical in the feedstock is recovered as the bed solids are dissolved, possibly in recycled weak wash, and recombined with sulfur recovered from the gas stream to regenerate pulping liquor used in 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, 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.



BLG process model inputs and outputs

Figure 9.1 Schematic of a MTCI Steam Reformer

As shown in Figure 1, the BLG process input and output streams are easily visualized, and can be summarized as shown in Figure 2. There are four separate input streams and three separate output streams. The input streams consist of the feedstock stream, in this case concentrated black liquor (BL), the bed fluidizing steam, the fuel gas combusted in the pulsed heaters and the air stream required for pulsed heater combustion. The third stream, the fuel gas for combustion in the pulsed heaters, can be natural gas or a recycled fraction of the BLG product gas. The output streams consist of the BLG bed solids, the product gas, and the flue gas from the pulsed heaters.

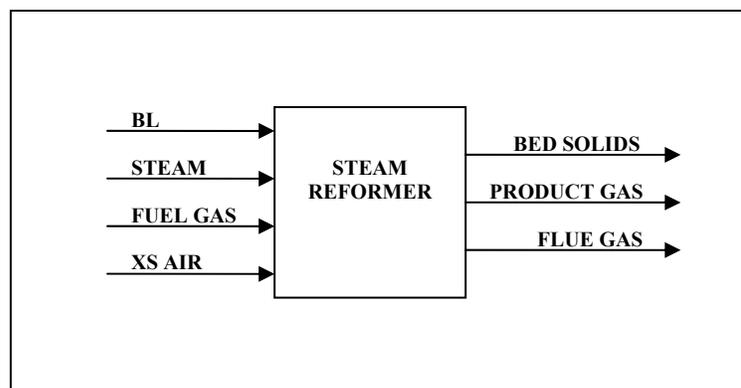


Figure 9.2 Stream structure for BLG model

Although the input and output streams are not complex, the compositions of the BL input stream and the product gas stream certainly are. The black liquor is comprised of all organic and inorganic material recovered from the pulping process, constituting a complex matrix of lignin fragments, cellulose, hemi-cellulose and various ionized inorganic species. The BLG product gas consists of a gas matrix containing all volatile species generated in the steam reforming reactions, as well as minute amounts of dust particles. The remaining streams are made up of either a single compound or simple mixtures.

BLG process model assumptions and parameters

At the outset of any process model construction, the level of detail in the model must be determined relative to its intended use and predictive capabilities. The purpose of constructing this BLG model was the desire to incorporate a BLG block into a full mill WinGEMS simulation, where the interaction of the BLG and other mill unit operations could be evaluated in terms of process variables of interest to the user. The model developed for this application bases the material and energy balances around the steam reformer on empirical relationships rather than first principles. This approach allows for the prediction of model output streams based on the given BL input stream and process parameters, as well as the back-calculation of the required amounts of bed fluidizing steam and energy supplied through the pulsed heaters to sustain the endothermic steam reforming reactions.

To simplify the BLG model and its control a number of parameters were identified and utilized for user input and reaction constraints internal to the model. These parameters, outlined in Table 1, include process operating variables such as temperature, reduction ratios and conversion efficiencies similar to those found in the WinGEMS[®] KFURN block (7). Several of the defined parameters and other considerations made regarding the BLG model were based on process data provided by MTCL. As a result, the range of operating conditions that can be used with the model in process simulations is limited by the original data. With increasing amounts of process data available for various pulping operations, this range will be increased. At present simulations incorporating the BLG model should be constrained to the default values indicated in the block documentation. In addition to the user defined parameters outlined in Table 1, available process data was used to determine the selective generation of gaseous components formed by sulfur and carbon, as well as particulate matter in the product gas.

Table 9.1 **BLG user defined block parameters**

User Defined Parameters	Units
Gasifier Operating Temperature	(deg C)
Steam Requirement for bed fluidization	(mol total H₂O / mol total C)
Heat of formation for Dissolved Wood Solids	(kJ/kg)
Dissolved Wood elemental fractions	
C	fraction
H	fraction
O	fraction
Sulfur reduction ratio	fraction
Chloride reduction ratio	fraction
Total Carbon conversion ratio	fraction

BLG process model algorithm

The material balances were calculated based on the elemental composition of the black liquor fed to the gasifier, the fluidizing steam, and the parameters outlined in Table 1. The sequence of calculations is outlined in Table 2.

Table 9.2 Algorithm for BLG material balances

Calculation order	Item	Comment
1	Calculate BL elemental composition (wet)	Organic fraction of C, H, O, based on input parameter
2	Calculate required fluidizing steam	Based in input parameter
3	Calculate Sulfur balance	Based on sulfur reduction ratio and sulfurous gas component split ratios
4	Calculate Chloride balance	Based on chloride reduction ratio
5	Calculate Sodium balance	
6	Calculate Potassium balance	
11	Calculate Carbon balance	Based on total carbon conversion ratio and parameters controlling the formation of carbonaceous compounds
8	Calculate Oxygen balance	
9	Calculate Hydrogen balance	
10	Calculate Solid stream output	Summation of all solids species
11	Calculate Gas stream output	Summation of all gaseous species

The BLG energy balances were calculated based on the Gulichsen total enthalpy method (8). In simple terms, the net total enthalpy of a system is computed as the difference between the sum of total enthalpies of the reactants and the corresponding sum of total enthalpies of the products (Eq. 1). In turn, the total enthalpy of a substance is calculated as the sum of its isothermal heat of formation, the sensible heat above 25 °C, the latent heat of fusion or evaporation, and the heat of solution and dissolution (Eq. 2).

$$\text{Equation 1.} \quad Q = H_{\text{Reactants}} - H_{\text{Products}}$$

$$\text{Equation 2.} \quad H = \Delta H_{f\text{STP}} + \int_{298\text{ °K}}^{T_2} C_p dt + \Delta H_{\text{agr}} + \Delta H_s$$

The overall BLG system material balance was calculated using the composition of the BL input stream. The stream components were used to define compounds present in the BL and compute their total enthalpies. Subsequent summation with the total enthalpy of the fluidizing steam yielded the total enthalpy of the reactants. The total enthalpy of the products was computed by summation of all the output components' total enthalpies generated in the bed solids and product gas streams. The difference between these two values was assumed to represent the amount of energy required to sustain the endothermic steam reforming reactions, and as such, used to back-calculate the amount of energy required for BLG operation. As shown (Eq. 3), this value minus an assumed system heat loss based on design parameters was used to determine the amount of fuel gas required for the pulsed heaters.

$$\text{Equation 3.} \quad \text{BLG } Q_{\text{Required}} = H_{\text{Reactants}} - H_{\text{Products}} - Q_{\text{BLG Heat Loss}}$$

Thermodynamic properties for the involved species were determined using the JANAF tables (9), the handbook of Chemistry and Physics (10) and the NIST Chemistry Webbook (11).

Integration of BLG block into WinGEMS

The WinGEMS Block Developers Kit was used to integrate the model into the simulation software. The appropriate code for the block, including the material and energy balance calculations, was generated in Compaq Visual FORTRAN[®]. Some hurdles to the successful development of this WinGEMS block, were in

particular, related to the material balance. WinGEMS uses a hardwired variable array for stream components that allows for easy information transfer between blocks. This array is not modifiable, and contains most stream components that would ever be used by a pulp and paper process engineer. However, the product gas stream, as an example, created through gasification contains several stream components that are not included in this variable array. When a user defines a new stream component, he/she has the option of assigning a dummy variable number to the new stream component. These dummy variables are essentially open slots carried in the stream component variable array, and can be accessed by any block. This capability was exploited in the code for the BLG block, where several stream components were designated to specific dummy variables. As a result, when building a new simulation involving the BLG block, the user defined stream components must be designated as the correct dummy variable for proper functionality. This and other considerations are addressed in the block reference file for the BLG WinGEMS block.

The completed BLG block was debugged in a simple WinGEMS simulation shown in Figure 3.

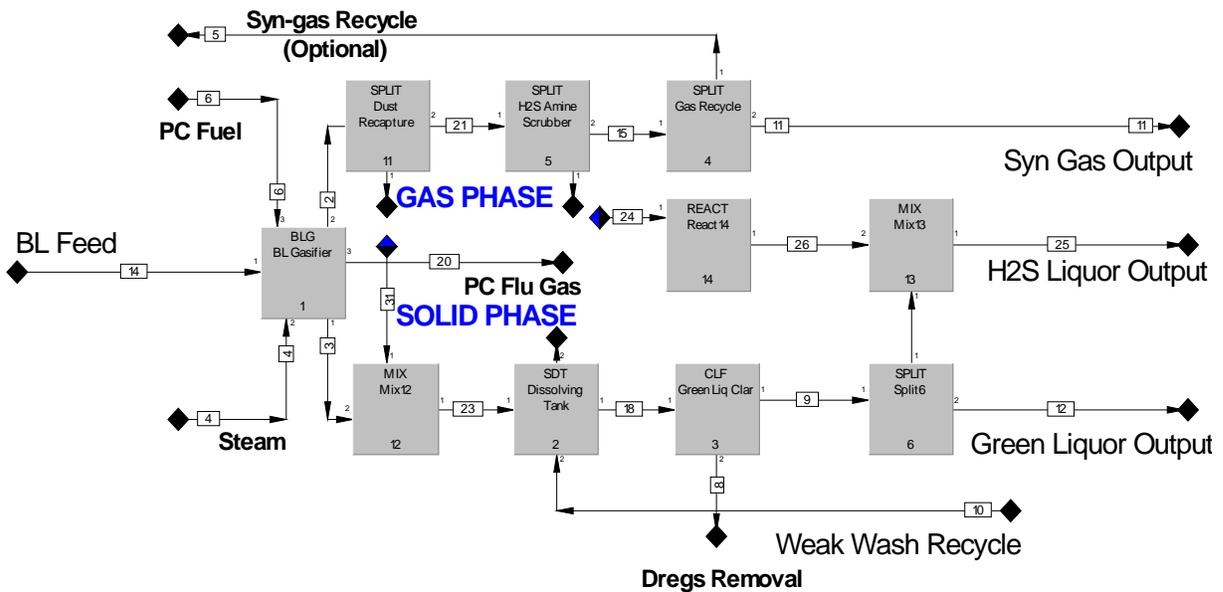


Figure 9.3 WinGEMS simulation using integrated BLG block model

The simulation outlined in Figure 3 was used to predict the BLG process outputs based on the BL feed stream and selected process parameters outlined in Table 1. The values were compared to process data supplied by MTCI, and the comparison used as validation of the BLG block as a functional tool for the given conditions.

A black liquor feed of 142 metric tons per hour was fed to the BLG block at 80% solids. The parameters outlined in Table 1 were set to match data provided by MTCI. The predicted output stream components and the calculated percent error, as compared to MTCI process data, are shown in Table 3.

Table 9.3 Predicted BLG process streams and comparisons to MTCI process data

BLG Output	% difference rel. MTCI process data	Solid components	% difference rel. MTCI process data
Gas Phase output		Gas Phase dust output	
CH ₄	0.8000	Na ₂ CO ₃	0.0240
C ₂ H ₆	0.0020	Na ₂ SO ₄	0.0404
C ₂ H ₄	0.0160	NaCl	0.0164
C ₃ H ₆	0.0018	K ₂ CO ₃	0.0001
C ₃ H ₈	0.0000	CaCO ₃	0.0000
Phenols	0.0790	C	0.0017
Acetone	0.0243	Solid Phase output	
H ₂ S	0.0340	Na ₂ CO ₃	0.0044
CH ₃ SH	0.0019	Na ₂ SO ₄	0.0415
(CH ₃) ₂ S	0.0080	NaCl	0.0235
(CH ₃) ₂ S ₂	0.0020	K ₂ CO ₃	0.0013
CO	1.2000	CaCO ₃	0.0000
CO ₂	1.2000	C	0.0018
H ₂	0.7600	Fluidizing Steam Input	1.1000
N ₂	0.0000	Fuel Input for Pulsed Heaters	1.3000
O ₂	0.0000		
H ₂ O (v)	0.2480		
HCl	0.0137		

As shown in the table, there is very good agreement between the predicted values and the MTCI reference data. The largest discrepancies are found in the components of CH₄, CO and CO₂, as well as in the values for the fluidizing steam and fuel requirements for the pulsed heaters. Work is currently underway to improve these differences. The overall results indicate that the developed model can accurately predict BLG unit operations under the given conditions. In addition to continuous updating of the process material and energy balances, work is in progress to explore the BLG model predictive capabilities under a range of typical process conditions. For instance, carbon conversion rates are critical in black liquor gasification as they affect the system efficiency and profitability. Low levels of carbon conversion can lead to tar build up and equipment fouling, as well as negatively affecting the heat value of the BLG product gas (12). A case study to investigate the effect on the predicted BLG product gas stream at various levels of carbon conversion is underway.

CONCLUSIONS

The predictive capability of the developed BLG WinGEMS block was validated by comparison to manufacturer's process data. The model generates output and back-calculated input streams with good agreement to values provided by MTCI for the gasification of black liquor.

Several obstacles were overcome in the creation of the block, including requirements on user defined stream components. Considerations for the employment of the BLG block in WinGEMS simulations are addressed in the block reference.

FUTURE WORK

The BLG block is currently being used to investigate the effects of varying carbon conversion ratios. These efforts are seen as further validation of the predictive capabilities of the model, which is envisioned to be used

in full mill simulations to explore the implications of modified pulping technologies on current pulping operations.

ACKNOWLEDGEMENTS

The authors thank the U.S. Department of Energy for the financial support of this work, and also Pacific Simulation and MTCI and TRI for their assistance and guidance; in particular Barry Malmberg (Pacific Simulation), Ravi Chandran and Lee Rockvam (MTCI), and Dan Burciaga and Dave Newport (TRI), who made this work possible.

REFERENCES

1. Consonni, S., Larson, E.D., Katofsky, R., Proc. ASME Turbo Expo 7: 1 (2004)
2. Consonni, S., Larson, E.D., Katofsky, R., Proc. ASME Turbo Expo 7: 15 (2004)
3. Lindstrom, M., Kirkman, A., Jameel, H. et al., Proc. TAPPI Fall Technol. Trade Fair pp. 1417-1429 (2002)
4. Patrick, K., Pap Age 119(7): 30 (2003)
5. Berglin, N., Lindblom, M., Ekbom, T., Proc. TAPPI Fall Technol. Trade Fair pp. 527-537 (2002)
6. Ekbom, T., Berglin, N., Lindblom, M., Int. Chem. Recovery Conf. Vol. 2: 843 (2004)
7. "WinGEMS 5.3 help manual:KFURN block reference" Pacific Simulation, Moscow, ID (200x)
8. Gullichsen, J., Proc. IUPAC/EUCEPA Symp. Recovery of Pulping Chemicals (Helsinki) p. 211-234 (1969)
9. Malcolm W. Chase, Jr., NIST-JANAF thermochemical tables, 4th ed., American Chemical Society; Woodbury, N.Y., American Institute of Physics for the National Institute of Standards and Technology, Washington, D.C. (1998)
10. Lide, D.R., CRC Handbook of Chemistry and Physics, 85th ed., Online Edition, <http://www.hbcpnetbase.com/> (2005)
11. NIST Chemistry Webbook., available online <http://webbook.nist.gov/chemistry/> (2005)
12. Sricharoenchaikul, V., Frederick, W.J., Grace, T.M., JPPS, 23(8): J394 (1997)

10. WINGEMS SIMULATION OF NET PROCESS VARIABLE OPERATING COSTS RESULTING FROM BLG INTEGRATION WITH SPLIT SULFIDITY AND POLYSULFIDE PULPING

Unpublished

WINGEMS SIMULATION OF NET PROCESS VARIABLE OPERATING COST RESULTING FROM BLG INTEGRATION WITH SPLIT SULFIDITY AND POLYSULFIDE PULPING

Mathias Lindström, Ved Naithani, Hasan Jameel, Adrianna Kirkman

Department of Wood and Paper Science

North Carolina State University

Raleigh, NC 27695-8005

USA

ABSTRACT

Black liquor gasification enables the separation of sodium and sulfur in pulp mill chemical recovery operations, thus creating a viable recovery system for pulping processes like polysulfide-anthraquinone, alkaline sulfite-anthraquinone or mini-sulfite sulfite-anthraquinone. These technologies could dramatically improve pulp yield and overall process economics. A previously developed WinGEMS model for low temperature black liquor gasification has been used to evaluate the integration of BLG combined with modified pulping technologies into the kraft process. Case studies were performed in WinGEMS comparing full mill simulations of a kraft process using modified continuous cooking to BLG processes with split sulfidity and polysulfide-anthraquinone pulping. The net variable operating costs for each case were determined from a set of cost factors. The obtained results indicate that implementing BLG with the investigated modified pulping technologies would lead to increases in the net variable operating cost per oven dry ton pulp produced ranging from 1.8 to 3.9% compared to the kraft-MCC base case. It was also found that the cost of kiln fuel and the price of power sales to the grid drive the relative cost performance of the evaluated cases. When comparing the BLG cases to the MCC reference, the net variable operating cost break even point based on lime kiln fuel cost ranges from \$47 to \$38 per barrel of kiln fuel depending on the BLG process, which is much lower than currently available prices. When performing similar comparisons of net variable operating costs based on variable power sales price, significant cost savings could be realized in all BLG processes at prices for power sold to the grid above 5 ¢/KWh.

INTRODUCTION

The implementation of black liquor gasification into conventional chemical recovery operations presents many benefits and opportunities relative to current chemical recovery technologies. The separation of sodium and sulfur into different streams will allow for the regeneration of a variety of pulping liquors that could be used to maximize pulp yield, and even design pulp properties according to market demand. In addition to the potential benefits applicable on the pulping side, BLG would also increase the efficiency of combined heat and power generation in the mill. The utilization of combined-cycle power generation will create energy management alternatives driven by the relative costs of steam production and electricity and their day to day impact on operating margins. The overall net result of BLG implementation could mean improved pulp mill operations and significant production cost savings (1-3).

The Tomlinson Recovery Boiler, in spite of being a mature proven technology, has the disadvantages of low thermal efficiency, low power to heat ratio and the risk of smelt/water explosions. Gasification technology addresses some of these concerns. Moreover, it allows for the separation of sodium and sulfur which in turn can be exploited to optimize pulping operations using modified pulping technologies such as those listed below.

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

Modifications to the kraft process, such as split sulfidity and polysulfide pulping would demand the smallest changes to current prevailing chemical recovery and pulping operations, and are the focus in this effort.

To simulate pulping operations using BLG combined with these processes in WinGEMS, a model for black liquor gasification had to be developed and integrated into the software. This work has previously been reported (4). The following is a brief discussion of the assumptions made for the simulated unit operation of the MTCI low temperature steam reformer and the model functionality.

THE MTCI LOW-TEMPERATURE STEAM REFORMER

A simplified schematic of the MTCI system is shown in Figure 1. It consists of a fluidized bed reactor that is indirectly heated by multiple resonance tubes of one or more pulse combustion modules. Recovered black liquor is fluidized with superheated steam and injected into the reactor. Sulfur and sodium are separated as the majority of the sulfur forms volatile compounds and exits with the gas output stream, whereas the sodium forms various metal salts, mainly carbonates and exits with removed bed solids.

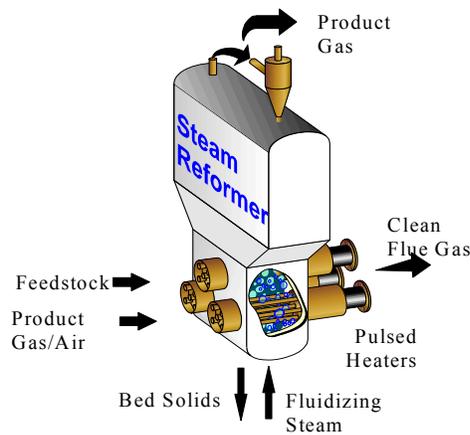


Figure 10.1 Schematic of a MTCI Steam Reformer

As shown in Figure 1, the BLG process input and output streams are easily visualized, and can be summarized as shown in Figure 2. There are four separate input streams and three separate output streams. The input streams consist of the feedstock stream, in this case concentrated black liquor (BL), the bed fluidizing steam, the fuel gas combusted in the pulsed heaters and the air stream required for pulsed heater combustion. The third stream, the fuel gas for combustion in the pulsed heaters, can be natural gas or a recycled fraction of the BLG product gas. The output streams consist of the BLG bed solids, the product gas, and the flue gas from the pulsed heaters.

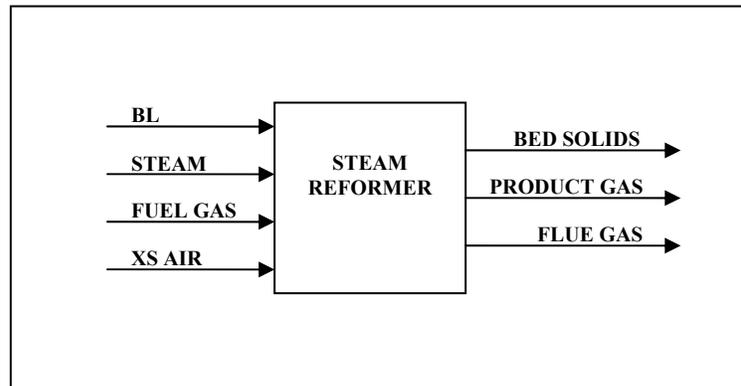


Figure 10.2 Stream structure for BLG model

Although the input and output streams are not complex, the compositions of the BL input stream and the product gas stream certainly are. The black liquor is comprised of all organic and inorganic material recovered from the pulping process, constituting a complex matrix of lignin fragments, cellulose, hemi-cellulose and various ionized inorganic species. The BLG product gas consists of a gas matrix containing all volatile species generated in the steam reforming reactions, as well as minute amounts of dust particles. The remaining streams are made up of either a single compound or simple mixtures.

INTEGRATION OF THE BLG MODEL AND CHEMICAL RECOVERY UNIT OPERATIONS IN WINGEMS

The developed BLG model was used in a full mill simulation case study comparing a conventional kraft process to BLG processes with modified pulping operations using split sulfidity and polysulfide-anthraquinone pulping. The reference kraft process simulation was envisioned as a bleached mixed southern softwood market pulp mill, producing 1000 oven dry metric tons of brown pulp, followed by an ODEopD bleaching sequence. All process unit operations were assumed to be conventional, with commonly accepted input parameters and efficiencies. In the simulated BLG cases, the kraft recovery loop has been modified with a BLG unit replacing the recovery boiler, and subsequent unit operations for syngas clean-up and pulping liquor generation designed for either split sulfidity or PSAQ pulping operations. Recovered black liquor from the pulping process was concentrated in conventional multiple effect evaporators and concentrated to 80% solids. Make-up chemical was added to the concentrated black liquor as salt cake, prior to gasification. In all BLG cases an amine system is used to capture the syngas H_2S , and the generated gasifier bed solids are processed through conventional green liquor recausticizing unit operations. In the BLG case with split sulfidity a portion of the generated green liquor is used to scrub absorb the H_2S captured from the syngas, generating high sulfidity green liquor. This liquor is then causticized in a separate slaker unit prior to being returned to the BLG-SS pretreatment vessel. In the BLG-PSAQ cases, the captured H_2S is put through a Klause process to generate elemental sulfur with the simultaneous release of the major portion of CO_2 that was co-absorbed in the amine scrubber. This elemental sulfur is then added to a portion of the recausticized (now) white liquor, generating very high sulfidity polysulfide liquor which is returned to the pretreatment vessel. The clean syngas is combusted in a gas turbine coupled to a condensing steam turbine to produce the process steam demand while generating power.

WINGEMS CASE STUDIES OF KRAFT-MCC AND BLG WITH SS AND PSAQ PULPING

Four chemical pulping processes were evaluated in separate full mill WinGEMS simulations. Each process represents an individual case in the study, where the kraft-MCC case was used as a reference for comparisons to the different BLG cases. The pulp yields for the simulated processes were based on generated laboratory data (5-7). In all BLG cases, the clean syngas was compressed and combusted in a combined cycle power plant for the production of process steam and power. The simulated unit operations were in general the same in each of the evaluated cases, except for the modifications made to those down stream from the BLG unit, involving gas clean-up and the regeneration of pulping liquors for split sulfidity and PSAQ pulping. Table 10.1 shows an

outlined comparison of the major design differences and some important assumptions between the 4 different cases evaluated in this case study. When estimating the change in process steam demand and power production from the base case to the BLG cases, the following assumptions were made. The base case reference steam demand was met by the steam generated from the recovery boiler, and the overall process is a net consumer of power. In the BLG cases, the difference in steam demand between the base case reference value (~282 mt/hr) and the steam generated from syngas combustion (~19 mt/hr) was overcome through combustion of additional biomass in a hog fuel boiler. The hog fuel demand in the BLG cases was set to meet the process steam demand, resulting in additional power production, above and beyond what was generated in the kraft reference simulation.

Table 10.1 Input parameters and key assumptions for WinGEMS case study

	Kraft Base Case	BLG-SS	BLG-PSAQ2%	BLG-PSAQ3%
Liquor Parameters				
% EA on OD wood	19	19	19	19
Sulfidity	25	25	25	40
Pulping Operations				
Pretreatment	No	Yes (120 °C)	Yes (120 °C)	Yes (120 °C)
Continuous Digester	Yes (170 °C)	same	same	same
Yield Assumptions				
Pulping	45%	47%	47%	48%
Rejects and Spills	8.5% of solids flow	same	same	same
Bleach Plant	5% of solids flow	same	same	same
Power Demand				
Overall Process	Base Case Index = 0	same	same	same
Steam Demand (1000 psig)	282 mt/hr (Met in RB)	282 mt/hr	282 mt/hr	282 mt/hr
Power Generation				
KWh/ODtP	Base case Index = 0	BLGCC	BLGCC	BLGCC
Steam Generation (1000 psig)	Equal to demand	Controlled to BC	Controlled to BC	Controlled to BC

The following discussion addresses the generated output report from the WinGEMS case study. The values for the fiber line calculated from WinGEMS simulation data area shown in Table 10.2. As seen in the table, the total wood feed is altered from case to case to meet the 1000 ODt brown pulp production target. With increasing pulp yields resulting from the integration of BLG and modified pulping technologies, the total wood demand is thus decreased. However, with additional pretreatment and divided sulfur rich and lean streams, the total digester steam demand, as well as total liquor flow is increased. The values for the bleach plant operations are very similar, which should be expected since all pulps are assumed to respond to the ODED bleaching sequence in a similar fashion.

Table 10.2 Comparison of fiber line process parameters for each simulated case

	Unit	Kraft Basecase	BLG-SS	BLG-PS2%	BLG-PS3%
Digester					
Chips	ODtC/day	2424.12	2326.50	2326.57	2278.10
Brown Pulp Produced	ODtP/day	1000.00	1000.00	1000.00	1000.00
Digester Steam	kg/ODtP	1137.33	1227.63	1197.14	1216.28
Pulping Liquor (synthetic)					
Flow	mt/hr	159.63	201.91	191.83	205.51
TTA as NaOH	g/L	151.25	151.26	171.52	179.08
Sulfidity	%	24.97	21.70	21.12	31.95
Bleach Plant (ODED)					
BP Steam	mt/hr	30.47	29.81	30.21	30.06
OWL Flow	mt/hr	19.44	18.87	17.69	17.70
CIO2	mt/hr	0.99	0.99	0.98	0.99
NaOH	mt/hr	0.07	0.07	0.07	0.07
H2O2	mt/hr	0.69	0.70	0.69	0.70
Yield					
Brown Pulp	%	41.25	42.98	42.98	43.90
Bleached Pulp	%	36.52	38.08	38.08	38.89

The corresponding values calculated for the chemical recovery process parameters are shown in Table 10.3. As seen in the table, the increased liquor flow in the BLG cases, coupled with a higher BL solids concentration being fed to the BLG unit, the total steam demand for evaporation and concentration is increased relative to the kraft base case. However, the total flow, and total solids flow to the gasifier unit is lower in the BLG cases, leaving room for extra capacity in situations where the mill is recovery boiler limited. Worth noting is that the total syngas flow from the BLG unit to the gas turbine in the combined cycle power production unit is smaller for the BLG case with 3% PS charge on OD wood. Higher levels of sulfur in the liquor loop will lead to higher volumes of H₂S produced during gasification, which in turn increases the load on the sulfur recovery operations and a smaller amount of syngas available for power production. The greatest effect of BLG integration on the chemical recovery loop is the significant increase on the slaking load, with related increases on the lime kiln and the demand for lime kiln fuel.

The values calculated from the assumptions made around process demand and production of power and steam are shown in Table 10.4. The assumed steam demand for the process was indexed to the total amount of steam produced in the base case from the recovery boiler. This total energy available for steam production was determined from the WinGEMS model as 4.96*10⁶ Mcal/day, producing about 282 mt/hr of 1000 psig steam at 825 °F. In order to meet this steam demand index, the BLG process would have to make the same amount of steam from combustion of generated syngas, or from combustion of additional fuel sources. In this case study, the balance of the required steam was met through combustion of additional hog fuel. The hog fuel demand was controlled to generate the required reference of 282 mt/hr of high grade steam. In addition, the kraft base case was assumed to be a neutral producer of power, neither selling nor buying power to or from the grid. The reference index for power production is thus set to zero, meaning that any power produced in the BLG cases from combined cycle syngas conversion plus additional power generated in the CC steam turbines from the hog fuel boiler heat recovery, would be available for sale to the grid. This net amount of power varies in the BLG cases from 1941.4 to 1834.4 KWh/ODtP produced.

Table 10.3 Comparison of chemical recovery process parameters for each simulated case

	Unit	Kraft Basecase	BLG-SS	BLG-PS2%	BLG-PS3%
Evaporator					
Flow to evaporator	mt/hr	456.16	484.72	475.19	483.44
Solids to evaporator	%	17.35	15.83	16.49	16.47
Dissolved solids to evaporator	kg/ODtP	1899.34	1841.78	1880.54	1910.60
Steam used (evaporated)	kg/ODtP	1436.77	1604.60	1539.44	1567.54
Steam used (concentrated)	kg/ODtP	570.79	811.84	829.11	842.22
Boiler / Gasifier					
Flow to unit	mt/hr	122.73	94.15	95.70	97.53
Solids fired	%	66.29	80.20	80.10	80.17
Dissolved solids to unit	kg/ODtP	1952.53	1812.12	1839.70	1876.50
Amount Inorganic	kg/ODtP	586.63	562.10	588.07	670.31
Amount Organic	kg/ODtP	1365.91	1250.02	1251.63	1206.19
Energy available for Steam	Mcal/day	4.96E+06	2.83E+05	2.74E+05	2.56E+05
Syngas to Gas Turbine	mt/hr	na	47.71	45.47	42.47
Slaker					
Flow	mt/hr	229.45	302.56	289.90	308.24
Returned lime	kg/ODtP	313.01	489.44	497.80	532.84
Fresh lime	kg/ODtP	8.90	5.66	4.10	4.37
Make-up lime	mt/day	8.90	5.66	4.10	4.37
White Liquor make-up					
NaOH (make-up)	kg/ODtP	32.56	25.91	30.91	27.72
Na2SO4	kg/ODtP	14.07	22.26	11.49	19.56
Elemental Sulfur	kg/ODtP	0.00	0.00	0.00	0.00
Kiln					
Throughput	ODt/day	557.92	880.36	895.80	956.92
Fuel consumed	kg/day	55302.59	88577.27	90153.01	95363.40
Losses					
Na, as Na	kg/ODtP	22.48	21.14	22.43	23.22
S, as S	kg/ODtP	2.70	3.36	2.62	4.05
Water Usage					
Brownstock Washer Shwr Make-up	mt/hr	116.47	83.31	96.34	90.76
BP Wash Water	mt/hr	595.89	596.15	596.14	596.16
Dregs Washer	mt/hr	3.22	3.22	3.22	3.22
Mud Filter Mill Water	mt/hr	22.55	22.55	22.55	22.55
Mud Tank Cons. Reg. Mill Water	mt/hr	15.50	24.45	24.88	26.58
Scrubber Mill Water	mt/hr	143.06	175.85	164.47	175.48
Total	mt/hr	753.62	729.68	743.13	739.28

Dollar values based on best available data were assigned to selected operating variables, and the calculated values obtained from the comparative economical analysis between the kraft base case and BLG cases are shown in Table 10.5. The first two columns list the cost variables and their associated values. The remaining columns list the values calculated from data obtained through WinGEMS simulations of the kraft base case, and the three BLG case studies. The % DELTA column shows the calculated percent difference for the cost variables between each simulated BLG case study and the kraft reference. The net cost in the last table row indicates the variable operating cost in each case to produce one oven dry ton of pulp (1 ODtP). As shown in the table, this net cost increases from the kraft base case (\$169/ODtP) by up to 3.9% for the BLG cases with PSAQ pulping (\$176/ODtP). The driving force behind this effect is the increased load on the lime kiln that

Table 10.4 Comparison of power and steam process variables for each simulated case

	Unit	Kraft Basecase	BLG-SS	BLG-PS2%	BLG-PS3%
Steam Users					
Digester Steam	kg/ODtP	1137.33	1227.63	1197.14	1216.28
BP Steam	kg/ODtP	30.47	29.81	30.21	30.06
Green Liqour Heater Steam	kg/ODtP	57.71	103.59	81.71	84.62
MEE (evaporator)	kg/ODtP	1436.77	1604.60	1539.44	1567.54
MEE (concentrator)	kg/ODtP	570.79	811.84	829.11	842.22
BLG unit	kg/ODtP	0.00	352.77	355.92	343.86
Total Steam Demand	mt/day	3233.07	4130.26	4033.55	4084.59
Steam Demand (RB cap)					
Energy Available/Required for Steam	Mcal/day	4.96E+06	2.83E+05	2.74E+05	2.56E+05
Steam Production (1000 psig)					
Recovery Boiler	mt/day	6750.52	0.00	0.00	0.00
Hog Fuel Boiler	mt/day	0.00	6382.69	6394.36	6419.36
Gas Turbine (Syngas)	mt/day	0.00	385.31	373.63	348.64
Total Steam Production	mt/day	6750.52	6768.00	6768.00	6768.00
Power Production					
Recovery Boiler (Base Case net)	Mcal/day	0.00	na	na	na
Gas Turbine (TG) (Syngas)	Mcal/day	na	1669299.00	1663039.88	1577281.69
Condensing Steam Turbine	Mcal/day	697024.79	697024.79	697024.51	697024.85
Total Power Produced	Mcal/day	0.00	2366323.79	2360064.39	2274306.54
Net Power Produced from TG	kWh/ODtP	0.00	1941.40	1934.12	1834.39

Table 10.5 Comparison of case study variable operating cost parameters and net cost per ODtP produced

	Cost (USD)	Kraft Basecase	BLG-SS	% DELTA	BLG-PS2%	% DELTA	BLG-PS3%	% DELTA
Chips/kg	0.062	150.3	144.2	-4.2	144.2	-4.2	141.2	-6.4
NaOH/lb	0.145	10.4	8.3	-25.7	9.9	-5.4	8.8	-17.5
Na2SO4/lb	0.08	2.5	3.9	36.8	2.0	-22.5	3.4	28.1
Fresh Lime/lb	0.055	1.1	0.7	-57.3	0.5	-117.3	0.5	-103.6
Steam used/kg	0.006	19.4	24.8	21.7	24.2	19.8	24.5	20.8
Hog Fuel/kg	0.015	0.0	58.4	100.0	58.5	100.0	58.7	100.0
Kiln fuel/barrel	60	24.4	39.0	37.6	39.7	38.7	42.0	42.0
Water/1000 gal	0.095	1.7	1.7	-3.3	1.7	-1.4	1.7	-1.9
Total		209.7	280.9	25.4	280.7	25.3	280.9	25.4
Steam Produced/kg	0.006	40.5	40.6	0.3	40.6	0.3	40.6	0.3
Power Produced kWh/ODTP	0.035	0.0	67.9	100.0	64.2	100.0	64.2	100.0
Total	0	40.5	108.6	62.7	104.8	61.4	104.8	61.4
Net Cost		169.2	172.4	1.8	175.9	3.8	176.1	3.9

BLG will impose on the chemical recovery operations, combined with the assumption that additional hog fuel must be burned in the BLG cases to meet the process steam demand. These two cost factors, hog fuel and lime kiln fuel, are under the current assumptions a greater negative contributor than all the gains achieved through

BLG integration with respect to decreased wood costs, and the net process power produced from syngas conversion in the combined cycle which is available for sale to the grid. This result changes dramatically if the assumed cost of lime kiln fuel and/or the price of green power sold to the grid is altered. The effect of variable lime kiln fuel (oil) prices has been illustrated in Figure 10.3. The plotted graphs represent the net variable operating cost per OD ton pulp produced, calculated at different cost levels of lime kiln fuel while keeping all other cost factors constant. As seen in the figure, the relative effect of increasing fuel price on the process net variable operating cost is greater in the BLG cases compared to the MCC reference. This is an expected outcome, as the BLG cases require a greater volume of kiln fuel. More importantly, the graph clearly shows that the net variable operating cost for the BLG processes are lower than that of the MCC at lower fuel costs. The break even points for the SS and PS2% processes compared to the MCC process is at a fuel price of about \$47/barrel. The corresponding value for the PS3% process is about \$38/barrel. These results suggest that the negative effects on variable operating costs for BLG processes, stemming from an increased lime kiln load, could be overcome if a less expensive fuel alternative was available. The value used in the initial analysis was based on current market price and assumed to be \$60/barrel, well above the estimated break even points.

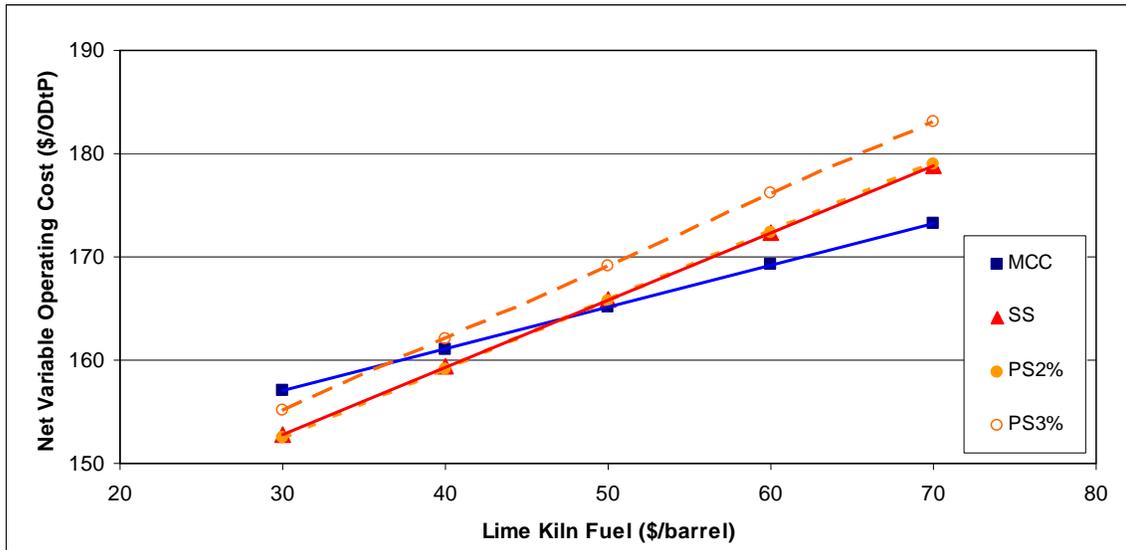


Figure 10.3 The effect of lime kiln fuel price on net variable operating cost, keeping all other cost factors constant (assuming green power sales price at \$3.5/KWh)

A similar analysis was performed to explore the effect of sales price of power generated in combined cycle operations and sold to the grid. The net variable operating costs were calculated by varying the power sales price and keeping all other cost factors constant. The calculated values for each simulated case are shown in Figure 4. The basic assumption around power consumption/production for the kraft-MCC process was that the reference mill was a neutral user/producer of power, and a change in power sales price would have no effect on the net variable operating cost for the MCC case. Thus, the blue line in the figure, representing the MCC case is flat over the explore range of power sales prices, whereas the calculated values for the BLG cases are highly sensitive to changes in the power sales price. The initial assumed price for power sold to the grid (\$3.5/KWh) was based on current market conditions, and at this level, the MCC process has a lower calculated net variable operating cost. However, as the sales price is increased the effect on the BLG cases net variable operating costs is dramatic and positive. In the current model, if the power sales price is increased from 3.5 to 6 \$/KWh, the net variable operating costs would decrease by about \$40/ODtP, with even greater cost savings realizable at higher power sales prices.

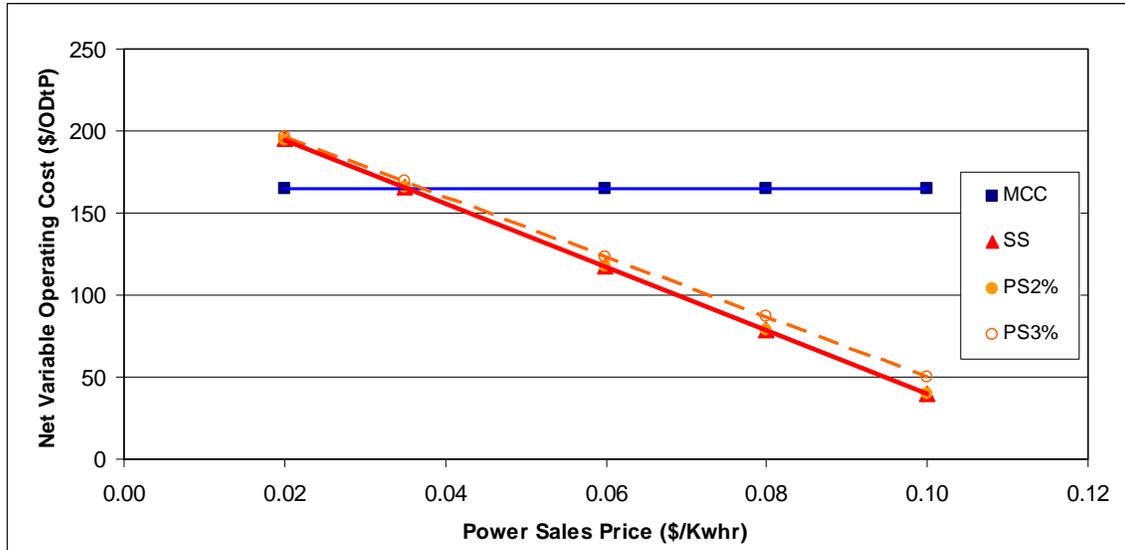


Figure 10.4 The effect of green power sales price on net variable operating cost, keeping all other cost factors constant (assuming lime kiln fuel price at \$60/barrel)

CONCLUSIONS

The overall conclusion from this simulation case study is that BLG integration into the kraft process is highly dependent on the price of lime kiln fuel and the price and amount of power produced from BLGCC conversion of syngas. Under the initial assumptions made in this case study, the significantly increased load on the lime kiln is not overcome by the benefits realized in pulping operations through the introduction of modified pulping technologies, nor by the additional revenue generated from the generation and sale of green power. However, if modifications could be made to the recausticizing unit operations, such as high sulfidity green liquor pretreatment, offloading the slaker and resulting load on the lime cycle, this would change. Another such approach would be auto-causticization in the white liquor stream. Also, as indicated in figures 10.3 and 10.4, if the lime kiln fuel cost is decreased or the power sale price increased, the BLGCC kraft process with split sulfidity or PSAQ pulping becomes a more economically favorable alternative than the conventional reference kraft process, based on variable operating costs. When comparing the BLG cases to the MCC reference, the net variable operating cost break even point based on lime kiln fuel cost is about \$47/barrel for the SS and PS2% processes, and about \$38/barrel for the PS2% process. This is significantly lower than assumed kiln fuel price of \$60/barrel used in this work. If the sales price for power to the grid was increased from 3.5 to 6 ¢/KWh cost savings of about \$40/ODtP could be realized in all BLG processes.

FUTURE WORK

Future work should be focused on exploring the effects of alternative pulping processes such as auto-causticization and mini-sulfite sulfite – anthraquinone pulping and the overall improvement on net variable operating costs that could be realized. More work should also be done in the area of combined cycle simulation in WinGEMS, as well as improvements in the BLG WinGEMS model.

REFERENCES

- 1) Lindstrom, M., Kirkman, A., Jameel, H. et al., Proc. TAPPI Fall Technol. Trade Fair pp. 1417-1429 (2002)
- 2) Consonni, S., Larson, E.D., Katofsky, R., Proc. ASME Turbo Expo 7: 1 (2004)
- 3) Consonni, S., Larson, E.D., Katofsky, R., Proc. ASME Turbo Expo 7: 15 (2004)
- 4) Lindstrom, M., Naithani, V., Kirkman, A., Jameel, H., "The Development and Validation of a Low-temperature Black Liquor Gasifier Model for Use in WinGEMS[®] TAPPI J. Vol. 5 No. 2 (2006) p.24

- 5) Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H.; "*Effects on Pulp Yield and Properties Using Modified Pulping Procedures Involving Sulfur Profiling and Green Liquor Pretreatment*"; Presented at 2004 Tappi Fall Technical Conference, Atlanta, GA, 2004
- 6) Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H. "*The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Properties*"; Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference; TAPPI Press: Atlanta, GA, 2005.
- 7) Lindstrom, M., Naithani, V., Kirkman, A., Jameel, H., "*The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Delignification* ", Proceedings TAPPI 2006 Engineering, Pulping and Environmental Conference, Atlanta, GA, (2006).

11 INTEGRATING BLACK LIQUOR GASIFICATION AND PULPING AND A REVIEW OF CURRENT TECHNOLOGY

Lindström, M; Jameel, H; Naithani, V; Kirkman, A; Renard, J; *"Integrating Black Liquor Gasification and Pulping; A Review Of Current Technology"*; IN. Materials, Chemicals and Energy from Forest Biomass, ACS Symposium Series, Argyropoulos, D. S., Ed.; Washington, ACS Books, 2006. (in Print, Scheduled for Public Release Dec 2006)

INTEGRATING BLACK LIQUOR GASIFICATION AND PULPING AND A REVIEW OF CURRENT TECHNOLOGY

Mathias Lindström, Hasan Jameel*, Ved Naithani, Adrianna Kirkman, and Jean Renard

Department of Forest Biomaterials Science and Engineering,
North Carolina State University, Raleigh, NC 27695-8005, USA

Gasification of black liquor could increase the flexibility and improve the profit potential of the paper industry. Its implementation would enable the application of modified pulping technologies, while creating a synthetic product gas that could be utilized in the production of value added products or electrical power. Black liquor gasification produces output streams that can be used with great benefit in modified pulping operations. Split sulfidity and polysulfide modifications to the kraft process lead to yield increases of 1-3% points with improved product quality. Modified sulfite pulping technologies resulted in yield increases of 5-18% points with much higher brightness and significant capital and operating cost savings.

Introduction

Biomass can be converted to power and/or fuels using a variety of technologies based around direct combustion, gasification and pyrolysis. In direct combustion, the amount of oxygen provided has to be sufficient for the efficient conversion of the carbon to carbon dioxide. In gasification the amount of oxygen is limited in order to produce a medium to low calorific gas, and in pyrolysis the biomass is heated to a very high temperature with limited oxygen to produce a mixture of gases and liquids with medium heating value.

One source of biomass that has typically been burned in a boiler to produce steam is black liquor, a by-product from the pulping process. Black liquor gasification (BLG) has some inherent advantages compared to the traditional combustion process. The efficiency of combustion is dependent on the mixing that occurs between the combusted material and oxygen, and gases burn more efficiently than either liquids or solids due to the improved contact between the oxygen and the fuel. In addition, the synthesis gas or syngas generated from gasification can be burned in a gas turbine. This is advantageous as the gas turbine can convert energy to electricity much more efficiently than a steam turbine, as used in a conventional chemical recovery system. The syngas can also be converted to other fuels, chemicals and materials via a wide range of proven chemical processes.

Presently, in a typical chemical pulp mill the black liquor is concentrated to greater than 65% dissolved solids and burned in a recovery boiler. The pulping chemicals are recovered in the smelt and the heat energy is converted to steam, which is used in a steam turbine generator to produce electricity. The typical thermal efficiency of a recovery boiler is generally 65-70%, and the thermal efficiency of the Rankine cycle for the conversion of steam to electricity varies from 30-38%, depending on the temperature and pressures of the different streams in the cycle. These values result in an overall system thermal efficiency of about 23% (1). On the other hand, if the black liquor is gasified, the syngas can after cleanup be combusted in a combined cycle for production of electricity. Combined cycle power generation entails the sequential utilization of a gas turbine followed by a steam turbine. The fuel gas is first burned in a gas turbine to produce electricity. The hot exhaust gas from the turbine is then passed through a heat exchanger to produce steam which is then used in a power-producing steam turbine. Implementing a gasifier with combined cycle cogeneration of power will increase the electricity production of the mill. A conventional steam cycle produces about 120-180 kWh/ton of steam, but a gasifier along with combined cycle power generation has the potential to generate 600-1000 kWh/ton of steam (2). Such a production of power would turn a pulp mill into a net exporter of electricity, and this potential is main motivation for the implementation of black liquor gasification.

In addition to the increased energy efficiency, gasification of black liquor has several other benefits relative to the traditional combustion recovery process. BLG process operation is inherently very stable and also flexible with regard to feed stock and load requirements. It is possible to process most any biomass material and stable operation can be maintained despite upset feed stock flows, even complete interruptions. BLG has

the potential to revolutionize the chemical recovery cycle and, through the separation of sodium and sulfur, enable the utilization of modified pulping technologies. These pulping technologies will increase yield or reduce wood demand, improve product quality, decrease chemical usage and more importantly simplifying the chemical recovery process. A simplification of the chemical recovery process will decrease the operating and capital cost for recovery. BLG would also decrease the malodor associated with the kraft process. Besides power generation, the resulting syngas can be used to generate bio-derived liquid fuels, bio-derived chemicals for the synthetic chemical and pharmaceutical industries, as well as H₂ for use in fuel cells.

Despite these benefits and opportunities, high capital cost and risk associated with new process implementation are impeding the implementation of BLG technologies in the industry. The synergy between BLG as increased energy generator and enabler of advanced pulping processes should increase the financial attractiveness of the realization of these new process concepts. Based on these observations, this paper will address the following topics:

- Review of BLG technologies and their status
- Review of modified pulping technologies enabled by BLG
 - Split sulfidity pulping
 - Polysulfide pulping
 - Alkaline sulfite with anthraquinone (AS-AQ)
 - Mini-sulfite sulfite pulping with anthraquinone (MSS-AQ)
- Effects on process economics of BLG implementation

The effects on overall process economics of enhanced power production and modified pulping technologies will then be discussed, and how the combined implementation of BLG with these technologies can improve the financial attractiveness of the BLG technology.

Black Liquor Gasification Processes

Figure 1 describes the typical process elements included in the gasification of black liquor. The black liquor is initially introduced into a process vessel, the black liquor gasifier, which can either be pressurized or operate under atmospheric pressure. In general terms, the process involves the conversion of hydrocarbons and oxygen to hydrogen and carbon monoxide while forming separate solid and gaseous product streams.

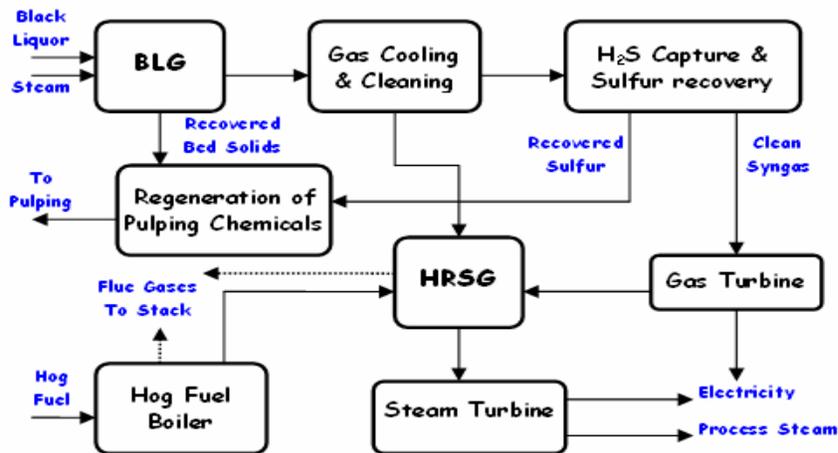


Figure 11.1 Simplified representation of BLGCC power/recovery systems

The inorganic material, including all sodium salts, leaves as a bed solid or smelt depending on the gasifier operating temperature. The bed solids or smelt is then slaked and recausticized to form a caustic solution. The volatiles, including most of the reduced sulfur species, leave as a syngas of medium BTU value. The major components of the syngas are H₂S, CO₂, CO, H₂O, and H₂. To prepare the syngas for other applications and to regenerate the pulping liquor, all sulfur must be separated from the syngas and then dissolved into the caustic solution prepared from the bed solids. The clean product gas is burned in a gas turbine and the hot flue gases are combined and used to generate steam in heat recovery steam generators (HRSGs). This steam is then used in a steam turbine and other process applications.

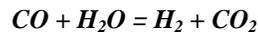
A review of the development of alternative recovery technologies to the Tomlinson recovery boiler has been given (3). The following discussion will focus on the gasification processes currently in commercial operation. Black liquor gasification technologies can be classified by the operating temperature (4). High temperature gasifiers operate at about 1000°C and low temperature gasifiers operate at less than 700°C. In the high temperature gasifier, the inorganic material form a smelt and leave in the molten form, while in the low temperature system, they leave as solids. The fuel value of the syngas produced is also dependent on the gasifying technology. Typically, gasification produces a fuel gas with heating values of 3-4 MJ/Nm³ using air and 89 MJ/Nm³ using oxygen (5).

Low Temperature Gasifier/Steam Reformer

The development of low temperature fluidized bed gasifiers is being pursued by ThermoChem Recovery International (TRI) in the USA and by ABB in Sweden. The TRI system uses steam reforming to generate the product gases. As opposed to exothermic incineration or combustion technologies, steam reforming is an endothermic process. The steam reforming vessel operates at atmospheric pressure and at a medium temperature. The organics are exposed to steam in a fluidized bed in the absence of air or oxygen with the following reaction:



The carbon monoxide produced in this first reaction then reacts with steam to produce more hydrogen and carbon dioxide.



The result is a synthesis gas made up of about 65% hydrogen. The TRI Steam Reformer technology, as shown in Figure 2, consists of a fluidized bed reactor that is indirectly heated by multiple resonance tubes of one or more pulse combustion modules. Black liquor is directly fed to the reactor, which is fluidized with superheated steam. The black liquor uniformly coats the bed solids, producing a char and volatile pyrolysis products which are steam cracked and reformed to produce a medium BTU gas. The residual char retained in the bed is more slowly gasified by reaction with steam. The sulfur and sodium are separated in that the sulfur becomes part of the gas stream and the sodium stays in solid form. Bed temperatures are maintained at 605-610 °C, thereby avoiding liquid smelt formation and the associated smelt-water explosion hazards.

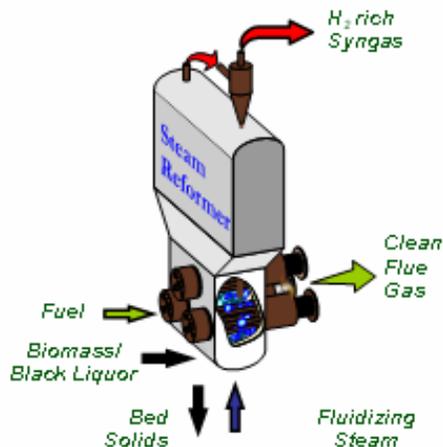


Figure 11.2 Schematic of MTCI Steam Reformer

Product gases are routed through a cyclone to remove the bulk of the entrained particulate matter and are subsequently quenched and scrubbed in a Venturi scrubber. A portion of the medium-Btu product gases can be supplied to the pulse combustion modules, and the combustion of these gases provides the heat necessary for the indirect gasification process. Low temperature gasification leads to complete separation of the sulfur and sodium in kraft black liquor to the gas and solid phase, respectively. Bed solids are continuously removed and mixed with water to form a carbonate solution. The inorganic chemical in the bed solids as well as the sulfur from the gas stream are recovered and used as cooking liquors for the mill. The product gas residence time in the fluid bed is about 15 seconds because of the deep bed (20 ft) used, while the solids residence time is about 50 hrs. These conditions promote extensive tar cracking and carbon conversion. In summary the steam reforming reactor vessel has three inputs; fluidizing steam, black liquor, and heat, and has three outputs; bed solids, hydrogen rich product gas, and flue gas (6).

High Temperature Gasifier

High temperature gasification stems from work initiated by SKF in the 1970s. The original patent for the technology was issued in 1987 and it has since been developed through a sequence of demonstration projects. The gasifier, as developed by Chemrec, is a refractory-lined entrained-flow reactor. In high temperature gasification (900-1000 °C), concentrated black liquor is atomized, fed to the reactor and decomposed under reducing conditions using air or oxygen as the oxidant. The initial chemical reactions involve char gasification and combustion and are influenced by physical factors like droplet size, heating rate, swelling, and the sodium and sulfur release phenomena. The resulting products, smelt droplets and a combustible gas, are then brought into direct contact with a cooling liquid in a quench dissolver. The two phases are separated as the smelt droplets dissolve in the cooling liquid forming green liquor. The exiting product gas is subsequently scrubbed and cooled for use in other unit operations. The split of sodium and sulfur between the smelt and gas phase is dependent on the process conditions. Typically, most of the sulfur leaves with the product gas and essentially all of the sodium with the smelt (7-9).

Current Status of BLG Technologies

The TRI steam reformer has been installed in two locations in North America, at the Norampac Mill at Trenton and the Georgia Pacific Mill at Big Island. The Trenton mill produces 500 tpd of corrugating medium using a sodium carbonate based pulping process. Prior to the start-up of the low-temperature black liquor gasifier in September 2003, the mill had no chemical recovery system. For over forty years the mill's spent

liquor was sold to local counties for use as a binder and dust suppressant on gravel roads. This practice was discontinued in 2002. The capacity of the spent liquor gasification system is 115 tpd of black liquor solids, and the syngas is burned in an auxiliary boiler (6).

Georgia-Pacific's mill at Big Island, Virginia, produces 900 tpd of linerboard from OCC and 600 tpd of corrugating medium from mixed hardwoods semi-chemical pulp. Like the Trenton mill, the Big Island mill uses a sodium carbonate process. In the past, the semi-chemical liquor was burned in two smelters providing chemical recovery but no energy recovery. Instead of replacing the smelters with a traditional recovery boiler Georgia-Pacific decided to install a low temperature black liquor gasification process. One difference between the two systems is that unlike Trenton, Big Island burns the generated product syngas in the pulsed combustors, so the product gas exiting the reformer vessel is cleaned prior to combustion (6).

The evolution of the high temperature gasifier has taken the technology from an air-blown process near atmospheric pressure to a high pressure (near 30 atm.) oxygen-blown process. Benefits realized through high pressure oxygen-blown operation are higher efficiencies, higher black liquor throughput and improved compatibility with down stream unit operations such as combined cycle power generation.

An air-blown pilot plant at Hofors, Sweden, was developed to verify the possibility of gasifying black liquor using an entrained-flow reactor operating at 900-1000 °C. The project showed that green liquor of acceptable quality could be generated; and the plant was dismantled in 1990. The Frövi, Sweden plant was designed as a capacity booster for the AssiDomän facility and was operated from 1991 to 1996, demonstrating the potential for black liquor gasification at a commercial scale. During its operation several technical problems were encountered and addressed. The identification of a suitable material for the refractory lining remained a problem. A subsequent commercial project was initiated in 1996 at the Weyerhaeuser plant in New Bern, North Carolina. The black liquor gasifier was more or less a scale-up of the Frövi plant, designed for a capacity of 300 tons of dissolved solids/day. In 1999 the process maintained greater than 85% availability. However, over the course of the project the plant experienced several technical problems, mainly related to the refractory lining, and it was shut down after cracks in the reactor vessel were discovered in 2000. After detailed studies and re-engineering, the gasifier operation at New Bern was resumed in the summer of 2003 (7). During the rebuild, it was retrofitted with spinel refractory materials developed at Oakridge National Labs in cooperation with other partners. The refractory material is in its second year of operation. The gasifier can burn up to 730,000 lb/day of solids or about 20% of the mill production (10). The syngas generated in the gasifier is currently burned in a boiler.

A pressurized air-blown demonstration project was established at the Stora Enso plant at Skoghall, Sweden, in 1994. The project showed the capability of a pressurized system to generate acceptable quality green liquor while maintaining high carbon conversion ratios. The process was converted to an oxygen-blown operation in 1997 resulting in a capacity increase of more than 60%. A second pressurized demonstration plant was completed in Piteå, Sweden, in 2005. The purpose of the project is to demonstrate high pressure operation (near 30 atm.) with associated gas cooling and sulphur handling unit operations required for a full-scale BLG process. Funding has been obtained for a scale-up project of the Piteå facility. The plant is designed for a capacity of 275-550 tDS/day and encompasses all the required unit operations, including the power island, for a BLG process with combined-cycle power generation (7).

BLG – The Cornerstone of the Biorefinery

The integrated forest biorefinery is a concept which, if implemented, has the potential to dramatically change the pulp and paper industry. The conversion of existing pulp mills into biorefineries is a natural progression when trying to realize the full potentials in the by-product streams from pulp and paper making. It is also a promising option for increasing the return on investment in an energy- and capital-intensive industry. The gasification of black liquor and biomass presents the best option for the generation of high value products from what today is essentially process waste (11). It is an inherently stable yet highly flexible technology that can be designed and sized according to the needs and requirements of individual mills. It allows for the recovery of any spent pulping liquor, and enables the generation of a wide array of liquors that can be used to optimize pulping chemistry, pulp yield and properties. It can be coupled with various other unit operations to

generate power or feedstocks for liquid fuels and bio-chemical processes, and even hydrogen for utilization in fuel cells. It is environmentally superior to current recovery boiler technologies and presents a carbon-neutral source for power generation and synthetic products. BLG is an enabler of the biorefinery and the technologies it encompasses (12).

The underlying fundamental for implementation of any new technology is the impact it will have on the overall process economics. Some deciding factors that will influence the implementation of BLG involve the cost-benefits associated with power generation and other high-value products that can be derived from the syngas. Another area of importance is the potential cost-savings that can be realized through process modifications and optimization. The effect on wood, chemical and fuel demand from changes in the pulping process can have a significant effect on the variable operating cost, capital investment and maintenance costs. Therefore, research exploring the impact of BLG on pulping technologies will be of great importance for the eventual implementation of this technology.

Pulping Technologies Enabled by BLG

The implementation of black liquor gasification into the Kraft recovery cycle would present several opportunities and potential benefits regarding pulp mill operation and process economics. Using black liquor gasification, the recovered entities of sodium and sulfur can be split into two separate fractions with varying degrees of separation dependent on the operating conditions and the technology used. The separation of these chemicals creates some opportunities in the pulping process which can be employed to increase the pulp yield, extend delignification and improve product quality. The following modified pulping technologies can be used in combination with black liquor gasification to realize these potential benefits:

- Split Sulfidity Pulping
- Polysulfide Pulping
- Alkaline Sulfite Pulping
 - Alkaline Sulfite- AQ (AS-AQ)
 - Mini-Sulfite Sulfide AQ Process (MSS-AQ)

Split Sulfidity Pulping

Modified kraft pulping processes have gained widespread acceptance, because they can be used to either extend delignification or to enhance the yield and pulp properties at a given kappa number. The basic principles of modified extended delignification consist of a level alkali concentration throughout the cook, a high initial sulfide concentration, low concentrations of lignin and Na^+ in the final stage of the cook, and lower temperature in the initial and final stages of the cook (13). BLG would enable a mill to generate a high sulfidity liquor which can be used to provide a high sulfide concentration during the initial phase of the cook. Figure 3 shows the basic concept design for generating liquors of different sulfide concentrations.

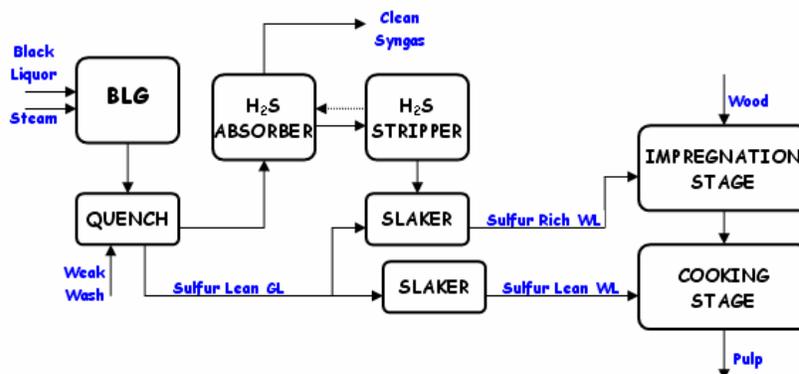


Figure 11.3 Schematic of unit operations in split sulfidity pulping

In split sulfidity pulping, it would be necessary to generate two streams of white liquor – one that is sulfide rich and another that is sulfide lean. Sulfur profiling would be the lowest capital cost process to implement to modify the pulping process especially for mills with a modified continuous or batch pulping process.

The concept of sulfur profiling, or split sulfidity pulping, employing a sulfur rich stream in the rapid initial phase, followed by a sulfur lean stream in the bulk and residual phase, has been investigated as a method for extending delignification or increasing yield (14-18). Compared to conventional kraft cooks of similar H-factor, split sulfidity pulping has been shown to enhance selectivity of the pulping reactions, resulting in increases in both lignin removal and pulp viscosity. Moreover, split sulfidity pulping has been shown to increase pulp yield and strength properties (19-21).

The effects of multiple stage cooking using sulfur profiling, has also been studied. The process showed a significant improvement in selectivity (22,23). Increased sulfide sorption resulted in both higher lignin-free yields and increased viscosities. At 30% overall sulfidity, the lignin-free yield was 0.6 to 0.9% higher and viscosity 8.89 to 10.4 mPa higher than conventional kraft. At increasing overall sulfidities, the yield advantage was reduced. Screened yield increased only slightly with higher sulfidity levels during impregnation. Similar findings were reported in subsequent work (24). Pulping work conducted at STFI found that sorption of sulfide increases with increasing hydrosulfide concentration, time, temperature and concentration of positive ions, but decreases with an increasing concentration of hydroxide ions (25). The potential for modifying softwood kraft pulping, by sulfur profiling has also investigated, where all of the sulfide was added to the beginning of the cook, a high hydrosulfide concentration could be maintained both in the initial phase and near the transition point from the initial to the bulk delignification phase (26).

The work described above is difficult to implement in a mill that utilizes conventional recovery technologies. However, BLG generates separate streams of sulfur and sodium, which will allow for independent sulfur and alkali profiling. Thus, the alkali profile can be adjusted independent of the sulfur concentration at any point in the cook. These opportunities were investigated at NC State University, exploring split sulfidity pulping of southern pine with different initial alkali concentrations. Based on a modified continuous cooking (MCC) laboratory procedure, different approaches were devised to explore split sulfidity and different initial alkali profiles (27,28). Two levels of initial alkali were investigated where a fraction of the available hydroxide was charged in the initial stage. The low initial alkali procedure used 11% of the alkali; and the corresponding value for the high initial alkali procedure was 33%.

The effects of split sulfidity and different levels of initial alkali on delignification and total pulp yield are presented in Figure 4. As shown, split sulfidity pulping produced lower kappa pulps at similar H factors relative the MCC procedure. The high initial alkali cooks generated pulps of lower kappa number compared to those of low initial alkali. The split sulfidity procedures produced pulp yields 1-2% greater than the MCC procedure, and the difference is more pronounced at higher kappa. Since the high initial alkali approach

produced higher yields and lower kappa numbers than the low initial alkali approach, this would be the preferred option. At similar kappa numbers the split sulfidity pulps had viscosities 5 to 10 cps greater than those of the MCC pulps. The high initial alkali pulps produced higher tensile and burst index values relative the MCC pulps at a similar tear index. The MCC pulps were slightly easier to refine relative to the split sulfidity pulps.

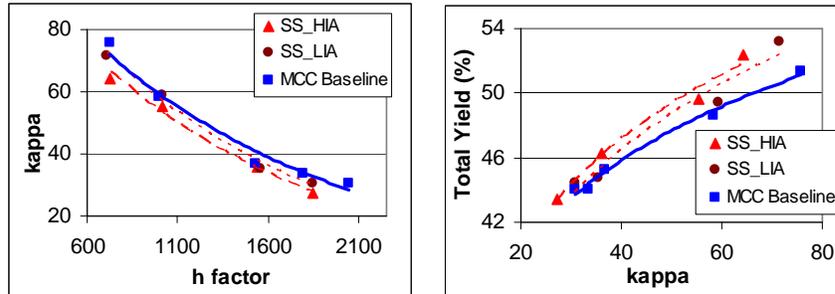


Figure 11.4 Delignification and yield results for split sulfidity pulping

The co-absorption of H_2S and CO_2 during the scrubbing in sulfur recovery, results in the production of $NaHCO_3$. During recausticization all sodium exiting the gasifier will be converted to $NaOH$. The conversion of $NaHCO_3$ to $NaOH$ requires twice as much lime compared to the conversion of $NaCO_3$ to $NaOH$. Thus, there is a two-fold increase in the amount of lime required to produce an equivalent amount of $NaOH$, and as a result, BLG will increase the overall causticization load.

The potential for in-situ causticization within the gasifier could dramatically affect the load on the recaust cycle and lime kiln. In current recovery operations, the sodium carbonate obtained from the slaking of the boiler smelt is converted to sodium hydroxide using calcium oxide. The byproduct calcium carbonate is then calcined in large rotating kilns to regenerate the calcium oxide. A 1000 ton per day pulp mill will use about 100,000 barrels of fuel oil per year to fire its lime kiln. Through novel chemistries it may be possible to carry out the causticization reactions directly within a black liquor gasifier. This could potentially eliminate the need for the lime cycle and the associated fuel costs (29).

Another alternative to in-situ causticization, avoiding the increase in causticization requirements, would be to pre-treat wood with green liquor. Previous work has demonstrated the feasibility of using green liquor in the impregnation stage, without increasing overall chemical usage (15,21). It has also been shown that the amount of sulfur adsorbed during the pretreatment decreases with higher $[OH^-]$ (30). By impregnating chips with high sulfidity, low pH liquor, a mill may enhance yield and further decrease the causticizing load. Figure 5 outlines the unit operations for a possible green liquor pretreatment process in conjunction with BLG.

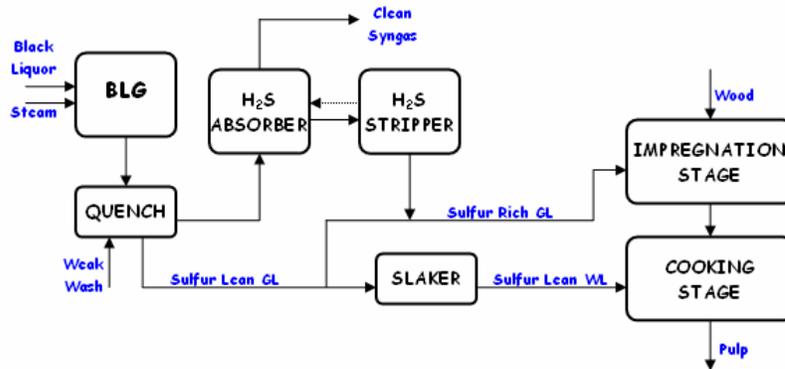


Figure 11.5 Outline of process using green liquor pretreatment

Comparing green liquor pretreatment and kraft pulping, the greatest relative cost-benefit from a decrease in causticization using green liquor pretreatment would be achieved in a situation where the level of TTA was the same in both processes. This requires that similar pulp kappa numbers must be attainable through both processes at the same TTA charge. Green liquor pretreatment pulping has been investigated (28). Pulping results show that green liquor pretreatment would return pulps of higher kappa at the same level of total titratable alkali, as shown in Figure 6. However, as shown in the figure it would be possible to achieve similar kappa number at the same level of system TTA by pulping to a higher H factor. Another option for decreasing the kappa number would be to increase the system TTA. Experiments performed with a 10% increase in TTA, labeled Hi-TTA, also resulted in a higher kappa number than the MCC baseline. In this study, if the TTA is increased by 20% the active alkali is the same in both processes, and the no causticizing benefits exist. The resulting pulp yield did not show any improvement with green liquor pretreatment, but the green liquor pretreated pulps had higher viscosity. These results did not show the yield benefit reported elsewhere, and may be the result from differences in pulping procedures (21).

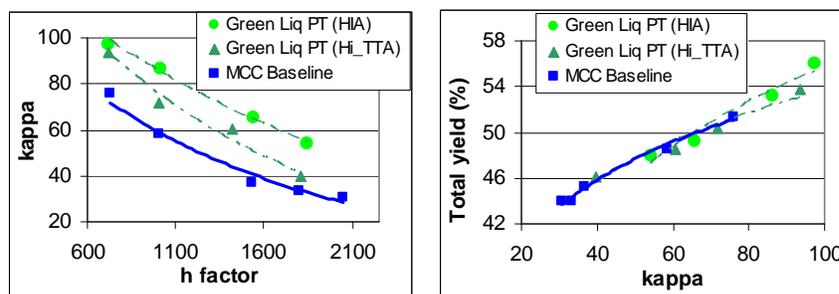


Figure 11.6 Obtained results for pulping using green liquor pretreatment

Polysulfide Pulping with Anthraquinone

The effect on pulping chemistry of polysulfide (PS), often in conjunction with anthraquinone (AQ) as additives to the Kraft process, has been explored for some time (31-36). Its effectiveness has been established, and it is typically reported that each percent of PS added increases the pulp yield by one percent (37,38). However, efficiently generating high concentrations of PS within the Kraft chemical recovery cycle is difficult. There are currently three primary competing processes available for PS generation, Chiyoda, MOXY™ and Paprilox® (39). These processes, in general terms, produce pulping liquors with PS concentrations of five to

eight grams per liter and PS selectivities ranging from 60 to 90 percent (40-43). This results in a PS limit of about 1% PS charge on oven dry wood for a mill operating at 25% sulfidity. However, a chemical recovery system based around BLG would allow for different pathways to generate PS liquors which would enable for higher charges of polysulfide. In addition, the separation of sodium and sulfur would allow for alkali profiling in conjunction with PS utilization. Figure 7 shows a schematic of PS process unit operations with BLG.

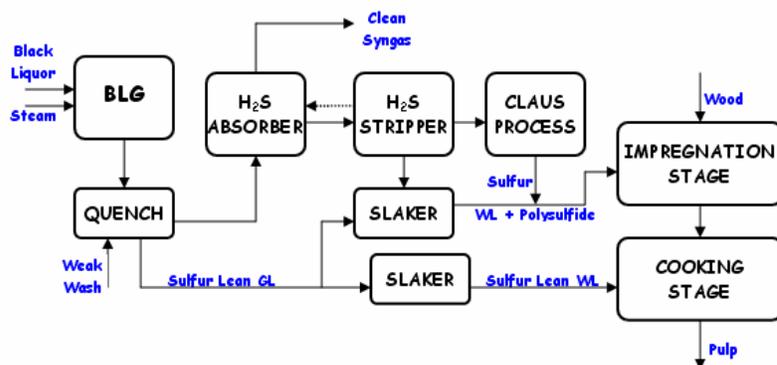


Figure 11.7 Outline of process using polysulfide

Research efforts in the area of PS have generally been in one of two major areas; work on PS pulping associated with PS utilization in Kraft process operations and/or associated PS generation technologies (40-47) and work investigating optimum parameters for PS pulping (48-50).

A smaller area of work has been based around the potential implementation of BLG and the opportunities created by the unrestricted management of sulfur and sodium as separate entities. The splitting of sulfur and sodium enables the application of polysulfide, sodium sulfide and sodium hydroxide independently of each other. Two processes have been described based on this concept. The ZAP process (Zero effective alkali in pretreatment), entails a two-stage pulping procedure, where the sulfur containing cooking chemicals (Na_2S and PS) were charged along with AQ to the wood in the pretreatment stage (51). In the subsequent cooking stage NaOH was added and the temperature increased. The obtained results using PS without AQ, indicate a potential yield benefit of 1% relative to conventional PS pulping at kappa 30. With the addition of AQ the yield benefit was increased to 1.5-2%. Additional results indicate even greater yield benefits at kappa 90. A different procedure called hyperalkaline polysulfide pulping has been suggested (52). The process utilizes two pretreatment stages followed by a cooking stage. In the first stage, alkali is charge to the wood at elevated concentrations, neutralizing the acids formed during the temperature elevation. PS is then charged in the second stage, followed by the cooking stage. The process resulted in a higher delignification rate, increased pulp viscosities and yield improvements of 1.5% as compared modified pulping without PS. Worth noting is that the bleachability and measured tear strength of the hyperalkaline PS pulps were similar to those of the Kraft reference pulp.

In addition to the capability for independent profiling of NaOH and PS, the implementation of BLG would allow for the conversion of all the sulfur in the cooking liquor to PS. This would enable higher PS charges than available through conventional technologies. The total amount of sulfur that is available is dependent on the sulfidity of the pulping liquor. Table 1 illustrates this balance displaying two examples of the partitioning of the total sulfur available in the system at 25 and 40% sulfidity. As seen in the table, PS charges slightly exceeding 2 % on wood is possible at 19.5% AA with 25% sulfidity. To enable higher PS charges the sulfidity must be increased and as shown in the table the corresponding value at 40% sulfidity is between 3 and 4% PS on wood.

Table 11.1 Demonstration of sulfur utilization as Na₂S (kraft) or Na₂S/PS (kraft-PS) and the system sulfur availability for PS generation

Cook Procedure	25% Sulfidity			40% Sulfidity		
	Tot. avail. Sulfur (S) (kg/ton)	S req. for PS (kg/ton)	S avail. as Na ₂ S (kg/ton)	Tot. avail. Sulfur (S) (kg/ton)	S req. for PS (kg/ton)	S avail. as Na ₂ S (kg/ton)
MCC	25.2	0	25.2	40.3	0	40.3
1% PS	25.2	10.0	15.2	40.3	10.0	30.3
2% PS	25.2	20.0	5.2	40.3	20.0	20.26
3% PS	25.2	30.0	- 4.8	40.3	30.0	10.3
4% PS	25.2	40.0	- 14.8	40.3	40.0	0.3

The effects of pulping southern pine with higher PS charges and alkali profiling was evaluated at NC State University. Table 2 shows a summary of the yield increases that were measured at various PS charges and sulfidities. At 40% sulfidity the impact of alkali profiling in the initial stage was also evaluated. Three different levels of alkali were investigated. In the low initial alkali (LIA) cook, 56% of the alkali was charged to the impregnation stage. The corresponding values for the medium initial alkali (MIA) was 65% and for the high initial alkali (HIA) 75%. The flexibility to optimize the alkali profile and PS use would only be possible in combination with BLG (53).

Table 11.2 Total yield improvement from PS procedures compared to 25% S MCC pulp

Cook ID	Estimated Yield at 30 kappa	Yield Improvement (% pts.)	Average Viscosity (cps)
MCC 25% S	45.2	n.a.	39.1
1% PS 25% S	47.7	2.4	38.6
2% PS 25% S	48.1	2.9	38.0
Cook ID	Estimated Yield at 30 kappa	Yield Improvement (% pts.)	Average Viscosity (cps)
1% PS 40% S LIA	46.7	1.5	49.5
2% PS 40% S LIA	47.3	2.1	51.6
3% PS 40% S LIA	47.4	2.2	55.7
3% PS 40% S MIA	48.9	3.7	47.7
3% PS 40% S HIA	45.8	0.6	46.7

At 25% sulfidity the kappa numbers with PSAQ were comparable to the MCC reference. The yield benefit was about 2% for a 1% PS charge, and about 3% for a 2% PS charge. At 40% sulfidity the kappa number decreased with increasing PS charge, and increasing levels initial alkali. The level of initial alkali had a significant effect on the yield. There is indication of an optimum condition for initial alkali charge, where too great or too low of an initial hydroxide concentration negatively affects the pulp yield. The work exploring MIA and HIA indicates that there exists a maximum in yield benefit as a function of initial alkali concentration. In the ZAP process using PSAQ a yield benefit of about 6% at 30 kappa was reported, where the initial alkali charge in the PS pretreatment stage was zero (50). They also showed that a minimum yield condition exists at a hydroxide concentration of about 0.3 mol/l. At hydroxide concentrations lower or greater than 0.3 mol/l, higher yields could be achieved. The results shown in Table 2 indicate that there also exists a maximum yield benefit at higher levels of initial alkali. The LIA procedure corresponds to an initial hydroxide concentration of about

0.6 mol/l, which is greater than the concentration reported for the yield minimum in the ZAP process. The maximum yield benefit was found around an initial hydroxide concentration of 0.9 mol/l. The effect of initial alkali on pulp yield should be further investigated to optimize the benefits of PS pulping.

Alkaline Sulfite Pulping

The use of anthraquinone as an accelerator to alkaline sulfite pulping led to the development of the AS-AQ process (54). The Mini-Sulfide Sulfite anthraquinone (MSS-AQ) pulping process was investigated in Sweden in the mid 1980's (55,56). Both the AS-AQ and the MSS-AQ process have some unique features outlined below (55-60):

- Pulp yield for linerboard is 10% pt higher than kraft at equivalent Kappa number and strength properties.
- The brightness of the AS-AQ/MSS-AQ linerboard pulp is considerably higher than the brightness of the corresponding kraft pulp: 40 % ISO and 18% ISO, respectively. This would be a considerable advantage for high quality printing on cardboard boxes for advertising.
- The need for the caustic room, lime kiln and associated energy usage is eliminated. This would be a very large capital savings, especially for greenfield mills and mills with major rebuilds.
- The yield advantage of AS-AQ/MSS-AQ over Kraft decreases rapidly as the kappa number decreases. However, because the AS-AQ/MSS-AQ pulps respond very well to oxygen delignification, it is possible to stop pulping at the defiberizing point (kappa 50) and to continue the delignification with oxygen and alkali while keeping most of the yield increase achieved at Kappa 50.
- The AS-AQ/MSS-AQ pulps are considerably brighter and also easier to bleach than the corresponding kraft pulps. ECF bleaching can be accomplished with lower ClO₂ usage. High brightness can be achieved with TCF sequences while producing a bleached pulp with acceptable pulp strength. If TCF bleaching becomes cost effective, the capital cost for the chlorine dioxide generators would also be eliminated.
- Lower TRS emissions results in a low odor mill.

The difference between the AS-AQ and MSS-AQ processes is the amount of sulfur that exists as sodium sulfide. In the AS-AQ process, all the sulfur exists as Na₂SO₃ with no Na₂S, while the mini-sulfide sulfite process uses a mixture of Na₂S and Na₂SO₃. The decision to utilize AS-AQ or MSS-AQ will depend on the amount of Na₂S that can be generated in pulping liquor during recovery operations, and on the potential improvements in delignification rate and pulp yield in MSS-AQ as compared to AS-AQ.

In the MSS-AQ process the total charge of alkali is about 22% Na₂O on OD wood, which is higher than for the kraft process (19% Na₂O). The delignification rate is slower than for the kraft process, and higher pulping temperatures (+ 18 °F) and anthraquinone addition (0.15% on OD wood) are required to obtain acceptable pulping rates. Preliminary optimization studies done at STFI (55,56) indicate that a sulfide ratio between 0.05 to 0.1 results in the lowest kappa number. The optimum also shifts to a lower value with increasing AQ charge. If the amount of sodium sulfide is increased above the optimum, the kappa number increases again.

Despite these significant advantages, the development of both the AS-AQ and MSS-AQ processes has not been pursued more aggressively because of the lack of an attractive chemical recovery process. Black liquor gasification combined with appropriate gas cleanup/absorber technology would present precisely such an alternative. The benefits of these two processes were compared for the production of linerboard.

AS-AQ Pulping Work

Two AS-AQ processes have been evaluated with southern pine: the traditional strongly alkaline, SA, and also the moderately alkaline, MA. It would be more attractive to operate at lower alkali charges since this would minimize the amount of NaOH that would be necessary in the process. When compared to the Kraft reference pulp, the moderately alkaline AS-AQ procedure produced pulps with a 10% yield benefit and a higher

ISO brightness. The pulp refined somewhat more slowly, had a higher apparent sheet density, a lower tensile index and burst index at similar tear index (61). Similarly, the strongly alkaline AS-AQ procedure returned a 5% yield benefit and a pulp of comparable ISO brightness.

MSS-AQ Pulping Work

When compared to the Kraft-AQ reference pulp, MSS-AQ pulping produced pulps with a 15-18% yield benefit and ISO brightness that was significantly higher. The yield and brightness of the different pulps are shown in Figure 7. The pulp refined more easily and at similar levels of tear index the MSS-AQ pulps had a slightly lower tensile and burst index (61).

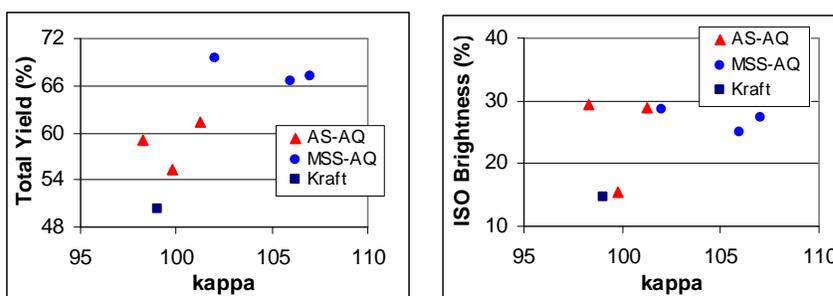


Figure 11.7 Total pulp yield and ISO Brightness versus kappa for Kraft, AS-AQ and MSS-AQ

Table 3 shows the chemical balance for the different processes in kg of chemicals required as Na₂O per oven dry metric ton pulp (ODtP). Integration of alkaline sulfite AQ into a mill would require the addition of sodium hydroxide to adjust the pH. The AS-AQ process operated at strongly alkaline conditions would require the conversion of 163 kg of NaOH. This would require a recausticization system to be operated at the mill, and therefore make this process alternative less attractive. In the mildly alkaline AS-AQ process the use of alkali can be decreased to 35 kg NaOH/ODtP.

Table 11.3 Chemical Requirements for Selected Options for production of 1 ODtP (all chemicals as Na₂O) converted to kg/ton

	Yield (%)	Wood (OD kg)	TTA (%)	NaOH (kg)	Na ₂ S (kg)	Na ₂ CO ₃ (kg)	Na ₂ SO ₃ (kg)
Kraft	50.0	2000	17.6	226	74	53	0
AS-AQ SA	55.4	1805	21.0	163	0	53	163
AS-AQ MA	60.0	1667	21.0	35	0	35	280
MSS-AQ1	66.6	1502	22.0	33	17	33	248
MSS-AQ2	67.3	1486	22.0	0	32	32	261
MSS-AQ3	69.6	1437	22.0	0	15	31	268

Some of the additional alkali required could be added as makeup chemical, but the 35 kg NaOH/ODtP is still greater than that required as makeup in most well operated mills. The MSS-AQ pulping process can be operated with no caustic, which would eliminate both the causticization process and the lime kiln. When the

sodium sulfide charge is 5% of the total chemical, 17 kg of sodium sulfide will have to be generated by absorption of the H₂S from the syngas. Alkaline sulfite methods generate pulp yields significantly greater than the Kraft-AQ procedure at similar kappa. The moderately alkaline AS-AQ procedure resulted in an additional 10 % yield benefit. MSS-AQ pulping resulted in yield increases ranging from about 15 to 20% as compared to the Kraft baseline. MSS-AQ and the moderately alkaline AS-AQ procedures generate pulps of significantly higher unbleached ISO brightness, ranging from about 25 to 30 %, as compared to the Kraft and strongly alkaline AS-AQ procedures with ISO brightness around 15 %. The higher pulp brightness indicates that there is a large potential for cost savings in bleaching operations if bleachable grade pulp was produced.

MSS-AQ with RTI Absorption Technology

Research Triangle Institute (RTI) has developed durable zinc oxide based regenerable desulfurization sorbents. The primary application for the technology has been removal of reduced sulfur compounds from hot coal derived synthesis gases and recovery of concentrated SO₂ streams. The product gases containing the sulfur compounds will be scrubbed to remove particulates and then sent to the RTI absorber. 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 active chemical for the alkaline sulfite pulping processes. Tests were conducted at 260 to 530°C and at pressures from 240 to 2000 kPa. In fixed bed sulfidation reactor tests, inlet H₂S 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 (61).

Black liquor gasification, RTI Absorption technology and MSS-AQ will have to be integrated into a chemical pulp mill to take advantage of the yield benefits, energy savings, capital savings and the increased power generation. The process flow-sheet with the above technologies integrated is shown in Figure 8.

The sulfur dioxide from the RTI absorber will be absorbed in the green liquor (sodium carbonate) to form the sodium sulfite liquor. An appropriate amount of the sulfur gases will be absorbed as hydrogen sulfide to produce the required amount of sodium sulfide. The RTI absorber serves the dual purpose of cleaning up the product gas and also regeneration of the chemicals. As shown in the process schematic, the causticization and lime kiln operations can be eliminated from the system as they are not needed in MSS-AQ pulping with BLG. This will result in significant capital and operating cost-savings (61).

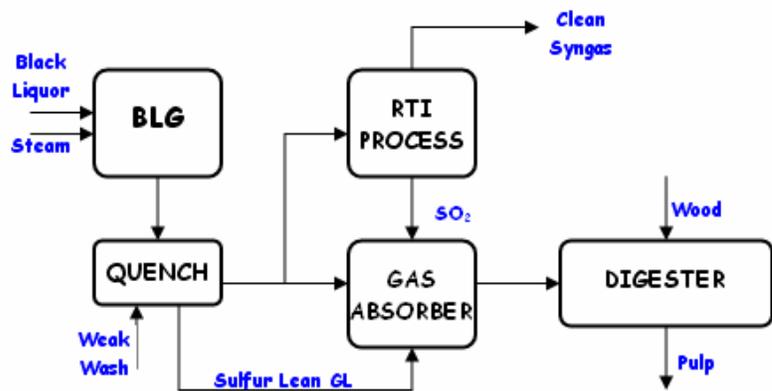


Figure 11.8 Schematic of the alkaline sulfite pulping processes with the RTI absorber

Economics of BLG Implementation

The overall economics associated with operating a BLG system will be impacted by the pulping process. The return on investment will also have a significant effect on how rapidly the technology will be implemented. The return on investment is dependent on the market price of oil, natural gas, and electricity, as well as the value of products that can be produced from the BLG syngas, and process savings achieved through BLG implementation. Work on forecasting the economic effects of BLG implementation, using analyses of existing and potential technologies will therefore be important. Areas of interests for these studies involve the exploration of markets for and economics of potential products, and the comparative analyses of different technologies and process options for their manufacture.

The BLG generation of a syngas high in hydrogen and carbon monoxide will allow for the production of a wide range of high value products currently unattainable with the Tomlinson recovery boiler. With different options for down-stream technologies following the BLG the capability exists to generate steam, power, or various bio-fuels and source materials for bio-chemicals processes such as (12).

- DME/Methanol
- Mixed alcohols
- Fischer-Tropsch liquids
- Syngas fermentation

Work has been done exploring the potential effects of modified pulping processes on the variable operating costs of pulp mill operations. To create a wider knowledge-base for future decision making regarding what products to manufacture and what process to use, more research is needed (11,62-65).

The Energy Group at the Princeton Environmental Institute has been a significant contributor to the work exploring the cost-benefits of BLG operation and associated technologies. Work has been presented showing the potential for different alternative products within the framework of the biorefinery concept, focusing on the combined cycle generation of electrical power (64-68). A comparison of the reported estimated capital investment required for installation of the different process options, including operations and maintenance costs, is displayed in Table 4. The values in the table are given as percent changes for each process option compared to the Tomlinson base case (BASE) indexed at 100.

Table 11.4 Estimated Cost Comparisons of Tomlinson and BLGCC Power/Recovery Systems Relative the Tomlinson BASE (index = 100), (68)

	<i>Tomlinson</i>		<i>BLGCC System</i>		
	<i>BASE</i>	<i>HERB</i>	<i>Low-Temp Mill-Scale</i>	<i>High-Temp Mill-Scale</i>	<i>High-Temp Utility-Scale</i>
Direct Costs	100	130	172	162	202
Non-Direct Costs	100	140	267	151	186
TOTAL INSTALLED CAPITAL COST	100	132	192	159	199
Annual Operating and Maintenance Costs	100	154	154	154	162

The different process options include Tomlinson alternatives with either a conventional or a high efficiency recovery boiler, and mill scale LT and HT BLG, as well as a utility scale HT BLG. The values were based on “Nth plant” level of technology maturity and reliability and have an estimated accuracy of ±30%. The capital requirement for the installation of BLG technologies is higher than for the Tomlinson recovery boiler. However, recovery operations built around a BLGCC system will convert the pulp mill to a significant net producer of electricity, compared to a mill using a Tomlinson boiler which is a net importer of electricity. The

kraft reference mill used in the study required a net import of 36 MW, compared to a net production and export of power to the grid of 22 MW and 126 MW, for the low and high temperature BLG processes, respectively. To meet the same process steam demand, additional fuel or biomass would have to be processed. In detailed work comparing the kraft reference mill to the LT and HT BLG processes, it was shown that the conversion efficiency of biomass to power was about 15% for the non-pressurized LT BLG, nearly 50% greater than for the reference kraft mill. For the two HT BLG processes the same values were about 19% for the smaller utility design (85% increase) and about 17.5% for the mill-scale design (70% increase). The work also indicates superior financial performance of the BLG technologies relative the kraft base comparison (66-68).

The internal rate of return (IRR) and net present value (NPV) were calculated for the different process options. Assuming a 2.5¢/kWh premium and a tax credit of 1.8¢/kWh for the production of renewable energy, the LT BLG process yielded an IRR of 20.9%/yr and a NPV of \$73 million compared to the kraft base case. The corresponding values for the HT BLG mill and utility scale processes were 34.8%/yr and \$138.5 million and 35.1%/yr and \$216 million respectively. Also indicated in the work is the distinct window of opportunity for the installation of the technology that exists in the near future, and that a lag in market penetration could be assessed as a loss of \$9 billion over a 25 year period measured in terms of energy costs and emission reductions (66-68).

Summary and Conclusions

Biomass can be converted to power and/or fuels using gasification. The gasification of black liquor produces output streams that can be used with great benefit in modified pulping operations with the additional production of power and other high value products. BLG with combined cycle power production can generate more electricity than combustion in a boiler given the same fuel, turning an integrated pulp and paper mill into a net exporter of electricity. Other options for syngas utilization are the generation of bio-derived liquid fuels, bio-derived chemicals for the synthetic and pharmaceutical industries, and H₂ for use in fuel cells.

As discussed in this paper, the implementation of a BLG system will have a dramatic effect on current pulp mill operations. In addition to the high value products made possible through the concepts related to the biorefinery, BLG will enable different modified pulping technologies through the separation of sulfur and sodium. A comparison of the different technologies enabled by BLG and their effects on the different pulping processes is given in Table 5.

Table 11.5 General Comparison of BLG Enabled Pulping Technologies

<i>Pulping technology</i>	<i>Effect on kappa</i>	<i>Effect on Yield</i>	<i>Effect on viscosity</i>	<i>Effect on properties</i>
Split Sulfidity	Lower kappa at same chemical charge	1-2% higher yield	Comparable viscosity	Improved strength properties
Green Liquor pretreatment	Higher kappa at same chemical charge	No/small benefit	Increased viscosity	Improved strength properties
Polysulfide-AQ	Similar to lower kappa at same chemical charge	1-2% yield increase per % PS charged	Increased viscosity (ZAP slight decrease)	Similar properties, but lower tear strength (Hyperalkaline-PS has comparable tear)
AS-AQ	Higher kappa at same total chemical charge	5-10% yield increase	Comparable viscosity	Somewhat lower strength, much greater brightness, easy to bleach
MSS-AQ	Higher kappa at same total chemical charge	15-18% yield increase	Comparable viscosity	Somewhat lower strength, much greater brightness, easy to bleach

As shown, modifications to the kraft process, using split sulfidity, green liquor pretreatment and polysulfide pulping, can generate increased rates of delignification, improvements in pulp yield, viscosity and strength properties, but not all at the same time. Further optimization of these technologies could have a significant effect on the kraft process. Alkaline sulfite 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, resulting in very significant cost-savings.

The overall economics associated with BLG implementation will have a significant effect on how rapidly the technology will be implemented. Analyses of the costs and benefits associated the installation of BLGCC technologies compared to conventional kraft operations using recovery boilers indicate increases of 20.9% in the internal rate of return and \$73 million in the net present value for a mill-scale low temperature BLG process. The corresponding values for a mill-scale high temperature BLG process are 34.8% (IRR) and \$138.5 million (NPV). Above and beyond these cost-benefits, additional benefits could be realized from modified pulping operations and the production of other high value products.

References

1. Nilsson, L.J.; Larson, E.D.; Gilbreath, K.R.; Gupta, A. *Energy Efficiency and the Pulp and Paper Industry*; ACEEE: Washington D.C./Berkeley, CA, 1995.
2. Jahne, F. "Commercial Success of Gasification Technology", *Tappi J.* **1999**, 82(10): 49.
3. Whitty, K.; Verrill, C.L. "A Historical Look at The Development of Alternative Black Liquor Recovery Technologies and The Evolution of Black Liquor Gasifier Designs", *Proc. 2004 TAPPI Int. Chem. Rec. Conf.*; TAPPI Press: Atlanta, GA, 2004; p 13-33.
4. Stigsson, L., "ChemrecTM [Kvaerner Chemrec AB's] Black-Liquor Gasification", *Proc. 1998 TAPPI Int. Chem. Rec. Conf.*; TAPPI Press: Atlanta, GA, 1998; p 663-674.
5. Grace, T.M.; Timmer, W.M. "A Comparison of Alternative Black Liquor Recovery Technologies", *Proc. 1995 TAPPI Int. Chem. Rec. Conf.*; TAPPI Press: Atlanta, GA, 1995.
6. Rowbottom, B.; Newport, D.; Connor, E. "Black Liquor Gasification at Norampac", *Proc. 2005 TAPPI Engineering Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
7. Chemrec ; URL <http://www.chemrec.se>; 2005.
8. Whitty, K.; Ekbohm, T.; Stigsson, L. "Chemrec Gasification of Black Liquor"; published on website URL <http://www.chemrec.se/forsta.htm>; 2000.
9. Lindblom, M. "An Overview of Chemrec Process Concepts"; Presentation at the Colloquium on Black Liquor Combustion and Gasification; Park City, Utah, May, 2003.
10. Erickson, D.; Brown, C. "Operating Experience with Gasification Pilot Project"; *Tappi J.* **1999**, 82(9).
11. Farmer, M. "Adaptable Biorefinery: Some Basic Economic Concepts to Guide Research Selection"; *Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
12. Burciaga, D. "Black Liquor Gasification: The Foundation of The Forest Bio-Refinery "New Value Streams"", *Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
13. Johansson, B.; Mjoberg, J.; Sandstrom, P.; Teder, A. "Modified Continuous Kraft Pulping - Now a Reality"; *Svensk Papperstidning--Nordisk Cellulosa.* **1984**, 87(10): 30-35.
14. Herschmiller, D.W. "Kraft Cooking with Split Sufidity- A Way to Break the Yield Barrier"; *Proc. Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998; Vol. 1 pp 59.
15. Andrews, E.K. Ph.D. thesis, North Carolina State University, Raleigh, NC, 1982.
16. Olm, L.; Tisdat, G. "Kinetics of the Initial Stage of Kraft Pulping"; *Svensk Papperstidning--Nordisk Cellulosa.* **1979**, 82(15): 458-464.
17. LeMon, S.; Teder, A. "Kinetics of Delignification in Kraft Pulping (1). Bulk Delignification of Pine"; *Svensk Papperstidning--Nordisk Cellulosa,* **1973**, 76(11): 407.
18. Olm, L.; Tormund, D.; Jensen, A. "Kraft Pulping with Sulfide Pretreatment-Part-1 Delignification and Carbohydrate Degradation"; *Nord. Pulp Pap. Res. J.* **2000**, 15, 62.
19. Jiang, J.E; Herschmiller, D.W. "Sulfide Profiling for Increased Kraft Pulping Selectivity"; *Proc. 1996 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1996, p. 311-318.

20. Lownertz, P.P.H.; Herschmiller, D.W. "Kraft Cooking with Split White Liquors and High Initial Sulfide Concentration: Impact on Pulping and Recovery"; Proc. 1994 TAPPI Pulping Conference; TAPPI Press: Atlanta, GA, 1994, p. 1217-1224.
21. Andrews, E.K.; Chang, H-m.; Kirkman, A.G.; Eckert, R.C. "Extending Delignification in Kraft and Kraft/Oxygen Pulping of Softwood by Treatment with Sodium Sulfur Liquors"; Proc. Japan Tappi Symposium on Wood pulp chemistry; TAPPI Press: Atlanta, GA, 1982.
22. Mao, B.; Hartler, N. "Improved Modified Kraft Cooking. (1). Pretreatment with a Sodium Sulfide Solution"; Paperi ja Puu. **1992**, 74(6): 491-494.
23. Mao, B.; Hartler, N. "Improved Modified Kraft Cooking. (2). Modified Cooking Using High Initial Sulfide Concentration"; Nordic Pulp and Paper Research J., **1992**, 7(4): 168-173.
24. Mao, B.; Hartler, N. "Improved Modified Kraft Cooking,4: Modified Cooking with Improved Sulfide and Lignin Profiles"; Paperi ja Puu. **1995**, 77(6/7): 419-422.
25. Olm, L.; Backstrom, M.; Tormund, D. "Pretreatment of Softwood with Sulfide Containing Liquor Prior to Kraft Cook"; Proc. 1994 TAPPI Pulping Conference; TAPPI Press: Atlanta, GA, 1994; 29.
26. Jiang, J.E.; Greenwood, B.F.; Phillips, J.R.; Stromberg, C.B. "Improved Kraft Pulping by Controlled Sulfide Additions"; Proc. 7th ISWPC Conference; CICCST: Beijing, China, 1993.
27. Andritz Inc.; Personal communication; Oct, 2003.
28. Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H.; "Effects on Pulp Yield and Properties Using Modified Pulping Procedures Involving Sulfur Profiling and Green Liquor Pretreatment"; Presented at 2004 Tappi Fall Technical Conference, Atlanta, GA, 2004.
29. Van Heiningen, A.; Schwiderke, E.; Chen, X. "Kinetics of the Direct Causticizing Reaction Between Black Liquor and Titanates During Low Temperature Gasification"; Proc. 2005 TAPPI Engineering, Pulping & Environmental Conference; TAPPI Press: Atlanta, GA, 2005.
30. Lopez, I.; Chang, H-m.; Jameel H.; Wizani, W. "Effect of Sodium Sulfide Pretreatment on Kraft Pulping"; Proc. 1999 TAPPI Pulping Conference; TAPPI Press: Atlanta, GA, 1999; pp135.
31. Li, Z.; Li, J.; Kubes, G.J. "Kinetics of Delignification and Cellulose Degradation During Kraft Pulping with Polysulfide and Anthraquinone"; JPPS. **2002**, 28(7): 234-239.
32. Griffin, C.W.; Kumar, K.R.; Gratzl, J.; Jameel, H. "Effects of Adding Anthraquinone and Polysulfide to the Modified Continuous Cooking (MCC) Process"; Proc. 1995 TAPPI Pulping Conference; TAPPI Press: Atlanta, GA, 1995; 19-30.
33. Jiang, J.E. "Extended Delignification of Southern Pine [*Pinus spp.*] with Anthraquinone and Polysulfide"; TAPPI J. **1995**, 78(2): 126-132.
34. Jiang, J.E. "Extended Modified Cooking of Southern Pine [*Pinus*] with Polysulfide: Effects on Pulp Yield and Physical Properties"; TAPPI J. **1994**, 77(2): 120-124.
35. Landmark, P.A.; Kleppe, P.J.; Johnsen, K. "Pulp Yield Increasing Process in Polysulfide Kraft Cooks"; Tappi J. **1965**, 58(8): 56.
36. Vennemark, E. "Some Ideas on Polysulfide Cooking"; Svensk Papperstidning. **1964**, 67(5): 157.
37. Kleppe, P.J.; Minja, R.J.A. "The Possibilities to Apply Polysulfide-AQ in Kraft Mills"; Proc. Breaking the yield barrier symposium; TAPPI Press: Atlanta, GA, 1998, Vol. 1, pp 113.
38. Sanyer, N.; Laundrie, J.F. "Factor Affecting Yield Increase and Fiber Quality in Polysulfide Pulping of Loblolly Pine, Other Softwoods, and Red Oak"; Tappi J. **1964**, 47(10): 640.
39. Luthe, C.; Berry, R. "Polysulphide Pulping of Western Softwoods: Yield Benefits and Effects on Pulp Properties"; Pulp. Pap. Can. **2005**, 106(3): 27-33.
40. Munro, F.; Uloth, V.; Tench, L.; MacLeod, M.; Dorris, G. "Mill-Scale Implementation of Paprican's Process for Polysulphide Liquor Production in Kraft Mill Causticizers - Part 2: Results of Pulp Mill Production Trials"; Pulp. Pap. Can. **2002**, 103(1): 57-61.
41. Tench, L.; Uloth, V.; Dorris, G.; Hornsey, D.; Munro, F. "Mill Scale Implementation of Paprican's Process for Polysulfide Liquor Production in Kraft Mill Causticizers. Part-1 Batch Trials and Optimization"; TAPPI J. **1999**, 82(10): 120.
42. Yamaguchi, A. "Operating Experiences with the MOXY Process and Quinoid Compounds"; In Anthraquinone Pulping: Anthology of Published Papers 1977-1996; Goyal, G.C., Ed.; TAPPI Press: Atlanta, GA, 1997; pp 287-291.
43. Nishijima, H.; et al., "Review of PS/AQ Pulping to Date in Japanese Kraft Mills and the Impact on Productivity"; Proc. 1995 TAPPI Pulping Conference; TAPPI Press: Atlanta, GA, 1995; 31-40.
44. MacLeod, M.; Radiotis, T.; Uloth, V.; Munro, F.; Tench, L. "Basket Cases IV: Higher Yield with Paprilox™ Polysulfide-AQ Pulping of Hardwoods"; TAPPI J. **2002**, 1(10): 3-8.

45. Olm, L.; Tormund, D.; Bernor Gidert E. "Possibilities to Increase the Pulp Yield in a Kraft Cook of [the] ITC-Type"; Proc. *Breaking the yield barrier symposium*; TAPPI Press: Atlanta, GA, 1998; Vol. 1, 69-78.
46. Hakanen, A.; Teder, A. "Modified Kraft Cooking with Polysulfide: Yield, Viscosity, and Physical Properties"; TAPPI J. **1997**, 80(7): pp 86,93,100, 189-196.
47. Jiang, J.E.; Crofut, K.R.; Jones, D.B. "Polysulfide Pulping of Southern Hardwood Employing the MOXYRG and Green-Liquor Crystallization Processes"; Proc. *1994 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1994; pp 799-806.
48. [Gustafsson, R.](#); [Ek, M.](#); [Teder, A.](#) "Polysulphide Pretreatment of Softwood for Increased Delignification and Higher Pulp Viscosity"; JPPS. **2004**, 30(5): 129-135.
49. [Mao, B. F.](#); [Hartler, N.](#); "Improved Modified Kraft Cooking,3: Modified Vapor-Phase Polysulfide Cooking"; TAPPI J. **1994**, 77(11): 149-153.
50. Lindstrom, M.; Teder, A. "Effect of Polysulfide Pretreatment When Kraft Pulping to Very Low Kappa Number"; Nordic Pulp Paper Res. J. **1995**, 10(1): 8-11.
51. Olm, L.; Tormund, D. "ZAP Cooking- Increase Yield in PS and PS-AQ Cooking with Zero Effective Alkali in the Pretreatment Stage"; Nordic Pulp Paper Res. J. **2004**, 19(1): 6.
52. Brannvall, E.; Gustafsson, R.; Teder, A.; "Properties of Hyperalkaline Polysulphide Pulps"; Nordic Pulp Paper Res. J. **2003**, 18(4): 436-440.
53. Lindstrom, M.; Naithani, V.; Kirkman, A.; Jameel, H. "The Effect of Integrating Polysulfide Pulping and Black Liquor Gasification on Pulp Yield and Properties"; Proc. *2005 TAPPI Engineering, Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
54. Nomura, Y.; Wakai, M.; and Sato, H. "Process for Producing Pulp in the Presence of a Quinine Compound"; Japanese Patent 112,903, 1967; Canadian Patent 1079906, 1980.
55. Dahlbom, J.; Olm, L.; Teder, A. "Characteristics of MSS-AQ [Minisulfide-Sulfite-Anthraquinone] Pulping - A New Pulping Process" TAPPI J., **1990**, 73(3): 257-261.
56. Olm, L.; Wiken, J.E.; Olander, K. "Alkaline Sulfite Pulp: Competitor to Sulfate Pulp"; Svensk Papperstidning--Nordisk Cellulosa. **1986**, 3(4): pp 75-77,85.
57. [Borgards, A.](#); [Patt, R.](#); [Kordsachia, O.](#); [Odermatt, J.](#); [Hunter, W. D.](#) "Comparison of ASAM and Kraft Pulping and ECF/TCF Bleaching of Southern Pine [Pinus spp.]" Proc. *1993 TAPPI Pulping Conference*; TAPPI Press: Atlanta, GA, 1993; Vol. 2, pp 629-636.
58. Patt, R.; Schubert, H.L.; Kordsachia, O.; Oltmann, E.; Krull, M. "Chlorine-Free Bleaching of Sulfite and ASAM Pulps on the Laboratory and Pilot-Plant Scale"; Papier. **1991**, 45(10A): V8-V16.
59. Ingruber, O.V.; Stradal M.; Histed, J.A.; "Alkaline Sulfite-Anthraquinone Pulping of Eastern Canadian Woods"; Pulp and Paper Canada. **1982**, 83(12): 79-84, 87-88.
60. Virkola,N.E.; Pusa,R.; Kettunen, J.; "Neutral sulfite AQ Pulping as an Alternative to Kraft Pulping"; Tappi J. **1981**, 64(5): 103-107.
61. Jameel, H.; Lindstrom, M.; Naithani, V.; Kirkman, A. "Alkaline Sulfite Pulping and its Integration with the TRI Process"; Proc. *2005 TAPPI Engineering, Pulping & Environmental Conference*; TAPPI Press: Atlanta, GA, 2005.
62. Lindstrom, M.; Kirkman, A.; Jameel, H. et al., "Economics of Integrating Black Liquor Gasification With Pulping: Part I – Effect Of Sulfur Profiling"; Proc. *2002 TAPPI Engineering, Pulping & Recycling Conference*; TAPPI Press: Atlanta, GA, 2002.
63. Berglin, N.; Lindblom, M.; Ekbom, T. "Preliminary Economics of Black Liquor Gasification with Motor Fuels Production"; Presentation at the Colloquium on Black Liquor Combustion and Gasification; Park City, Utah, May, 2003.
64. Larson, E.D.; Haiming, J.; "Biomass Conversion to Fischer-Tropsch Liquids: Preliminary Energy Balances"; Proc. *4th Biomass Conference of the Americas*; Elsevier Science Ltd: Oxford, UK, 1999.
65. Williams, R.H.; Larson, E.D.; Katofsky, R.E.; Chen, J. "Methanol and Hydrogen from Biomass for Transportation"; Energy for Sustainable Development. **1995**, 1(5): 18.
66. Larson, E.D.; Consonni, S.; Katofsky, R.E. "A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry – Final Report"; prepared with support from the American Forest & Paper Association and the U.S. Department of Energy's Office of Biomass Programs (available from the authors) (Oct. 8, 2003).
67. Consonni, S.; Larson, E.D.; Katofsky, R.E. "An Assessment of Black Liquor Gasification Combined Cycles Part A: Technological Issues And Performance Comparisons"; Proc. *ASME Turbo Expo 2004 Power for Land, Sea, and Air*; ASME: 2004.

68. Larson, E.D.; Katofsky, R.E.; Consonni, S. “*An Assessment of Black Liquor Gasification Combined Cycles Part B: Emissions, Costs and Macro-Benefits*”; Proc. ASME Turbo Expo 2004 Power for Land, Sea, and Air; ASME: 2004.

12 APPENDICES

12.1 Notes on pump calibration and operation

The cart based American LEWA dual head piston pump, was purchased from Hydrocorp Inc., represented by Mr. Gene Prather (Am LEWA representative):

- (919) 518-1800
- (919) 518-2800
- gprather@hydrocorpinc.com

The operators manual is contained in a black spiral three ring binder and will be stored with Dr. Hasan Jameel. The following are some operational notes on how to set up and use the pump.

Note: Never run the pump against a closed line, as the piston will generate enough force to almost immediately cause the rupture disks in the pump assembly to fail. The rupture disk performance and replacement information is contained on the plates attached to the pump assembly.

The pump flow rate is calibrated by stroke length and pump motor speed. The stroke length is adjusted from zero to 15 mm by turning the wheels on top of each pump head. If the dial is set to zero, it is possible (and permissible) to run the pump motor without displacing the piston. The pump motor speed is controlled using the electrical control zero to sixty (0-60) Hz. The pump was during this project operated at a 200 ml/min flow rate. The pump is wired to match the 3 prong outlet on the south wall of the pulping lab (Biltmore 1103) next to the hallway door behind the EKA digester. If the pump is moved, appropriate power compatibility must be ensured!

12.2 Protocol for simulated MCC pulping

Protocol for MCC procedure – NCSU, January '04

The following procedure was developed from information provided by International Paper, and is aimed at laboratory simulation of modified continuous cooking. The protocol involves a three stage procedure, involving two liquor additions (see Liquor addition/transfer protocol) and using the stage II and III temperature to reach the desired h factor under a fixed total cooking time.

Table 1. Outline of MCC protocol

	Cumulative % TTA	L/W	Stage Temperature (°C)	Time at Temperature (min)
Stage I	65	3.5	120	15
Stage II	85	4.1	155-166	70
Stage III	100	4.5	155-166	120

Stage I.

The first stage is organized as a traditional lab batch cook using the M&K digesters. 65 % of the TTA is placed in the digester with the chips and dilution water required to meet a liquor:wood ratio of 3.5:1. The cook is then heated to 120 and held at temperature for 15 minutes. At this point a BL sample for residual effective alkali (REA) determination is collected and the first liquor addition is initiated.

Stage II

The second stage follows the first liquor addition. During Stage II the digester is heated to a predetermined temperature that over the span of the cook will result in the desired final h factor. The cook is held at temperature for 70 minutes, at which point a BL sample for REA determination is collected and the second liquor transfer is initiated. (Optional – An additional BL sample can be collected when at any point after the first liquor addition to monitor the REA.)

Stage III

The third stage follows the second liquor addition. In Stage III the digester is held at the predetermined temperature (see above) for 120 minutes. A sample of BL is collected for analysis at the end of the cook during the blow. (Optional – An additional BL sample can be collected when at any point after the second liquor addition to monitor the REA.)

The pulp is then defibered using the mixer (chips are evenly distributed in two buckets and each bucket is mixed for 5 minutes) and screened. Screened yield, rejects and total yield are determined.

Suggested BL sample collection points for REA determination

At the completion of stage I

(optional) Anytime after the first liquor addition and sufficient mixing

At the completion of stage II

(optional) Anytime after the second liquor addition and sufficient mixing

At the completion of stage III, during the blow of the cook

12.3 Protocol for Polysulfide generation

Polysulfide (PS) liquors were generated and their concentration determined based on procedures developed from work published by Dorris and Uloth at Paprican.

PS liquor was generated by dissolving elemental (sublimated) sulfur into a Na_2S solution, so as to generate a 10% PS liquor. This was accomplished by placing 160g of elemental S in 1600 ml of Na_2S solution (50 gpl as Na_2O), and mixing the solution continuously heated to 50-60 deg C under a N_2 atmosphere. The basic equipment used was a 2000 ml E-flask (reaction vessel) with a modified stopper to allow for a thermometer and continuous circulation of N_2 , a stirrer hot-plate and Teflon coated magnetic bar. The mixture was allowed to react until the visible sulfur particles had gone into solution, turning the solution deep orange/amber. This takes 4-12 hrs depending on the relative concentrations of elemental sulfur and Na_2S solution. The PS concentration of the generated PS mixture can then be determined through the Dorris and Uloth gravimetric procedure. The PS solution should be stored separated from oxygen, by vacuum seal or by floating a layer of mineral oil on top of the PS solution. The PS solution is stable for some time, depending on the storage conditions.