GO-PF13a
(08/01)

U.S. DEPARTMENT OF ENERGY
GOLDEN FIELD OFFICE

PROPERTY INVENTORY CERTIFICATE-ASSISTANCE

Grant/Cooperative Agreement No.	Grantee/Recipient
GO10626	Georgia Institute of Technology/Lucian A. Lucia

Based on the Grantee/Recipient records, and in accordance with the Property Standards set forth in 10 CFR 600.130 through 600.137 (600.230-600.233 for States), all real and personal property provided by, or partially or wholly funded by, DOE, and now in the custody of the Grantee/Recipient is listed and accounted for below.

I. REAL PROPERTY (Real estate)(10 CFR 600.132/600.232)

A. Federally-Owned: ☒ NO ☐ YES (If yes, attach list the property)
B. Acquired With Project Funds: ☒ NO ☐ YES (If yes, list below and complete C)
C. ☐ The property will continue to be used for the purposes authorized by the award.
☐ The property is no longer needed and DOE disposition instructions are requested.
☐ The property is no longer needed for the purposes of the award, and DOE approval is requested to use the property for project(s) listed below:

II. NONEXPENDABLE PERSONAL PROPERTY (Equipment)(10 CFR 600.134/600.232)

A. Federally-Owned: ☒ NO ☐ YES (If yes, attach list of property)
B. Acquired With Project Funds: ☒ NO ☐ YES
C. Acquired With Project Funds and Exempt: ☒ NO ☐ YES (If yes, explain why and attach list)

D. Acquired With Project Funds and NOT Exempt: Property in inventory at a unit fair market value of $5000 or more: ☐ NO ☐ YES (If yes, complete (1)-(3) below)
(1) ☐ Property will continue to be used for the purposes authorized by the award.
(2) ☐ Property is no longer needed for Project, and shall be used in the following federally-sponsored activity/activities:
(3) ☐ Property is no longer needed for Project or other federal activities, and:
☐ Grantee/Recipient requests DOE disposition instructions.
☐ Grantee/Recipient wishes to retain the property and:
Fair Market Value of the property is estimated at ______________
Basis of estimate: ______________

III. EXPENDABLE PERSONAL PROPERTY (10 CFR 600.135/600.233

A. ☐ There is residual inventory exceeding $5000 in aggregate fair market value. (If checked, continue.)
B. ☐ The property will be used on other federally-sponsored activities.
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D. The Aggregate Fair Market Value of the property is ______________
Basis of estimate of value is ______________

Name:	Signature:	Title:	Date:
Lucian A. Lucia		Assoc. Prof. Chem., North Carolina State University	28 January 2005

To be completed by the Government:

Project Officer Signature:	Date:
Recommended Property Disposition:	
Property Officer Signature:	Date:

FINAL TECHNICAL REPORT FOR THE US DEPARTMENT OF ENERGY

Project Title: **NOVEL PULPING TECHNOLOGY: DIRECTED GREEN LIQUOR UTILIZATION (D-GLU) PULPING**

Covering Period: January 1, 2001 to January 31, 2005

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Recipient: Georgia Institute of Technology, Institute of Paper Science and Technology (IPST), Atlanta, GA 30332-0620

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Lists of Figures, Tables and Appendices

I. Executive Summary

Maximizing the capital effectiveness of pulp and paper operations to increase profitability is one of the highest priorities for our industry. A logical way to achieve this goal is to target advances in the rate and selectivity of kraft pulping, the most fundamental part of our operations, without incurring significant capital costs. **High sulfidity pretreatment of wood chips is one of the most promising means available to achieve significant pulping improvements.** Several of the most attractive economic benefits obtained from this technology are decreased mill energy demands, stronger pulp, higher pulp yields, and lower effective alkali consumption in the digester.

The feasibility of high sulfidity pretreatment was a direct result of the development of the fundamental principles of *modified kraft pulping*:

- Hydroxyl ion (caustic) concentration should be maintained constant throughout the cook, but should initially be low.
- *Hydrosulfide ion concentration should be high at the early part of cooking.*
- Dissolved matter concentration should be kept low, particularly near the end of cooking.

<u>High concentration of the hydrosulfide ion in the early part of the cook</u> is critical to ensure the most efficient operation of kraft pulping. The hydrosulfide ion greatly increases the hydrolysis reactions of lignin by preventing re-condensation of alkaline pulped moieties and provides a degree of stabilization for carbohydrates. It therefore offers the distinct opportunity to increase the productivity of pulping by potentially accelerating delignification reactions and protecting carbohydrates. As a result, use of two separate (split) white liquor additions at different sulfidities has been suggested to obtain the optimal sulfide and hydroxide profiles according to the modified kraft pulping themes above. The "split sulfidity" technique, however, requires a high sulfidity impregnation stage and a lower sulfidity cooking liquor in the latter part of pulping. Although the split sulfidity technique has received considerable research attention, it nonetheless suffers from the drawbacks of significant modifications to the pulping operation.

Our work has been examining the economic benefits of hydrosulfide pretreatment of pulp by taking advantage of green liquor, one of the lowest capital means available to the mill. We have begun to critically evaluate and optimize in the laboratory the use of <u>green liquor</u>, an easily accessible and rich hydrosulfide source in kraft pulp mills, as part of a pretreatment stage to a kraft cook. Green liquor results from the water dissolution of the smelt leaving the combustion furnace. Normally, it is converted to cooking "white liquor" by addition of lime (CaO) to give a NaOH rich liquor. Green liquor, however, is naturally rich in hydrosulfide ion (approximately 37 g Na_2O/L) and poor in hydroxide ion (approximately 15 g Na_2O/L). Past work has shown that using this liquor as a pretreatment stage for a conventional kraft pulp results in pulps with substantially higher viscosities and strengths.[1] We have conduct proof of concept experimental designs and determined that green liquor provides significant pulping benefits. Some of the benefits that we have collected at both the lab and mill scale include:

1. Lower active alkali demands in the digester by almost 30%.
2. Reductions up to 15% in the total chlorine multiple consumption in a D(EOP)DED bleach sequence for an oxygen-delignified pulp.
3. A 10% gain in tear strength at constant tensile (70 mN/g).
4. Yields from 1-3% depending on the raw material and cooking procedure.

Green liquor pretreatment of North American wood species has promising benefits for our operations. Questions of the feasibility of employing this technology for our pulping operations, the necessary strength of green liquor, and the resultant pulp properties will become cornerstone objectives for our work. The overall preliminary cost calculations suggest that the energy balances (causticization, pulping, and bleaching) strongly favors use of the technology. Although the 0.5L/kg odw wood level conflicts with others[3] who contend that 2 L/kg is necessary for benefits, it has been suggested that lower green liquor charges still provide the benefit of thiolignin formation (resulting from pretreatment) which at a minimum green liquor level (to be determined) greatly expedite delignification. Simultaneously, carbohydrate aldehyde end groups are reduced to thioalditols, thus preventing peeling. Again, these latter benefits do not need a significant green liquor charge on a mole-gram basis since delignification is aided by thiolignins and only aldehyde end groups in carbohydrates (which have thousands of degrees of polymerization) need to react. Interestingly, small amounts of polysulfide have been claimed to form during the thiolignin-induced delignification process that can also stabilize carbohydrates. We have determined that the use of a novel sulfur additive (thiourea, $0.19/lb) can greatly enhance the currently available benefits of the technology.

Ultimately, **the use of green liquor to enhance North American pulping operations** will be available from the gains in knowledge we will access in a follow up project to this current project that will focus on implementation at a North American kraft mill.

II. Introduction

We have determined that the controlled delivery of mill green liquor (GL) in a mild (temperature and time) pretreatment phase before cooking can significantly enhance pulp properties. Moreover, we have preliminarily determined that the inclusion of inexpensive and benign nitrogen-based pulping additives that improve the uptake of sulfide into chips can augment the yield and strength of pulp, while reducing the energy required for pulping. Indeed, DOE-funded work done by Tschirner in this area has demonstrated the value of including pulping additives (mainly penetrants) that provide better uptake of pulping chemicals.

The benefits of the additive-reinforced GL pretreatment pulping not only include pulp yield and alkali savings, but significant energy savings in the digester and the lime kiln. Not surprisingly, a number of paper companies have expressed their support for attempting a version of our GL-pretreatment technology.

II.A. Energy Savings

Market Information	
Industry:	Forest Products
Process:	Chemical Pulping
Annual Market Production:	53.13 million tons
Fuel/Steam Energy Use:	3.78 million Btu/ton
Electricity Energy Use:	1.27 million Btu/ton

User Inputs	
Annual Market Growth Rate:	0.0%
Year of Technology Introduction:	2005
Market Penetration Curve:	10 Year Market Saturation
% of Market Production Technology will Impact:	100.0%
% Energy Savings Fuel/Steam:	30.0%
% Energy Savings Electricity:	30.0%
Solid or Liquid Waste Reduction:	10 lbs per 1000 lbs of product
Non-Combustion Air Pollutants Reduction:	5 lbs per 1000 lbs of product

II.B. Technology Impacts

	2005	2010	2015	2020
MARKET PENETRATION *	4.4%	29.3%	78.9%	97.1%
MARKET (Million tons)	2	16	42	52
ENERGY SAVINGS				
Fuel/Steam Energy Savings (trillion Btu)	2.65	17.65	47.53	58.50
Electricity Savings (trillion Btu)	0.891	5.931	15.97	19.65

N/A = not applicable

* Percent penetration of the market the user selected that their technology will impact, not the percent penetration of the entire market, unless the user selected that their technology will impact 100% of the total market.

User Explanations	
Technology Description:	An economic pulp catalyst in conjunction with a green liquor pretreatment phase can provide significant savings in energy and pulp yield for kraft mills. The work proposed in this manufacturing breakthrough in collaboration with our industrial consortium will help to develop the basic engineering and environmental protocols for future implementation at a selected kraft mill.
% of Market Production Technology will Impact:	The savings in yield, chemicals, and energy are significant and generate approximately $1-2 million/year for a bleached kraft mill. The industry has the technological prowess to implement this technology as well as the economic incentive. The capital expenditures are also low in comparison to the ROI.
Year of Technology Introduction:	We are currently collaborating with both IP and Samoa Pacific and Cellulose on our proposal and we expect that a reasonable date for full use based on our research data will be about 2 years from now.
Energy Savings Percentages:	H-factor reduction by 33% Lime kiln offloading by 35% Refining energy reduction by 20% Faster paper machine by 15%
Other Wastes and Pollutants:	Reduction in numbers of green liquor dregs Less black liquor burned in recovery, lower CO2 and other volatiles Reduction in time for cook, reduction in mercaptans

III. Body of the Report

Year 1

Y1/Q2:

1.1: Characterization of furnish with respect to lignin and carbohydrate changes (NMR and IEC)
Changes of carbohydrates components for green liquor pretreatment modified pulping have been analyzed by HPAEC-PAD. The differences of sugars in pulps under various pulping conditions have been investigated. The effects of the active alkali charges, sulfidities, pretreatment condition,s and surfactants on carbohydrates in pulps were investigated, and some important results have been achieved.

- The results acquired indicate that the pulps yield gain by green liquor pretreatment modified mainly come from the more glucose remaining in pulps.
- Higher digester sulfidities do not necessarily translate to more benefits beyond a certain point (due to absorption limits)
- Select surfactants additives appear some unique function to preserve sugar components, and contribute to increase carbohydrates yield.
- AQ appears to work also to preserve mannose.

1.2: Establish correlation between cooking condition and pulp products
1.2.1 Chemicals absorption properties during green liquor pretreatment

Alkali and sulfide absorption status are a key issue focused on green liquor pretreatment modified pulping. The effects of pretreatment conditions on absorption were investigated in our research, and the relationship of pretreatment conditions and pulps qualities were demonstrated. Some important data have been acquired.

- From the absorption and liquor analysis, it appears that 1 L of GL/kg wood will provide maximum benefits.
- Sulfide is absorbed much more quickly than alkali, although at higher temp./time absorption is equivalent.
- The reductions in AA for the cook are partially explained by the alkali absorption in the chips during pretreatment.

1.2.2 Green liquor pretreatment pulping

Some benefits have been demonstrated by pretreating wood chips with green liquor to modifying kraft pulping, green liquor is effective to improve pulping process and pulp qualities and reduce pulping cost.

- The lower kappa numbers and better delignification selectivity could be observed by increasing GL concentration, which indicated that GL pretreatment mainly contributes to delignification.
- 3%-5% higher pulp yields and about 30% pulp viscosity increasing for GL modified pulps as compared to conventional kraft pulps.
- AQ, PS, and surfactants demonstrate some improved effects on GL modified pulping. The synergistic effects of green liquor and additives will be further investigated.
- Green liquor Pretreated pulps require about 40% less alkali than conventional kraft cook to achieve a given kappa number and 37-41% less alkali than conventional kraft to get a particular yield

General scientific conclusions

- Absorption of the various GL components provides rational for some effect of process
- Physical property preservation appears to be a function of maintaining the glucose polymer
- It is feasible to implement the process at 1.0L/kg wood levels
- Preliminarily, it appears to surpass the ability of modern kraft processes to manufacture pulp in an economic sense (faster, better properties, and higher yields)

Y1/Q3:

1.2: Evaluation of the value and proof of principle of this pulping technology for US hardwood and softwood furnishes

- As adequately demonstrated at our past annual review at the DOE meeting in Louisville, KY (03/01), we have established that the technology works according to the principles derived by STFi (*see .ppt presentation*). We have completed preliminary studies with both SW and HW species to establish proof of principle and are exploring the remarkable basis for the validity of this technology.

2.1: Rationale for GL pretreatment with respect to preliminary pulp qualities and strength properties

- After pretreatment, the concentrations of sulfide and alkali inside wood chips and in pretreatment liquor display a pronounced difference; it is evident that much higher concentrations of both sulfide and alkali are in the wood chips as compared to the bulk liquor. The results demonstrate a specific sulfide absorption response for the wood chips during the pretreatment procedure. The response will be further investigated.

- A multi-regression set of experiments have been designed by means of the central composite experimental method to investigate the absorption characteristics of green liquor as a function of pretreatment parameters, kinetic mechanism of sulfide and alkali uptake, lignin structural changes during the pretreatment process, and the control of pretreatment as related to pulp qualities.

- GL pretreatment pulp appears to have 8-10% higher tear strength at same tensile index as compared to conventional kraft pulp.

2.2: Determine the optimal methods to increase yield of pulp based on previous results

- An important goal to attain in the GL pretreatment process is pulp processing, which could strengthen pretreatment efficiency and contribute to a further reduction in chemical dosage used in cooking. It will also serve to increase pulp yield even further. From our preliminary forays in this area, we have determined that approximately 30% savings can be realized in active alkali for cooking by a patentable improved pretreatment process. This new invention is based on an additive-modified GL pretreatment technology for which we are currently applying for a patent.

- Based on lab digester experimental data, the active alkali required for modified GL pretreated pulp to reach a given kappa number is six absolute percentage points lower than that of conventional kraft pulp (12% compared to 18%).

2.3: Characterization of GL modified pulp with respect to lignin structural changes and pulp quality

- Preliminary ^{31}P NMR analysis indicated that the pulps modified by GL pretreatment have more uncondensed lignin structures and more aliphatic hydroxyl groups in the residual lignin than that of conventional kraft pulps. The increase of pretreatment liquor concentration may contribute to increased uncondensed and aliphatic structural content and the higher pretreatment temperature may result in a reduction in uncondensed lignin structures and higher content of phenolic groups (may make the pulp more bleachable by oxygen).

- A change in the cooking sulfidity from 15% to 30% evidently affected the nature of residual lignin in PS additive pulping since an increase of phenolic and *p*-hydroxyphenyl hydroxyl groups were observed. In AQ-added GL pulping, slight changes of lignin nature were observed that will be explored further in accompanying projects.

- The preliminary results indicate that the pulping process must indeed by targeted to reduce lignin condensation reactions for any significant improvement of oxygen delignification or ensuing bleaching. The beneficial uncondensed lignin structures for oxygen delignification of SW pulps are guaiacyl-based.

- Pulping modified by green liquor pretreatment may produce more easily oxygen-delignified pulp, in which the nature of residual lignin may be characterized as a higher ratio of uncondensed to condensed phenolic groups. It appears that changes in the ratio of aliphatic hydroxyl to phenolics may benefit pulp bleachability.

General scientific conclusions:

- We believe that beside chemical absorption during pretreatment, some chemical reactions may be induced by means of a proper catalytic effect whose synergistic effects possibly result in a lignin structural change under proper pretreatment conditions and easier removal during kraft cooking. This new finding provides a new approach to develop improved GL pretreatment pulping strategies.GL pretreatment results in more uncondensed phenolic and aliphatic hydroxyl groups in residual lignin structure. GL dosage and temperature influence the nature of residual lignin. The ratios of uncondensed to condensed phenolics and aliphatic hydroxyl to phenolics increase as an increase in GL charge, and decrease at higher pretreatment temperatures.

- The higher uncondensed phenolic structures in residual lignin could improve oxygen delignification, which may result in a greater kappa number reduction during oxygen treatment. The beneficial uncondensed lignin structures during oxygen delignification are guaiacyl in nature. The higher ratio of aliphatic hydroxyls to phenolics may also provide a benefit for oxygen delignification trials that will be more fully incorporated into next year's work.

Y1/Q4:

3.1 Establish correlations between pretreatment conditions, absorption characteristics, structural changes, reaction kinetics, and preliminary pulp properties.

- The preliminary experimental design matrix results indicate that the pretreatment conditions appear to have a profound impact on pulp qualities. In general, the increase of GL charge and temperature results in a decrease in pulp yield; the ratio of liquor to wood does not appear to demonstrate an independent effect on pulp yield, which is affected by a host of other experimental parameters. An optimal pretreatment time for higher pulp yield does exist under different pretreatment temperatures.

- GL charge in the pretreatment stage shows positive impact on delignification. A linear correlation has been determined to exist between GL charge increase and pulp kappa number decrease, but GL charge has no obvious impact on the selectivity of delignification. GL concentration in the pretreatment liquor contributes to improvements in both selectivity of delignification and pulp kappa number. A lower temperature and longer time could have benefit for both better delignification selectivity and lower pulp kappa number.

3.2 Investigate strengthened GL pretreatment and optimize the process.

- The preliminary results from the additive strengthened GL pretreatment pulping show a tremendous improvement in chemical savings and improved pulp properties. Compared to conventional kraft pulping, almost 50% alkali savings are observed, and over double higher pulp viscosity could be achieved at a similar kappa number and higher pulp yield.

- Through an additive pretreatment, pulp delignification could be accelerated during the pretreatment process. The post cooking can therefore be conducted in a shorter time and at lower level of active alkali usage.

3.3 Provide rationale for GL pretreatment.

- The kinetic investigation on delignification indicates that GL pretreatment not only affects chemical absorption into wood, but also contributes to delignification; approximately 10% lignin can be removed during the GL pretreatment process. Compared to conventional kraft pulping, the bulk delignification phase after GL pretreatment is achieved more quickly and ends earlier than witnessed in conventional cooking. This indicates that there is a tremendous potential to reduce the cooking time and accrue significant energy savings.

- The consumption of both caustic alkali and sulfide during post cooks is reduced compared to a conventional kraft cook. The reduction in the chemical consumption is among the principal reasons for the benefits of higher pulp yield and viscosity. Further investigations on the chemical basis of carbohydrate stabilization are ongoing to reveal the mechanism of GL modified pulping.

General scientific conclusions:

- The experimental results reveal that the GL pretreatment is not a simple physical absorption process as generally thought. The chemical reactions appear to occur in the pretreatment phase and result in lignin partly removed from the wood material. Some changes in the lignin structure and carbohydrates are induced during the pretreatment process. Thus, pretreatment technology is a new potential research target that requires further investigation for further significant economic modification of the pulping process.

- A comprehensive investigation of GL pretreatment in conjunction with the pulping process and pulp qualities demonstrates the beneficial impact of pretreatment conditions and their interrelated effects on the pulping process and pulp properties. Results indicate that the higher GL charge is helpful in achieving a lower pulp kappa number, but it is not critical for increases in delignification selectivity. A better selectivity can be obtained by an optimal GL concentration in which GL is used at a lower level more compatible with the overall mill operation (reducing evaporator loads, providing caustic requirements). The experimental data also indicate that better pulp viscosity and higher pulp yield can be achieved by using moderate pretreatment conditions.

Year 2
Y2/Q1:

2.1.2 Establish a mathematical model using a central composite experimental design.

- From the central composite experimental design, the relationships among GL pretreatment parameters, chemical absorption, pulping selectivity and pulp qualities have been correlated. The equations deduced from the experiments describe the contributions of each pretreatment condition and the optimal impact on pulping. Based on the regression analysis, significant regular correlations among sulfide and alkali absorption with pulping and pulp qualities have been demonstrated.

- Based on the equations acquired from the regression of the experimental data, the pulping selectivity is mainly influenced by the GL concentration, pretreatment temperature, and time. Using the higher GL concentration, but under the lower GL charge at a temperature below 90ºC for 90 minutes achieves the best pulping selectivity. For acquiring better preliminary pulp qualities, the interactive effects of pretreatment parameters exhibit significant correlation: the lower GL dosage under the higher concentration and the higher temperature for shorter time or lower temperature for the longer time are optimal pretreatment parameters.

2.1.3 Rationale for GL pretreatment with respect to preliminary pulp qualities and strength properties.

- The GL pretreatment process showed a significant influence on preliminary pulp qualities and strength properties. Each pretreatment variable shows different contributions to pulping and pulp qualities. The increase of GL charge would strengthen delignification to reach a lower kappa number, but impair pulp viscosity and decrease pulp yield. However, a higher GL concentration through adjusting the ratio of pretreatment liquor to wood can provide a higher pulp yield with better viscosity and better pulping selectivity. These results indicate that it is possible to use lower GL at an industrially feasible level for impregnation to benefit both pulp properties and energy efficiency.

- The experimental results indicate that fortified sulfide impregnation through GL pretreatment before the kraft cook mainly contributes to enhanced delignification to acquire a lower pulp kappa number other than impact carbohydrate protection. However, the ratio of sulfide to hydroxide demonstrated a critical impact on pulping selectivity and pulp strength whereby the higher ratio of sulfide to hydroxide would benefit both pulping selectivity and pulp properties.

- GL modified pulping can be further improved through a potentially patentable additive pretreatment process, in which the H-factor of the whole pulping process can be reduced by as much as 10-20%. *This demonstrates that the novel modified pulping technology can provide much more efficient energy utilization for a typical kraft mill.*

General scientific conclusions:

- GL pretreatment parameters are able to influence the pulping and pulp qualities. The GL concentration in the pretreatment liquor rather than the GL charge shows a critical impact on pulping and pulp properties. In our range of experiments, the dosage of GL in the pretreatment did not exhibit an obvious impact on pulping selectivity. The lowest kappa pulp with good viscosity could be attained by using the highest concentration of pretreatment liquor, which also provided the best pulping selectivity and highest pulp yield.
- During GL pretreatment, using a higher GL charge and higher concentration at the higher temperature for longer times resulted in a higher sulfide absorption into wood chips. But, because of the different absorption rates of each chemical in GL, a variety of pretreatment parameters would result in different ratios of sulfide to hydroxide after pretreatment. In the general, a higher GL charge would result in a lower ratio of sulfide to hydroxide, whereas a higher concentration of pretreatment liquor, higher pretreatment temperature, and longer time would be helpful for increasing the ratio of sulfide to hydroxide. However, an increase in carbonate absorption is mainly affected by higher GL charge and concentration. The results demonstrated that different absorption characteristics of the chemicals in GL resulted in varied chemical absorptions under different pretreatment conditions, and thus have a significant impact on the cook and resultant pulp properties. It should also be realized that there are synergistic effects for all the chemicals in GL, not only sulfide, on pulping and pulp qualities.

- The profile of chemical absorption in GL pretreatment correlate well with pulping and primary pulp qualities. The experimental results conclude that the ratio of sulfide to hydroxide have a significant impact on pulping selectivity, in which a higher ratio would benefit pulping selectivity. When the ratio was 0.45-0.50, an increase in the ratio exhibited a positive linear relationship with pulping selectivity. The higher ratio of sulfide to hydroxide also slightly increased the screened pulp yield. The good linear relationships correlate among the pulp primary properties including kappa number and viscosity, and pretreatment chemical absorption, both sulfide absorption and the ratio of sulfide to hydroxide. These results indicate a synergistic effect exists between sulfide and hydroxide absorption which contributes to delignification.

Y2/Q2:

2.1.3. Rationale for GL pretreatment and cooking process
2.1.1. Analysis of sulfide absorption during pretreatment

- We have investigated the fundamental chemical reactivity of the hydrosulfide anion in the kraft pulps by several methods. First, we developed the idea that the anions are present in three forms (free, adsorbed, and chemically bound). The adsorbed and chemically bound forms are most likely responsible for gains in yield, pulp strength, and delignification enhancement during pulping. We explored the fate of the ions using elemental analytical techniques and determined that a large concentration of active sulfide is chemically bound in green liquor pretreated pulps (1.5% of total available in pretreatment liquor). This number increases as the temperature and/or charge go up. This result is significant since it provides a basis for the carbohydrate retention and strength, as well as the delignification enhancement during pulping and bleaching. Several relevant graphs from our work are shown below for illustration:

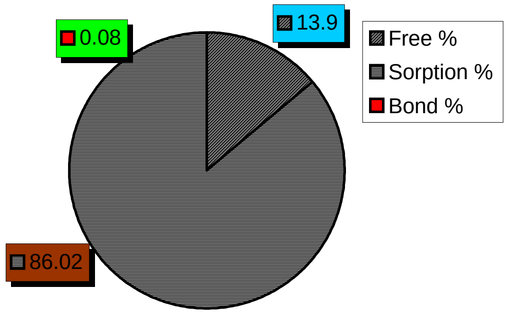


Fig. 1. Status of sulfide in wood chips after GL pretreatment (GL concentration 25%, 90ºC, 90 min).

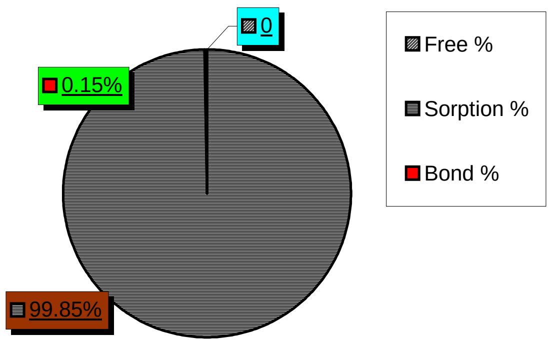


Fig. 2. Status of sulfide in wood chips after GL pretreatment (GL concentration 25%, 120ºC, 60 min).

- One of the most remarkable findings that we obtained which we discussed for the first time at the recent DOE review meeting is the application of a newly designed pulp catalyst system (under patent review): the inclusion of a pulping catalyst into the green liquor pretreatment provides many remarkable benefits which are even greater than found in the traditional green liquor pretreatment. We expect a tremendous acceleration in pulping time will result in many chemical processes including semi-chemical, CTMP, CMP, and kraft. We find that part of the explanation for the rate enhancement lies in the enhanced uptake of the sulfide anion (0.24%) by the wood as shown in the graph below:

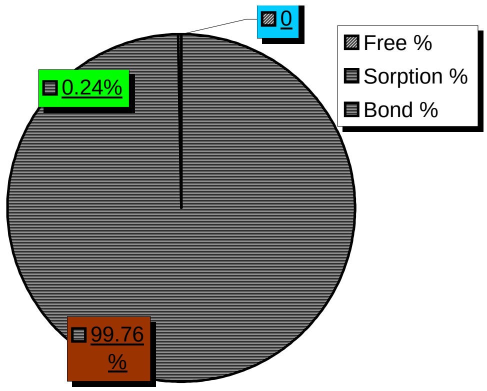


Fig. 3. Status of sulfide in wood chips after GL pretreatment (GL concentration 25%, 120ºC, 60 min, 2% proprietary additive).

2.2.1 Finalized investigation of economic additive to improve GL pretreatment pulping.

- We have endeavored to provide more data as part of a new offshoot of our current work (incorporated into a future DOE proposal) on the activity of the remarkable GL/pulping catalyst system. Herein we report the ability of the catalyst to significantly expedite pulping catalysis:

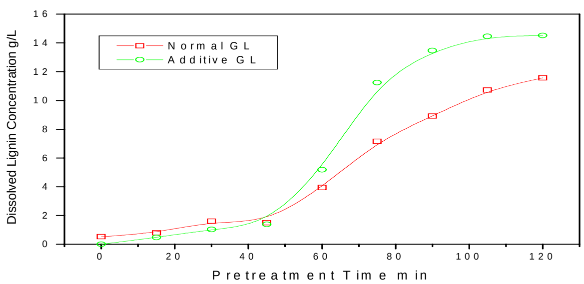


Fig. 4. Comparison of the dissolved lignin concentration for a normal GL pretreatment cook (squares) versus an pulping catalyst enhanced GL pretreatment cook (circles).
The kinetics of cooking are greatly enhanced due to the higher rate of delignification and diffusion into the bulk cook. In fact, we find that the uptake of all of the major cooking chemicals is significantly enhanced by the pulping catalyst system. Our results have shown thus far that this technology requires much more work to bring it to the market place, but we are much closer with the discovery of this fortuitous pulping catalyst system.

General scientific conclusions:

- GL pretreatment may function by providing a greater availability of sulfide-containing lignin and carbohydrate forms that help the efficiency of pulping and bleaching. Our work has shown that there exist three distinct forms of sulfide in the chips (free, absorbed, and chemically bound) which all behave differently. It is our contention that some of the major benefits in pulp final properties are a function of the chemically bound sulfur forms. This contention will require further exploration at either the end of this grant or a future DOE funding opportunity.

- The pulping catalyst appears to be a very promising way to improve uptake of sulfide by over 60% which may account for the enhanced delignification kinetics we have observed in this study.

Y2/Q3:

2.1.4. Rationale for GL pretreatment and cooking process

- Based on our investigation on sulfide's fundamental physical and chemical behavior during the pretreatment with green liquor, we have determined that various sulfide forms exist in wood that have different influences on wood delignification, and furthermore on final pulp properties. The results demonstrate that adsorbed and chemically bonded sulfide have a positive effect on lignin removal during the pretreatment; otherwise, the free sulfide in wood chips displays a negative influence on delignification. Therefore, optimization of the pretreatment process to ensure increased levels of effective sulfide forms is critical for improving kraft pulping. Several relevant graphs from our work are shown below for clarification of the latter concept:

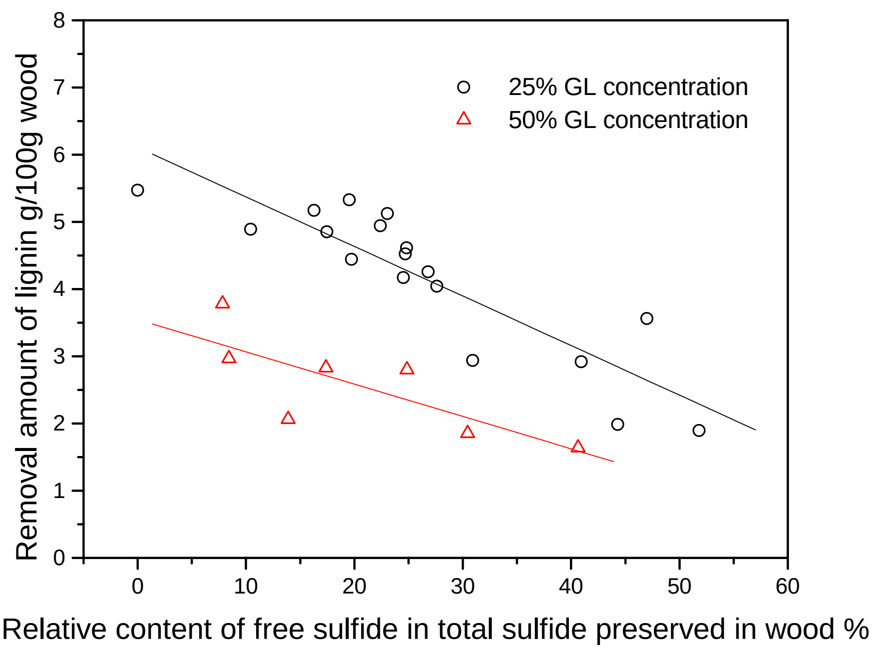


Fig. 1. Influence of free sulfide on the delignification of softwood chips after GL pretreatment (pretreatment temperature varied from 90ºC to 135ºC, time 30 min. to 90 min.).

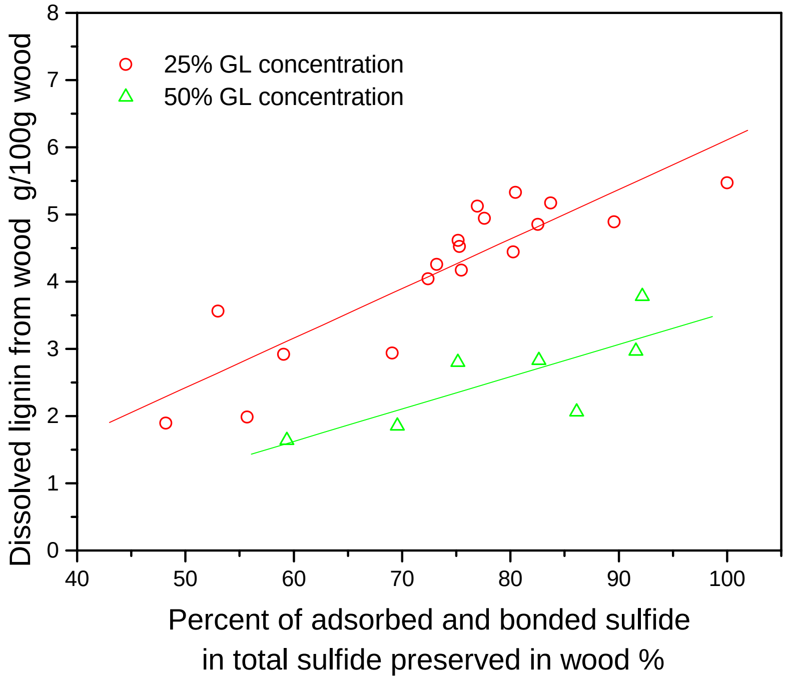


Fig. 2. Influence of adsorbed and chemically bonded sulfide in wood chips after GL pretreatment (pretreatment temperature varied from 90ºC to 135ºC, time 30 min. to 90 min.).

2.2.2 Optimization of the GL pretreatment process with respect to yield and strength

- Comparing the physical strength of pulps modified by GL pretreatment to conventional kraft pulps, benefits of higher tensile and tear strength from GL pretreatment have been observed. Gains as high as 7.8% and 12% in tensile and tear strength, respectively, could be acquired through GL modified pulping. Furthermore, we have attempted to improve the pretreatment process by means of additives, a very promising development in the optimization of pulping technology and pulp properties, which have provide improved pulp qualities, approximately 12% increase in tensile strength and 20% in tear strength, respectively, was observed compared to kraft pulp.
- We have investigated the intrinsic correlations of pulp properties with GL pretreatment, and the experimental results reveal that sulfide adsorbed by wood chips during pretreatment has a positive impact on pulp tensile and tear strength.

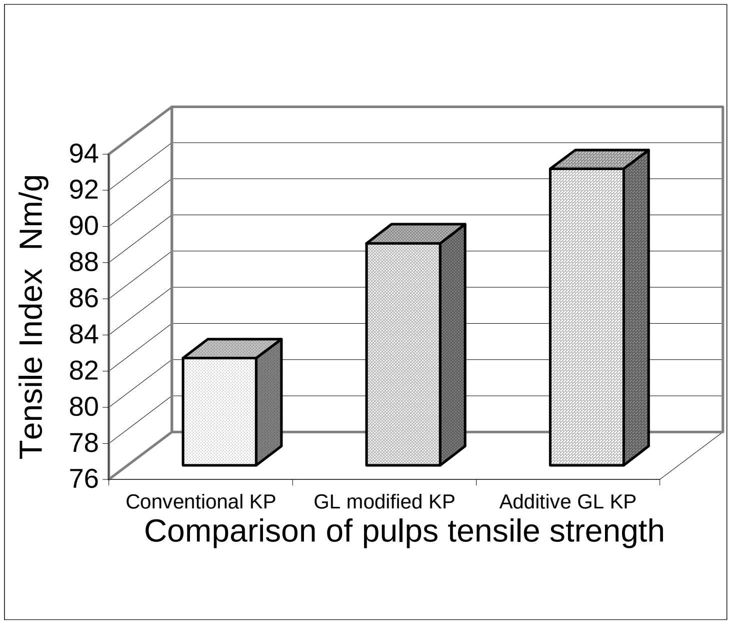


Fig. 3. Comparison of pulp tensile strength for GL modified pulp, additive GL modified pulp, and conventional kraft pulp (KP).

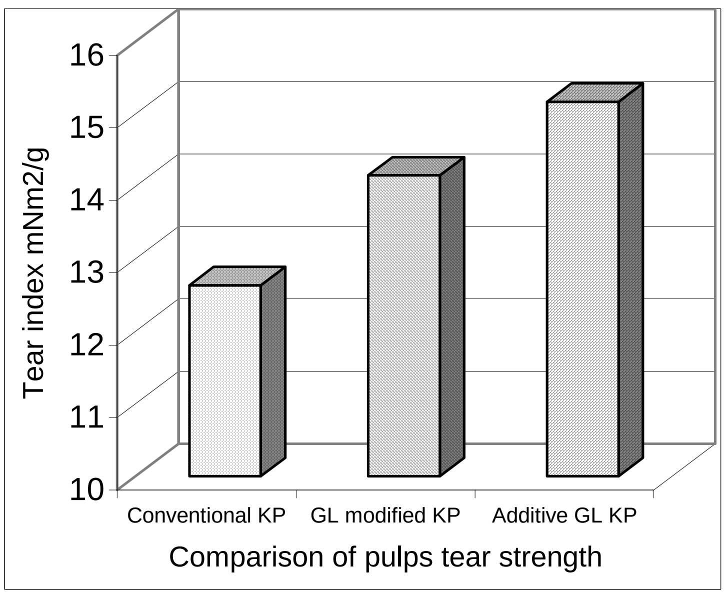


Fig. 4. Comparison of pulp tear strength for GL modified pulp, additive GL modified pulp, and conventional KP.

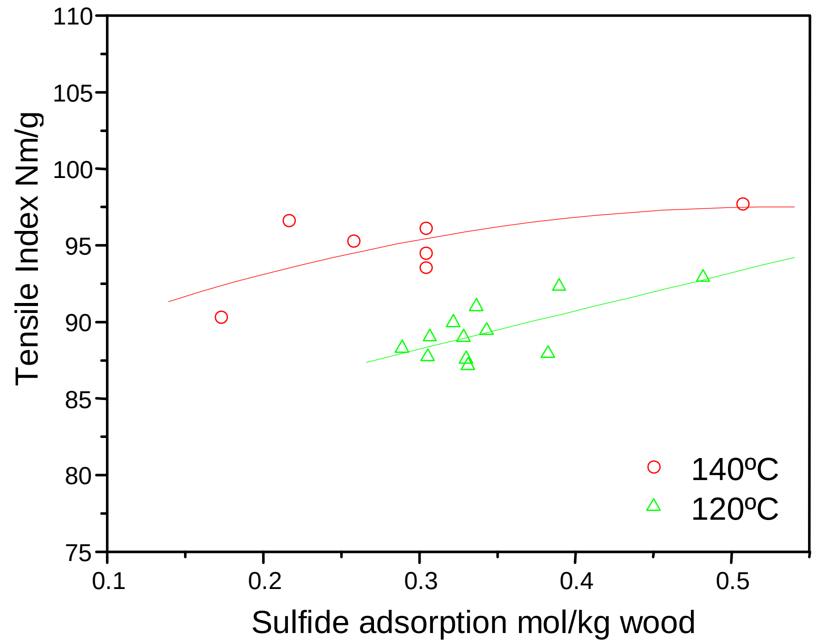


Fig. 5. Correlation of sulfide adsorption in the pretreatment with subsequent pulp tensile strength.

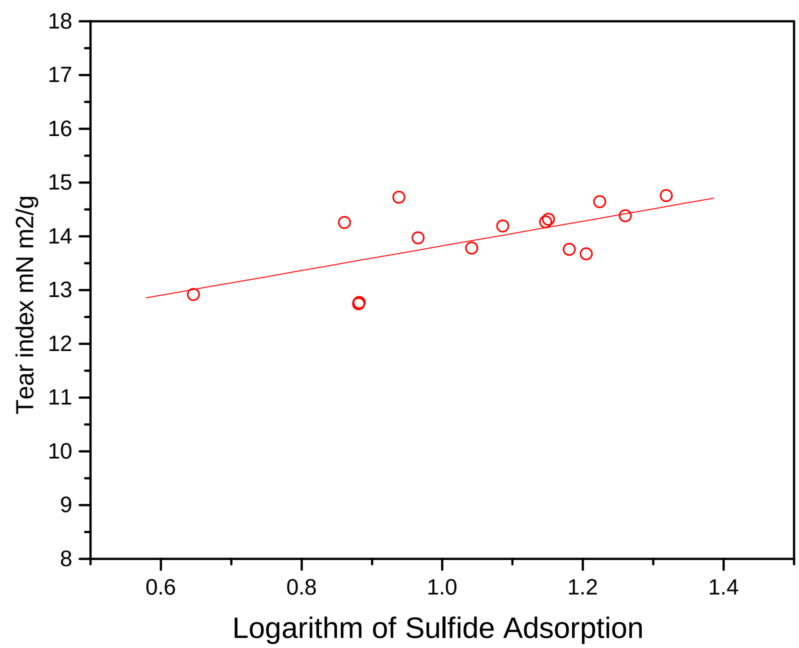


Fig. 6. Correlation of sulfide adsorption in the pretreatment with the subsequent pulp tear strength (100ºC-120ºC.).

General scientific conclusions:

- To better understand the rational of GL pretreatment function on pulping and bleaching, our work has demonstrated that various forms of sulfide exist in the chips after the pretreatment that had different effects on delignification: adsorbed and chemical bonded sulfide encourage lignin removal; however, the free sulfide in the wood chips displayed a negative effect on lignin dissolution. These results indicate that sulfide penetration into chips is effective for lignin removal in the pretreatment *only when it exists as adsorbed or bonded form.* Thus, optimizing the pretreatment process to remove increased amounts of lignin is possible. **The significance of the latter discovery is the potential to increasingly shift the delignification demand from the kraft cook to the pretreatment, delivering a remarkable savings in energy and chemicals, and significant benefits to pulp qualities.**
- In comparing pulp physical strength between GL modified and conventional kraft pulp, it was that GL modified pulp had better pulp strength (tensile and tear). By reinforcing GL pretreatment, pulp strength could be further improved. In attempting to develop a correlation between pulp strength and GL pretreatment, it was found that the higher levels of adsorbed or chemically bonded sulfide strongly correlated with higher pulp strength, but free sulfide did not have a positive impact on pulp strength.
- Our current work has provided new fundamental knowledge for the process of GL pretreatment for the modification of kraft pulping. First, adsorbed and chemically bonded sulfide in wood chips are very effective forms which have a positive correlation with lignin dissolution and pulp qualities; secondly, the significance of GL pretreatment is not only for preserving higher sulfide in chips as current theories indicate, but also for lignin removal during the pretreatment process – the latter might be very significant for efforts to improve pulping and bleaching. Furthermore, through optimization of GL pretreatment, reductions in cook time and energy consumption are feasible and are very desirable to pursue within the context of DOE funding.

Y2/Q4:

2.1.3. Rationale for GL pretreatment and cooking process

- Compared GL modified by catalyst addition with regular GL impregnation process, the additive process displays a catalytic effect on lignin removal in the pretreatment, as Figure 1 demonstrates. To compare the sulfide consumption in both GL pretreatment process, additive pretreatment consumed more sulfide than the regular pretreatment, and had 20% ~ 50% lower residual sulfide in the pretreatment. The result demonstrates the effect of the additive on sulfide activity in the GL which could subsequently catalyze lignin reactions with sulfide.
- Since lignin is more labile from the sulfide activity during the pretreatment, the delignification load is potentially diminished as confirmed from the rate of delignification in the both GL pretreatment process being higher than traditional kraft cooking. Thus, to reach a certain level

of delignification, less cooking time is needed for GL pretreatment pulping as shown in Figure 2 which directly translates to high energy savings and higher productivity.

2.2.1. Finalized investigation of economic additive to improve GL pretreatment pulping

- In comparison with kraft pulping (KP), GL pretreatment modified pulping and additive GL pretreatment pulping provide increased savings in energy, chemicals, and wood resources. The new technology appears to display remarkable economical potential interests. Compared to traditional KP, additive GL pretreatment pulping reduces energy consumption by 20%, and reduces the need for wood material and chemicals by as much as 8.3% and 40%, respectively. Figure 3 demonstrates the comparison in pulping costs.

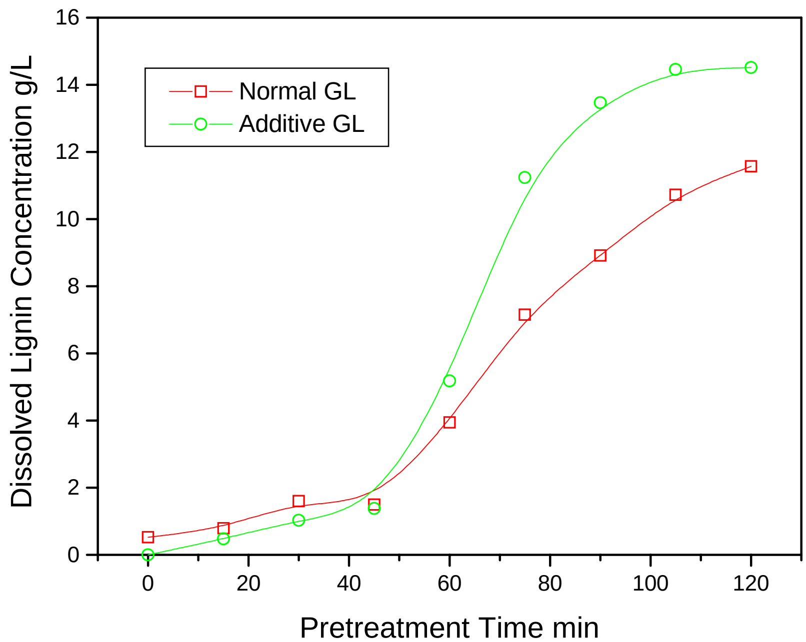


Fig.1. Comparison of normal and additive gl pretreatment delignification.

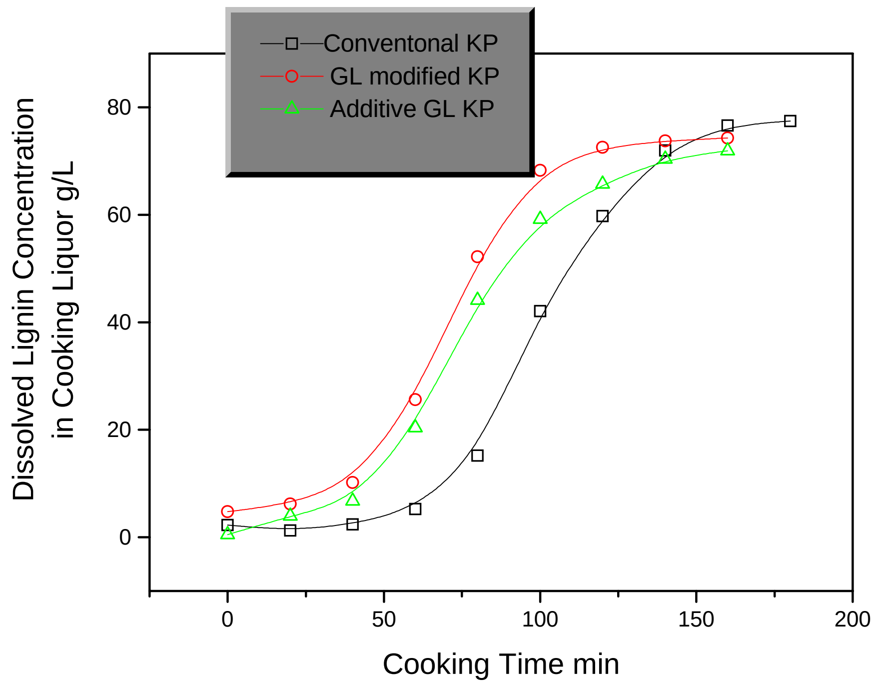


Fig.2. Delignification comparison of KP, GL KP, and additive GL KP cooking processes.

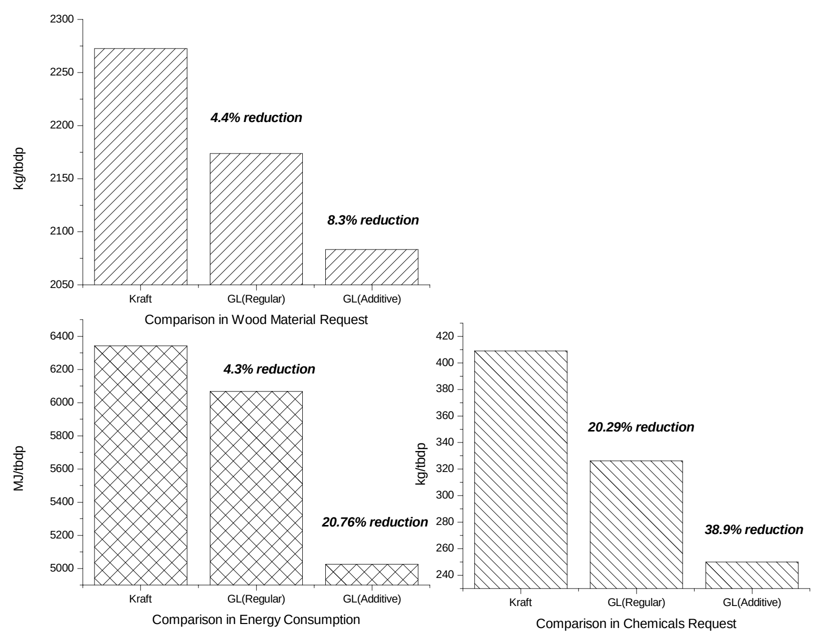


Fig. 3. Comparisons in energy, chemicals, and material consumption with Kraft, GL modified, and additive GL pulping.

2.4.1. Discussion of potential mill trials with suitable mill sponsors

Several pulping mills have been interested in improving kraft pulping by means of GL pretreatment technology as mentioned in the **BACKGROUND**. We are currently engaging in discussions and future preparations for mill trials.

General scientific conclusions:

Sulfide during kraft pulping functions as a nucleophilic reagent to react with lignin macrostructures, but this reaction usually occurs under high reaction temperature. We have determined that the pretreatment acts as a sulfide adsorption process. However, the application of an efficient catalyst system during the pretreatment enhances the nucleophilic effect of sulfide enhanced leading to the increased degradation reactions of the lignin macrostructures and subsequent removal in the GL pretreatment and kraft pulping.

Year 3
Y3/Q1:

3.1.3 Rational for GL modified pulping

We developed a novel strengthened GL pretreatment process, which uses an organic sulfur additive in the pretreatment. In this manner, the chemical effect of sulfide can be enhanced. Pulp qualities and the entire cooking process can be further improved. The following figures demonstrate the improvements of additive pretreatment pulping compared with conventional KP and regular GL pretreatment KP:

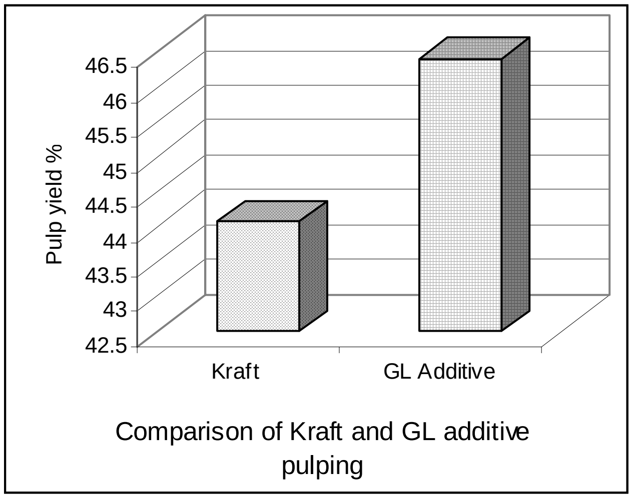


Figure 1. Pulp yield comparison (range of pulp kappa numbers is between 38 and 40.

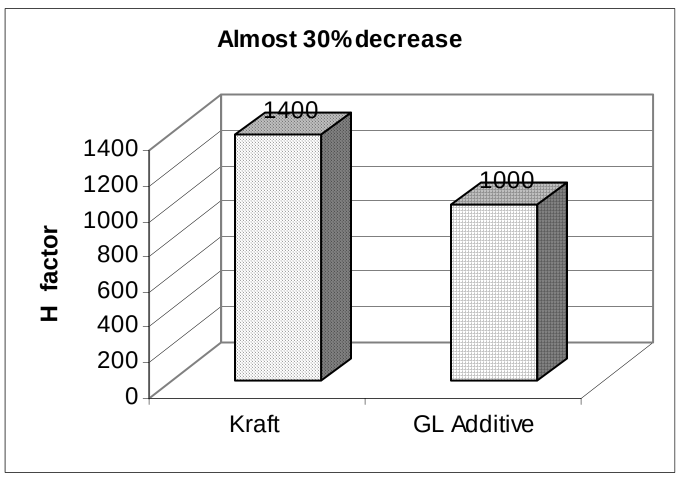


Figure 2. Shown above is a comparison of the H factors necessary for kraft and additive GL pulping to achieve a given Kappa (38 to 40).

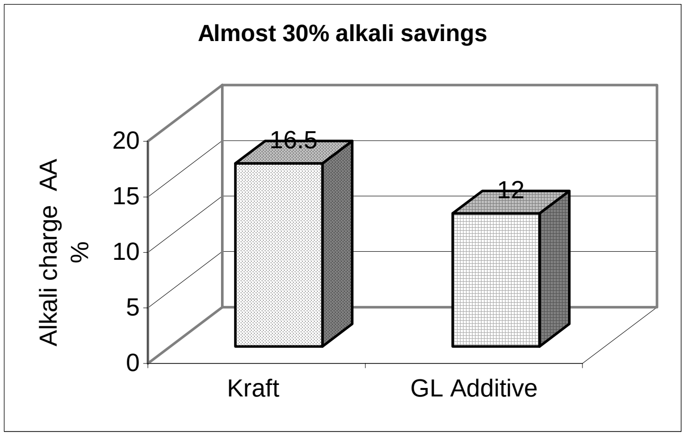


Figure 3. Shown above is a comparison of the alkali charges necessary for kraft and additive GL pulping to achieve a given Kappa (38 to 40).

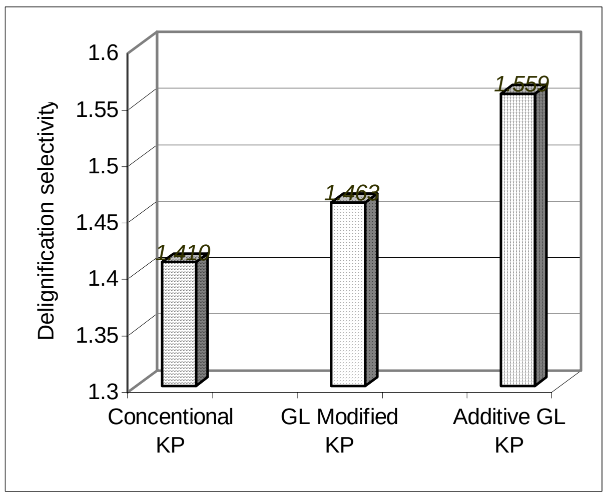


Figure 4. Comparison of the pulping selectivities for the KP, GL-modified, and additive-enhance GL cooking processes.

3.2.2 Develop WIN GEMS analysis of implementation at mill:

The balance of sodium and sulfur:

- Exiting digester = +0.00075 lb/lb Na, -0.23% sulfidity
- Exiting evaporators = +0.00043 lb/lb Na, +0.05% sulfidity
- Exiting WL clarifiers = -0.00022 lb/lb Na, +0.21% sulfidity

Boiler energy consumption:

- 1 st/d makeup salt cake necessary
- 1200 MBTU/d less steam energy available
- 2 st/d less makeup caustic required

3.2.3 Specific economic simulations given mill schematics

- 62% yield SW base ply, 56% yield SW top ply with 3% yield increase (base case)
- 4250 lb steam/BDMT (base case)
- 30% reduction for caustic chemical demands
- 97.8% reduction in solids flow to recovery boiler in GL case

Y3/Q2:

3.1.1 IEC, NMR analysis

- The investigation on the behavior of carbohydrate composition is significant for pulping chemistry and technology. However, the performance of carbohydrates in GL pretreatment have never been reported in the literatures. Our current work analyzed the changes in carbohydrate components in wood during GL pretreatment process, the regularity of sugar change and itscorrelation with pretreatment variables was investigated, which would provide new fundamental knowledge to understand the rational of efficiency of GL modified pulping technology.
- Totally, 15%-20% of carbohydrates in wood are removed from wood chips during GL pretreatment. Most of them occurred in the early stages of the pretreatment. Glucose and mannose are the main components of the lost carbohydrates.
- The pretreatment parameters have an obvious influence on carbohydrates; the main characteristics of carbohydrates in GL pretreatment are re-adsorption in neutral or slightly alkalinity conditions and substantial mannose dissolution. Both higher temperature and GL concentration strengthen both sugars dissolution and re-adsorption, as Figures 1 and 2 show.

3.2.1. Discuss potential mill trials

- To develop GL modification technology in industrial application, we are conducting specific experiments at various paper mill requests. The current results for Samoa company show that the reduction in alkali and better pulp qualities could be achieved by using GL pretreatment modified kraft pulping. (Figure 3)

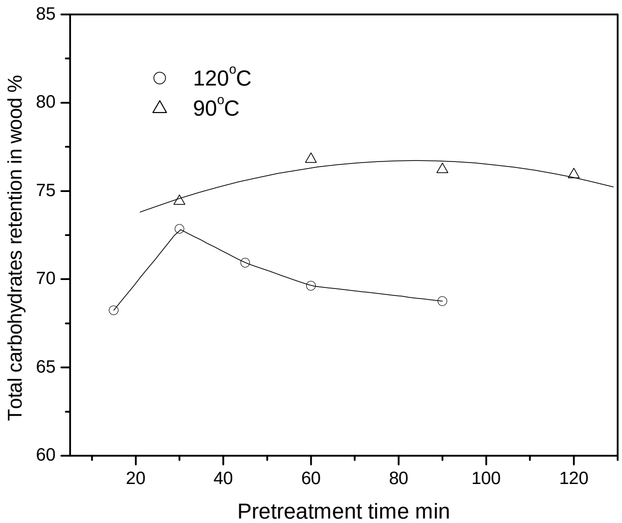


Figure 1. Changes in total carbohydrate during GL pretreatment

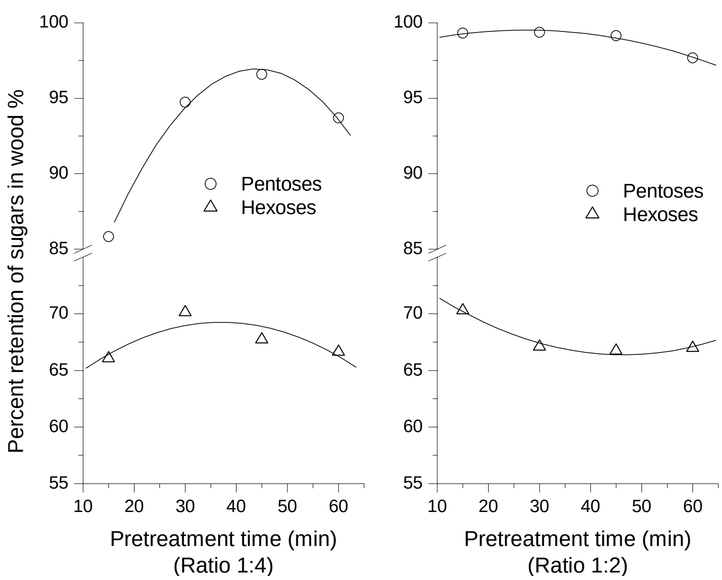


Figure 2. Comparison in pentose and hexose retention under varied GL concentration(120^{o}C)

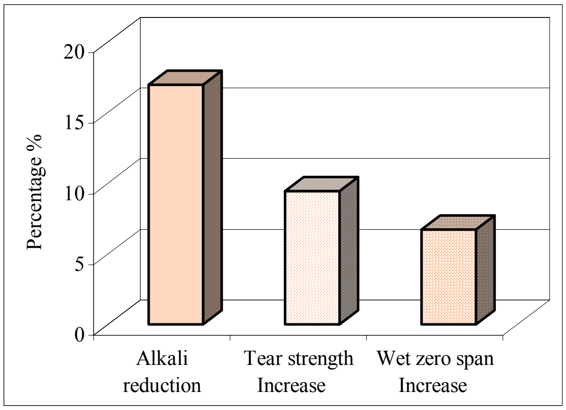


Figure 3. Comparison between conventional and GL modified KP

General scientific conclusions:

- Carbohydrates re-adsorption can occur in the pretreatment process, especially when the pretreatment process approaches near neutral environment. Pentoses are more apt to be re-adsorbed onto fiber than hexoses.
- Additive applied in the pretreatment can improve GL efficiency. Surfactants appear to have profound impact on carbohydrates retention; a suitable surfactant strikingly increases the sugar retention. The rational of surfactant function related to structure needs to be further investigated. Furthermore, other additives also show a positive influence on carbohydrates retention. The results demonstrate that the additive could play a significant role in the GL pretreatment to improve carbohydrates retention and delignification.
- During the pretreatment with green liquor, hydrogen sulfide ion reacts with wood components and is retained in wood by chemical bonding which could result in a higher carbohydrates retention by stabilization of sugars aldehyde groups.

Y3/Q3:

3.2.1 Discuss potential mill trials with Georgia Pacific or suitable mill sponsor

- Cooperation with our industrial partners have been made a exciting progress. The mill trials are discussing in detail with IP and Samoa.

3.2.4 OLI modeling of evaporator fouling

- How to handle the residual liquor after the pretreatment is very important issue that deals with the industrial application of GL pretreatment technology. Due to the extra process liquor produced from the pretreatment, characterized as high carbonate content, it is not feasible if transferring this sort of liquor into the evaporating system because the evaporation burden will increase. Our current efforts are to investigate direct causticizing of the pretreatment liquor, a simple and economical way to satisfy industrial demand. Overall, the same conversion level could be achieved in the direct causticizing process by using the residual pretreatment liquor compared to GL. The features of causticized liquor are satisfactory to reuse as white liquor. The impacts of pretreatment process on causticization are shown in Fig 1-2.

- High performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD) technology has been well used for analysis of carbohydrate components. However, the past work mainly focused on analysis of solid samples, wood and pulps, and the analytic methods only fit for solid samples. The analysis for process liquors is significant to understand carbohydrates chemistry mechanisms. In the current work, we established the optimal hydrolysis conditions for both pretreatment liquor and black liquor by using D-Optimal Experimental design, which could then be applied to analyze carbohydrate components in the process liquor.

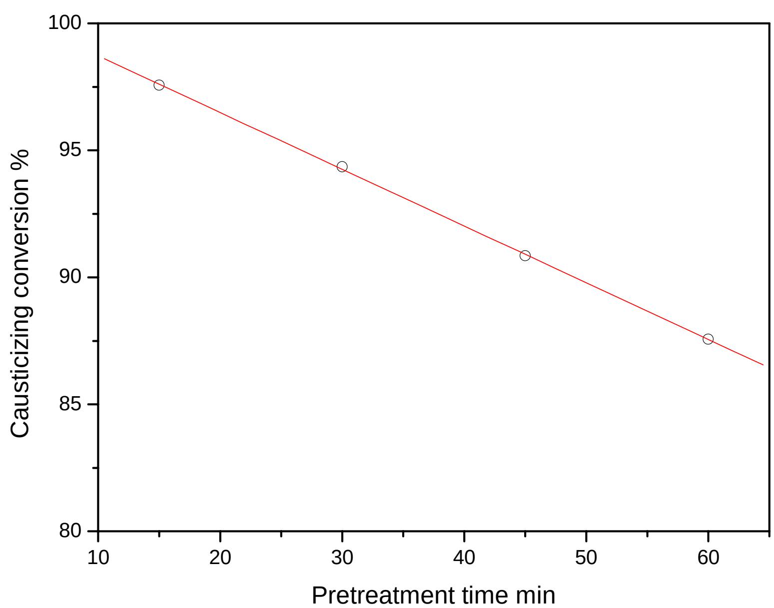


Figure 1. Influence of pretreatment time on causticizing conversion

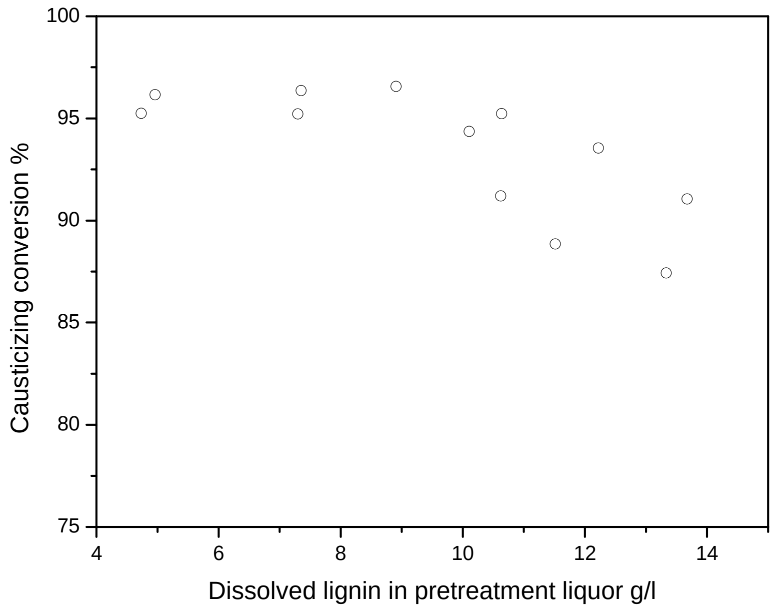
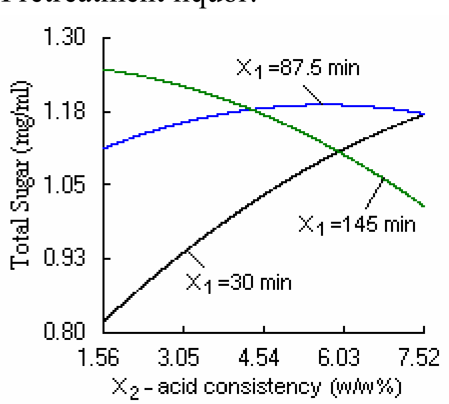
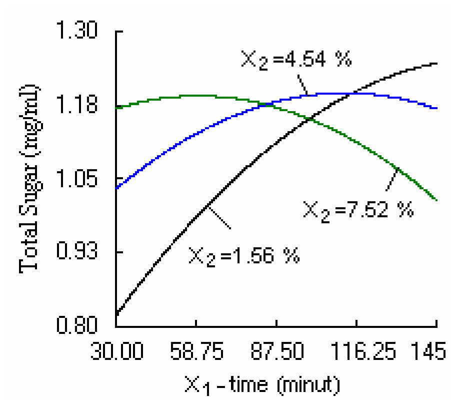
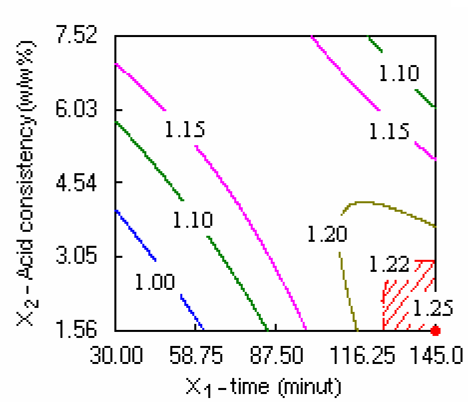


Figure 2. Correlation of lignin content in pretreatment liquor with causticizing conversion

Pretreatment liquor:







treatment liquor hydrolysis

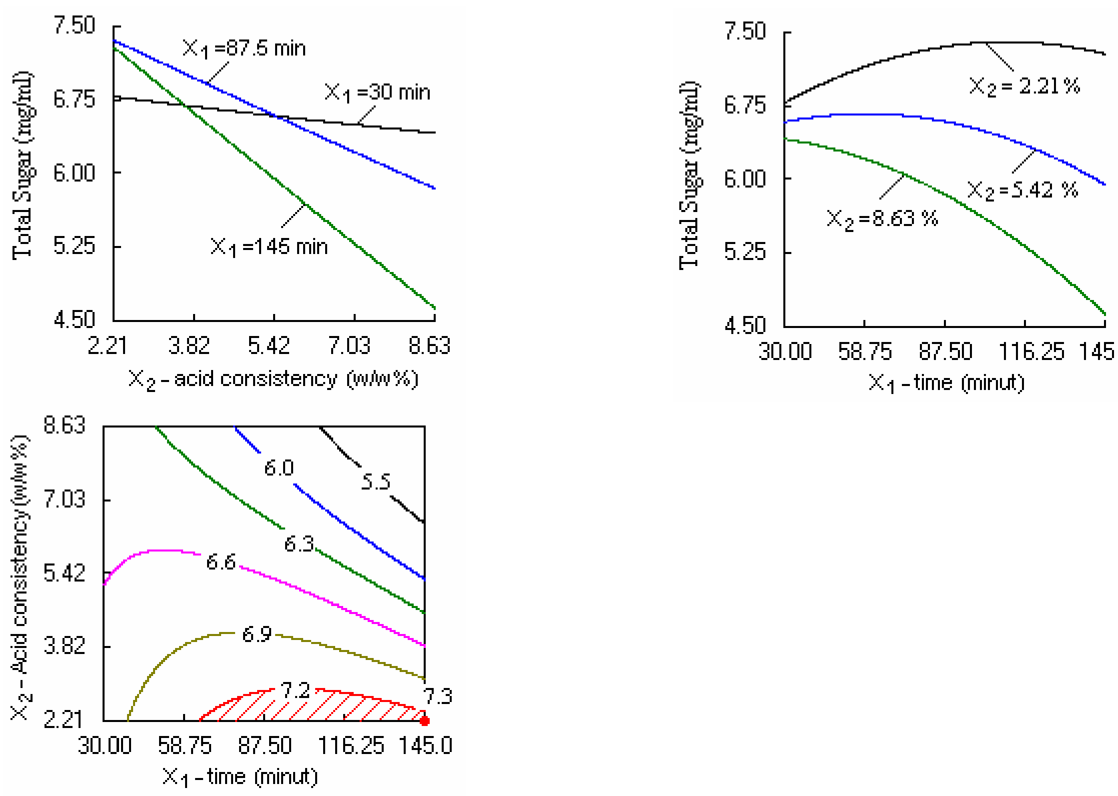


Figure 4. Optimal regression of black liquor hydrolysis.

General scientific conclusions

- The pretreatment parameter influence on the causticization of residual liquor. Both higher pretreatment temperature and longer time would decrease the causticizing efficiency. Lignin content in the pretreatment liquor can be correlated with causticizing conversion; when there is a lower lignin level in the pretreatment liquor, no obvious impact on causticization could be observed, however, at a high level of lignin content (>10 g/l), lignin increase resulted in a reduction in causticizing efficiency.
- To analyze carbohydrates in the process liquor by HPAEC-PAD, various types of liquors needed different hydrolysis conditions. For the pretreatment liquor, hydrolysis with a lower acid concentration for a longer time is preferred; in our experimental range, 1.5 % acid concentration and 145 min are the optimal conditions. Compared to pretreatment liquor, black liquor needs higher acid concentration to achieve the highest sugar yield. The favorable conditions for black liquor hydrolysis are 2.2% acid concentration and 145 min. where the regression equations that correlate sugars yield and hydrolysis parameters are described as follows:

Pretreatment liquor:
$Y=1.18086+0.06756X_1+0.02921X_2-0.07958X_1^2-0.03924X_2^2-0.14602X_1*X_2$
(Relevance Test: R=0.99)

Black liquor:

$$Y=131.76146-6.44777X_1-15.14776X2-6.51126X_1^2+0.20198X_2^2-11.43658X_1*X_2$$

(Relevance Test: R= 0.99)

X_1 : Hydrolysis time(min)

X_2 : Acid concentration(%)

Y3/Q4:

3.1.3 Rational for GL modified pulping:

● To apply GL pretreatment technology in a modern kraft pulping process, the suitability of GL modified technology was investigated as part of different pulping processes. The difference between conventional pulping and RDH pulping was compared. Figure1 shows the influence of RDH on pulp yield. One more percent point higher in pulp yield was obtained by using the presteaming process.

● Our previous reports have indicated the following benefits of additive GL pretreatment: higher pulp yield, shorter cooking time, and as much as one third of the total alkali used currently in conventional cooking for bleached grades was achieved. The current experiments further confirm the efficiency of additive GL modified kraft pulping. A similar pulp yield increase (approximately 2 absolute percentage points) was achieved with a concomitant 30% reduction in alkali charge at presteaming conditions, as shown in Figure 2.

● The synergistic effect of using surfactant, BL, and AQ either in the pretreatment or postcook were explored for optimization of GL pretreatment technology. Figure 3 illustrates the pulping selectivity in various processes associated with different additives. By using a combination of GL pretreatment and AQ additive kraft postcook, the pulping selectivity was tremendously improved. The results demonstrate that AQ could further exert an important impact in the post cooking process. Surprisingly, when using BL to replace water in GL pretreatment, the pulping selectivity also was improved. The mechanism requires further investigation.

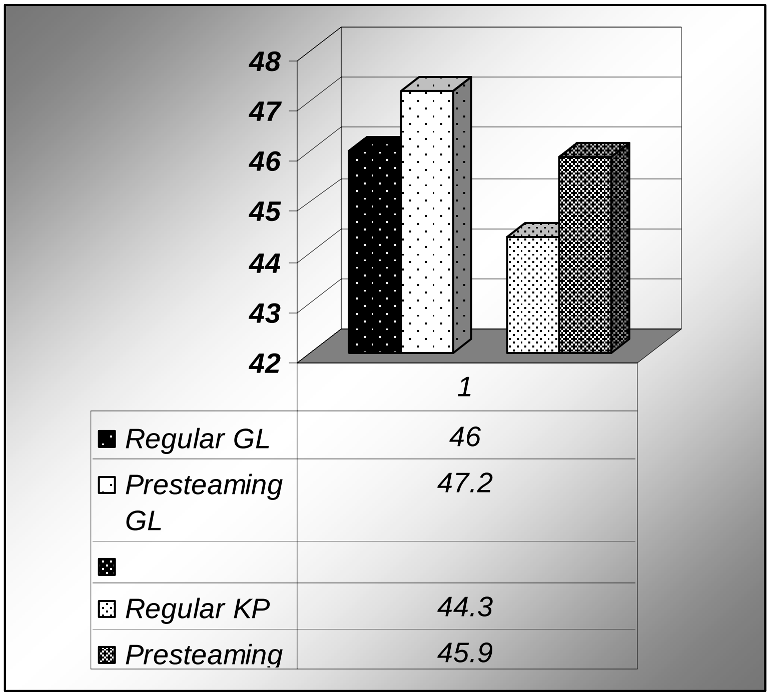


Figure 1. Influence of RDH on pulp yield.
(Kappa: No presteaming GL 31.3; Presteaming GL 30.8; Regular KP 30.6; Presteaming KP 30.2)

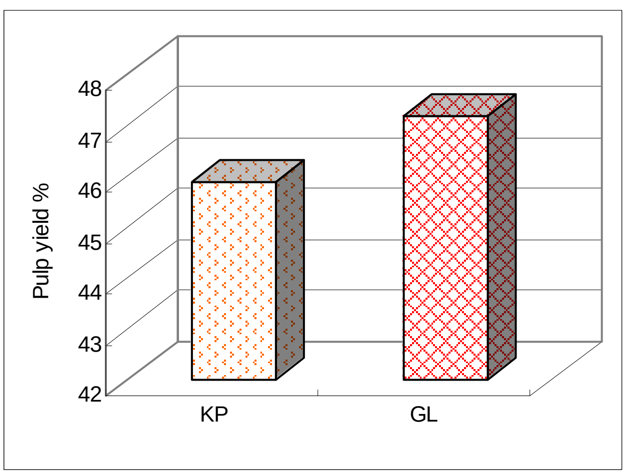


Figure 2. Comparison of pulp yield between kraft and additive GL modified pulping.
(With presteaming; Kappa: KP 30.21, GL 30.8)

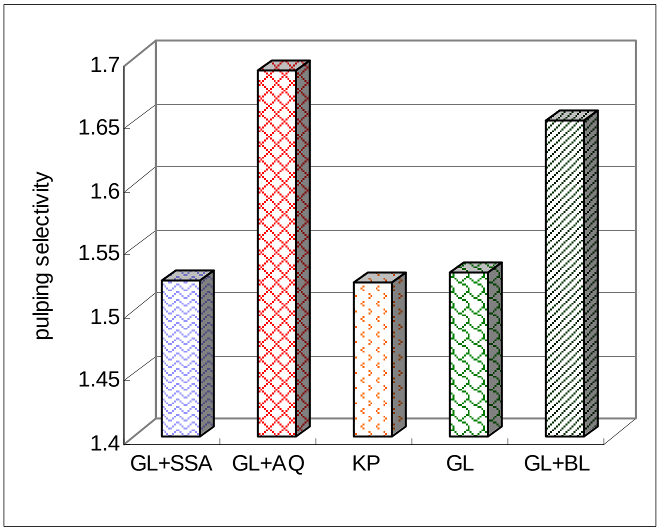


Figure 3. Comparison in various GL pretreatment processes
(GL+SSA: Surfactant additive in GL pretreatment;
GL+AQ: GL pretreatment followed by AQ additive Kraft cook;
KP: Regular Kraft cook;
GL: Additive GL pretreatment;
GL+BL: Combined GL with BL pretreatment.)

General scientific conclusions:

RDH pulping is influenced by pretreatment similarly to regular cooking. As we reported in previous work, the majority of carbohydrates removed in pretreatment phase are lost in the temperature ramp stage, about 25% of the total sugars in the wood. That indicates that a shorter, rapid ramp stage would benefit carbohydrates retention. Furthermore, RDH appears to accelerate the adsorption of sulfide into the wood chips. Through RDH pretreatment, 30% of the pretreatment time has been reduced; however, 100 % sulfide adsorption has been achieved. This result indicates that increased sulfide adsorption and decreased carbohydrate loss can be achieved by optimizing the pretreatment procedure.

Y4/Q1:

3.1.3 Rational for GL modified pulping

- After completing a typical GL pretreatment, the residual liquor contains a large amount of carbonate and some decomposed lignin and carbohydrates. Directly causticizing the residual liquor to produce white liquor for circulation of this part process liquor is a feasible method for industrial application of the GL pretreatment technology.

- The comparisons of causticizing conversion rates of various residual pretreatment liquors with GL are shown in Fig. 1. Overall, under regular pretreatment conditions (120°C, 30 min.; 90°C, 30-60 min.), the residual liquor showed similar causticizing conversion rates compared with the original GL. The data indicate that residual liquor could be directly causticized as is done in the normal GL process. In the case of using a higher pretreatment temperature or longer time, the causticizing conversion rate of the residual liquor would decrease due to the influence of higher levels of dissolved lignin. Fig. 2 demonstrates the influence of pretreatment time on conversion rate. Extending pretreatment time from 30 minutes to 60 and to 90 minutes, would cause conversion rates to drop 12%-15%.

- To verify the change of lignin content in the causticizing process, the lignin content in pretreatment liquor before and after causticizing was analyzed by UV. In the causticizing process more lignin remained in the residual liquor, approximately 70%-80%, while the rest of the lignin is part of the mud settling. As shown in Fig. 3, by increasing pretreatment time, a reduction in the lignin remaining in the residual liquor is decreased.

- The basis for lignin distribution in the liquor and in the settling can be correlated with lignin concentration in the residual liquor. A higher lignin concentration in the original residual liquor would result in less lignin settling with the carbonate mud, as shown in Fig. 4. The mechanism is not clear and needs to further investigation.

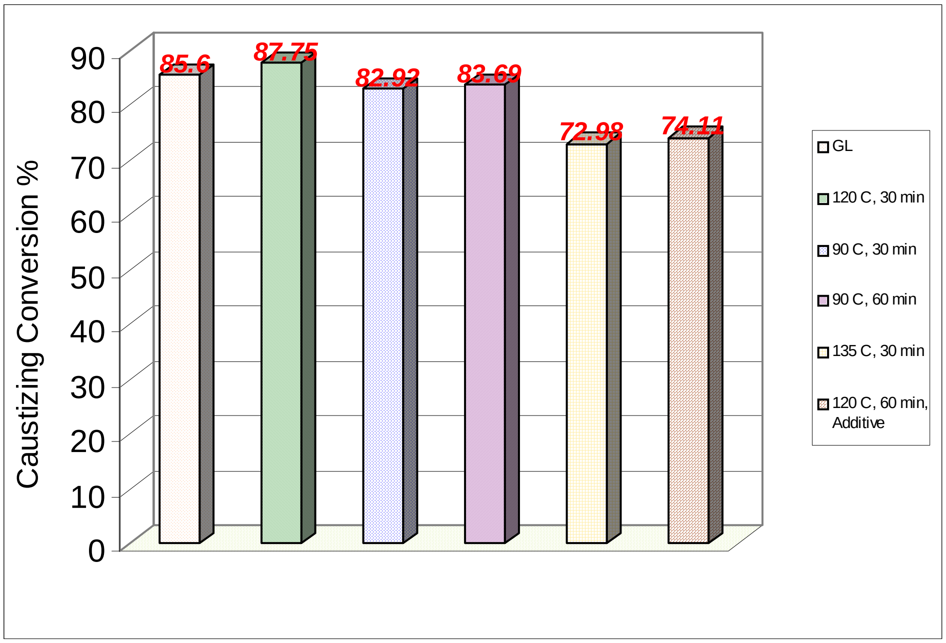


Figure 1. Comparison of causticizing conversion rates among various GL pretreatment liquors and original GL systems.

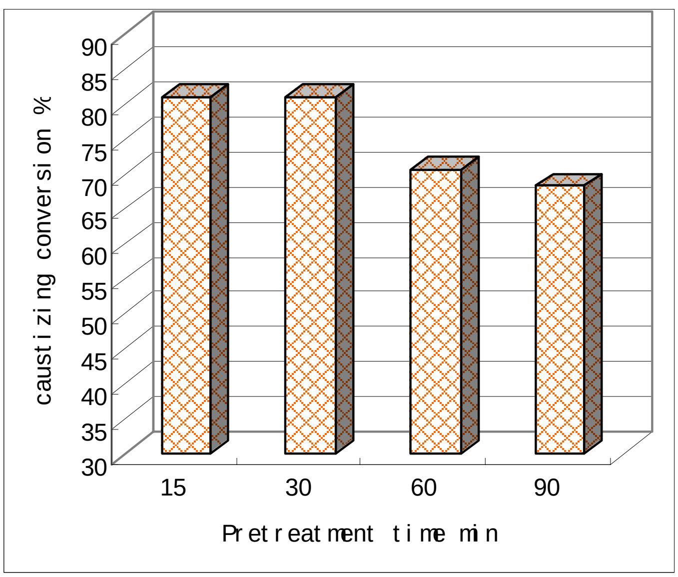


Figure 2. Impact of pretreatment time on causticizing conversion.

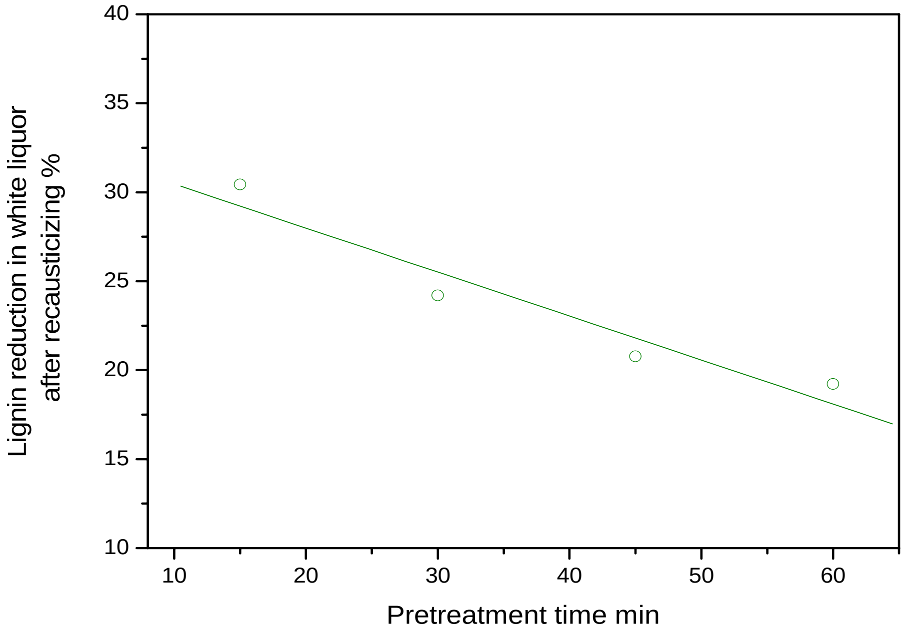


Figure 3. Impact of pretreatment time on lignin content in the WL.

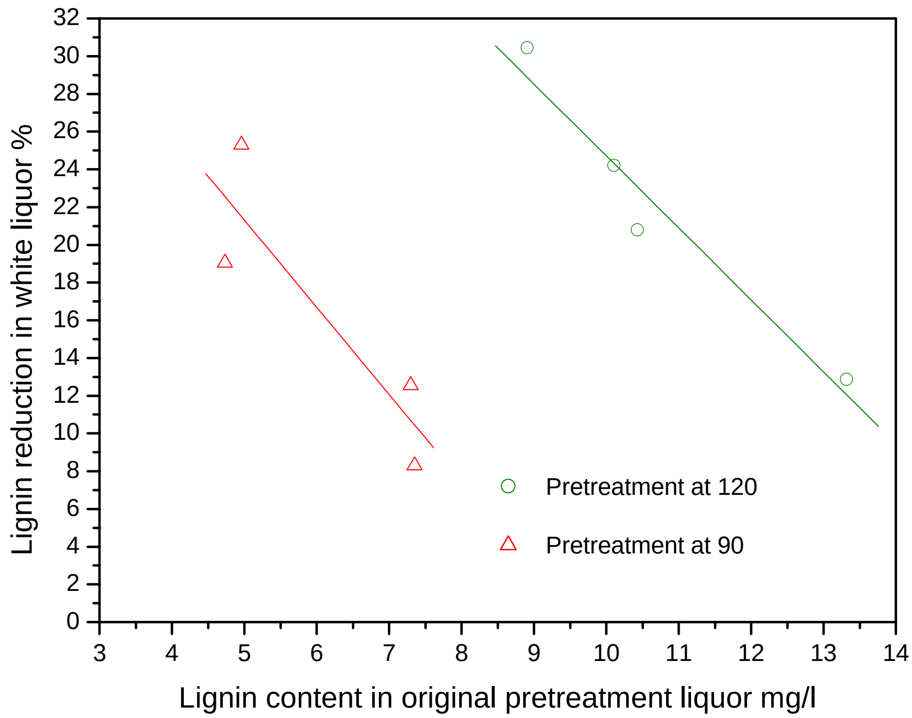


Figure 4. Correlation of lignin content in original pretreatment liquor and WL.

General scientific conclusions:

By using residual pretreatment liquor in a direct causticization process, similar alkali conversion rates could be achieved compared to normal GL conversion. Lignin dissolved in the residual liquor during the pretreatment has a profound influence on both causticizing conversion and lignin distribution in the settling and liquor. A higher lignin concentration in the residual liquor results in a lower alkali conversion rate and a higher lignin content in the white liquor. A full analysis still needs to be done.

Y4/Q2:

GL pretreatment has been shown to improve the efficiency of chemical performance for delignification. First, chemical consumption is well matched with lignin dissolution in each pulping stage, in which they mainly contribute to delignification; further, the function of hydrosulfide toward delignification is enhanced through GL pretreatment. A higher consumption ratio of hydrosulfide to hydroxide in the bulk phase pulping period correlates with a higher delignification rate. A linear relationship was shown to exist between lignin removal and hydrosulfide.

Delignification kinetics for GL-modified kraft pulping may also be modeled as a first-order process that includes three successive phases. Compared to conventional kraft pulping, the GL pretreatment pulping process has a higher delignification rate. The process accelerates the bulk delignification by 20 minutes and takes a shorter time for each consecutive stage. It is possible to reduce the whole pulping process by 30 minutes or longer. The average delignification rate may also be increased by as much as 30% compared to the kraft cook control.

Y4/Q3:

3.1.3. Rational for GL modified pulping

Our previous work investigated the kinetics of delignification for GL pretreatment modified pulping. Our most recent work continues to unveil the kinetic features of carbohydrates chemistry in the pretreatment and post cook.

Various carbohydrates tend to dissolve during both GL pretreatment and Kraft pulping in a linear manner as the temperature increases. However, the dissolution rate of carbohydrates in the GL pretreatment is much lower than that in the early stages of conventional Kraft pulping as shown in Fig. 1. For example, at the same temperature, much less carbohydrates are dissolved in GL pretreatment compared to the early stages of conventional Kraft pulping. The result indicates that the mild lower alkali conditions in GL pretreatment reduce carbohydrates losses in the chips during chemical penetration and adsorption.

In general, total carbohydrate removal in GL pretreatment can be divided into two stages as shown in Fig. 2: during the 90 minute period, total carbohydrate removal shows a linear increase as the process proceeds. After 90 minutes, there is no obvious change in the carbohydrate level. The result indicates that a different mechanism is in effect in this second period. A near neutral pH environment after 90 minutes of pretreatment is one reason for the observed decrease in carbohydrate losses. A readsorption of carbohydrates onto the wood chips is another possible explanation for the reduction in total carbohydrate removal as we reported in a previous report.

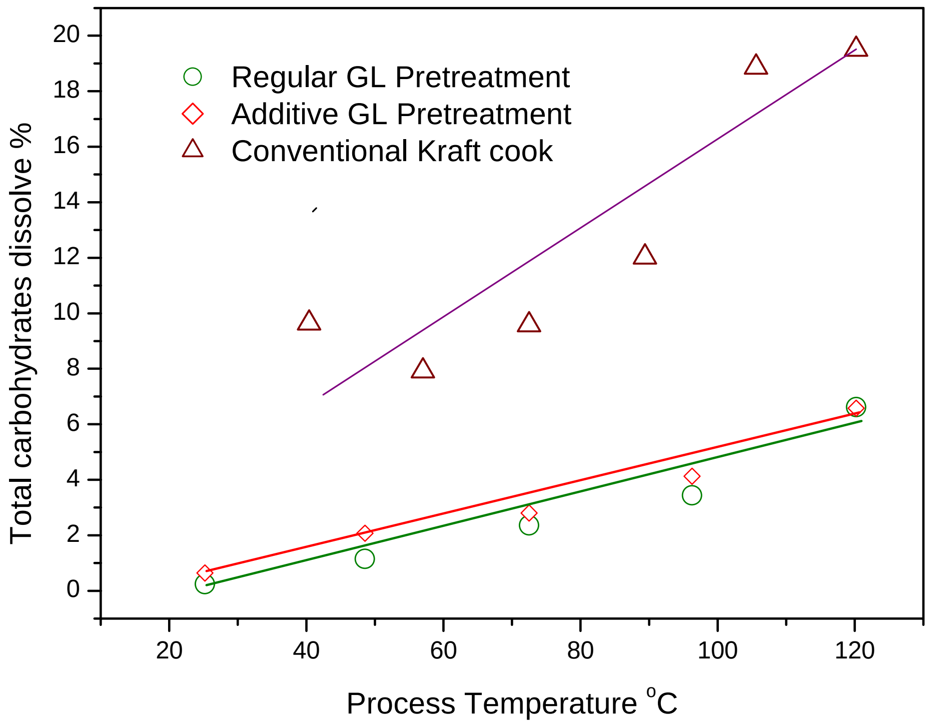


Figure 1. Comparison of total carbohydrates dissolution in GL pretreatment and the early stages of Kraft cooking.

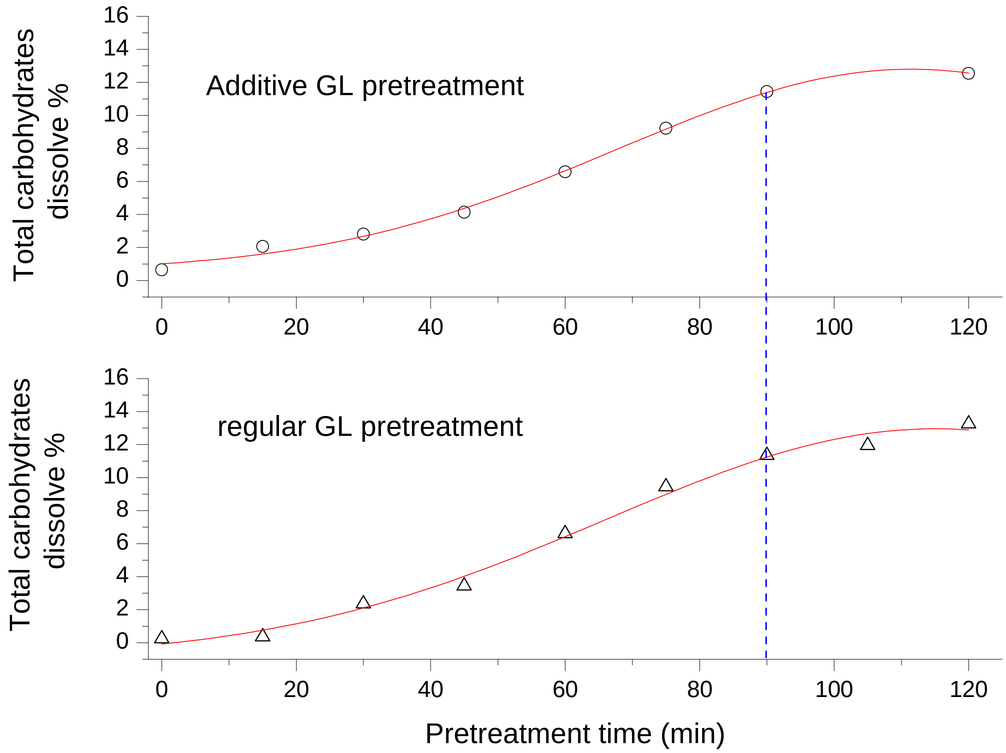


Figure 2. Kinetics of carbohydrate losses during GL pretreatment.

IV. Accomplishments

We have published fourteen paper on this subject and provided seven conference presentations on the subject as shown below:

Publications:

1. Singh, J.; Ragauskas, A.R.; Lucia, L.A. "Green Liquor Chip Pretreatment as a Feasible Method for the Enhancement of Softwood Pulp Chemical Properties," *Cell. Chem. Technol.* **2002**, 1-2, 173-181.
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We have had one mill examine our technology within the context of faster paper machine speeds and found good results. Our most important achievement, however, will be the implementation of this technology at a North American mill during 2005-2006. We have agreed in principle to coordinate a trial within this time period given the fact we have received additional funding from the US DOE from 2005-2009.

V. Conclusions

The technology described in this final report has significant commercial applications within a kraft mill, especially a brown mill, to improve pulp properties, significantly reduce energy requirements, and improve paper machine speed. We expect commercialization within the next two years given the industrial interest, government support, and results to date.

VI. Recommendations

We are continuing this work within the newly funded US DOE project "**HIGHLY ENERGY EFFICIENT D-GLU (DIRECTED GREEN LIQUOR UTILIZATION) PULPING (DE-FC36-04GO14308).**"

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