CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE MEETING

November 4-5, 1998

CHEMICAL PULPING AND BLEACHING

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CHEMICAL PULPING AND BLEACHING PAC MEETING

November 4-5, 1998 Agenda

Wednesday, November 4

9:00 Introduction (Don Dimmel/Tadas Macas)

9:10 Research lines, Future Consortium Project Selection (Earl Malcolm)

9:30 RAC report (Pat Bryant/Tadas Macas)

9:50 Fundamentals of Bleaching Chemistry - Project F015
(A) peroxide, laccase, hexenuronic acid (Art Ragauskas)
(B) singlet oxygen (Lucian Lucia)

11:00 Complete F015A and F015B Project Report Form + break

11:15 Selectivity of Ozone Bleaching - USDA Project 4168 (Don Dimmel)

11:35 Student research - Mike Zawadski

12:00 Complete 4168 Project Report Form (optional) + lunch

12:40 Report from Chemical Recovery closed mill research (Peter Pfromm)

1:00 Closed Mill Operations - Project F017 (Jim Frederick, Alan Rudie)

2:15 Complete Project Report Form for F017 + break

2:30 Environmentally Compatible Production of Bleached Chemical Pulp - Project F013 (Tom McDonough, Chuck Courchene)

3:15 Complete Project Report Form for F013 + break

3:30 Project F030 (Jian Li)

3:50 Project F014 (Art Ragauskas)

4:20 Complete Project Report Forms for F030 and F014 + break

4:35 Externally-funded projects:

- Trees with Built-in Catalysts - Project 4181 (Don Dimmel)
- Trees with Modified Lignin - Project 4226 (Don Dimmel)
- Energy Efficient Kraft Pulping for .... Low-Lignin Pulp - Project 4120 (McDonough)
- High Efficiency ClO_2 Delignification - Project 4159 (Tom McDonough)
- Low Capital ECF Bleaching – Project 4201 (Tom McDonough)

5:45 Complete Project Report Form for 4000 projects (optional)

6:00 Dinner

Thursday, November 5

8:00 IPST News, Project ROCIT (Earl Malcolm)

8:15-12:15 Committee Discussions

CHEMICAL PULPING AND BLEACHING
PROJECT ADVISORY COMMITTEE

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FY-2000 PLANNING SUMMARIES

DUES-FUNDED PROJECT SUMMARY

Project Title: Environmentally Compatible Production of Bleached Chemical Pulp
Project Number: F013
PAC: Chemical Pulping and Bleaching
Project Duration: 1 year
Project Staff:
Faculty/Senior Staff: T.J. McDonough, C.E. Courchene, J. Waterhouse
Staff: M. Turner, A. Shaket, M. Bliss
Project Funding:
Allocated as Matching Funds: $50,000
Proposed Budget: $250,000

RESEARCH LINE/ROADMAP:
Environmental Perfomance/RM5 - Reduce Emissions

BENEFITS TO INDUSTRY:
Improved environmental performance of pulp manufacturing facilities with minimum cost.

PROJECT OBJECTIVE:
Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

DELIVERABLES:
1. Assessment of alternatives for activation and catalysis of peroxide delignification of kraft brownstock.

2. Development of novel hardwood kraft bleach sequences based on Rapid D_0 technology and prehydrolysis.

3. Determine effects of delignification with ozone, chlorine dioxide, oxygen and their combinations on fiber characteristics and papermaking and end-use related pulp properties.

4. Leveraging of relevant externally funded research on one or more of the following topics:

   - Bubble size control to improve oxygen-based bleaching
   - ClO_2-based bleaching in closed-mill systems
   - Odor-free, low-kappa bleached pulp manufacturing process
   - Low-capital ECF bleaching sequences for closed mill systems
   - Distribution and control of nonprocess elements in closed bleach plants
   - Extended D(EOP) delignification

Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

Project Title: Fundamentals of Brightness Stability
Project Code/Project Number: F014
PAC: Chemical Pulping and Bleaching
Project Duration: FY 1999 - 2000
Project Staff:
Faculty/Senior Staff: Arthur J. Ragauskas and Lenong Allison
Staff:
Project Funding: $63,000
Allocated as Matching Funds: N/A

RESEARCH LINE/ROADMAP:

Improved Forest Productivity:

- Increase the yield of kraft-pulp equivalent fiber by 10%.
- Use of post treatments to give kraft properties.
- Modification of structure or composition of products.

BENEFITS TO INDUSTRY:

The projected benefits of this project are to improve the use high-yield fibers for papermaking applications.

PROJECT OBJECTIVES:

Provide a fundamental understanding of the chemical reactions that are initiated when high-yield pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases methods to eliminate or significantly retard the photoyellowing of high-yield pulps will be pursued.

DELIVERABLES:

1. Optimize photostabilization effects of $CaCO_3$ with FWA and UV-absorber.
2. Study photobleaching chemistry of acetylated lignin.
3. Examine use of 'practical' alternatives to lignin acetylation to photostabilize high-yield fibers.

Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

Project Title: Chemical Fundamentals of Bleaching
Project Code/Project Number: F015
PAC: Chemical Pulping and Bleaching
Project Duration: FY 1999 - 2000
Project Staff:
Faculty/Senior Staff: Arthur J. Ragauskas, Lucian A. Lucia, Lenong Allison, Ki-Oh Hwang
Staff:
Project Funding: $270,000
Allocated as Matching Funds: N/A

RESEARCH LINE/ROADMAP:

Environmental Performance:

- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.
- Reduce water usage in bleached kraft pulp production to 2,500 gallons per ton.

Improved Forest Productivity:

- Increase the yield of kraft-pulp equivalent fiber by 10%.

BENEFITS TO INDUSTRY:

The projected benefits of this project are to decrease the operating and capital costs associated with ECF bleaching of kraft pulps. Improvements in the selectivity of pulp bleaching chemicals are anticipated to yield enhanced physical properties of fully bleached kraft pulps. These objectives are to be accomplished while addressing current and future environmental performance requirements for bleaching kraft pulps.

PROJECT OBJECTIVES:

Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences. Understand the reasons for selectivity of reactions that occur in selected pulping and bleaching sequences. The research compliments Project F013 research on bleach process technology. Focus areas for this fiscal year are hexenuronic acids, biobleaching, high efficiency peroxide bleaching, and fundamentals of oxygen delignification.

DELIVERABLES:

1. Identify bleaching conditions that maximize efficient use of oxygen and hydrogen peroxide in (EOP) for D_0 bleached pulps.
2. Study pulping procedures to reduce hexenuronic acid content in hardwood kraft pulps. Evaluate the mechanisms involved in acidic peroxide treatment of hardwood kraft to decrease apparent kappa number.
3. Examine the use of laccase delignification technologies for high kappa pulps with respect to yield and physical properties.
4. Study the fundamental bleaching reactions of singlet oxygen in kraft softwood pulps as a function of light source and temperature and determine if the technology is patentable.

Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

RESEARCH LINE/ROADMAP:

Project Title:	Closed Mill Operation
Project Code/ Project Number:	CLDMIL/F017
PAC:	Chemical Pulping and Bleaching
Project Duration	2 years
Project Staff	
Faculty/Senior Staff:	Alan Rudie
Staff:	
Project Funding:	
Proposed Budget FY 99/00:	$120,000
Allocated as Matching Funds:	

RESEARCH LINE/ROADMAP:

4: Reduce water usage in Bleached Kraft Pulp production to 2500 gallons per ton.

BENEFITS TO INDUSTRY:

The industry is suffering from increased scale problems due to recent changes in bleaching practice and the continual need to reduce water use and wastewater discharge in the bleach plant. Development of NPE predictive capability to function with existing Mass and Energy balance simulators has become a priority in the industry. The pulp ion exchange process has been characterized in this project for the pH range 1-9, it is necessary to characterize the phenolic contribution to ion exchange (pH 9-10) to obtain complete predictive capability for metals management. To gain better control of the scale problem, the industry needs tools to and understand the precipitation and scaling process. Of particular interest is the evidence that nearly all bleach plants exceed the solubility limit of barium sulfate and calcium oxalate, but not all bleach plants have serious scaling problems. This conclusion comes from the bleach plant sampling effort of Pat Bryant where the minimum Barium and minimum sulfate concentrations were 3 times the solubility limit (using OLI) and a paper published by Per Ulmgren (Tappi 1997 Minimum Effluent Mill Symposium) indicating over 50% of the analyzed filtrate CaC_2O_4 was really a 500 Dalton micro-particulate. Since small crystals are thermodynamically unstable, determining the nature of the micro-particulate and if crystalline, the growth inhibitor, is of considerable interest and may provide a means to control scale.

PROJECT OBJECTIVES:

- Complete wood pulp ion exchange work to characterize NPE behavior at high pH.
- Initiate an investigate $BaSO_4$ and CaC_2O_4 precipitation, and scale.

DELIVERABLES:

1. Completed ion exchange models for NPE adsorption on wood pulp (high pH work).
2. Prevalence of bleach plant precipitates and correlation to scaling problems
3. Analysis of any organics associated with the precipitates and or scales.
    - Functional group (carboxylic acids?)
    - Molecular weight
    - Structural nature/origin (lignin, carbohydrate, extractives, process chemical)

Average Overall PAC Rating ____________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

Project Title:	**High Strength, High Yield Bleached Pulps**
Project Code/Project Number:	HSYBP/ F030
PAC:	Chemical Pulping and Bleaching
Project Duration:	FYR 2000
Project Staff:	
Faculty/Senior Staff:	J. Li, E. Malcolm, C. Courchene, D. Dimmel
Staff:	Tech. III
Project Funding:	$200,000
Allocated as Matching Funds:	$ 0

RESEARCH LINE/ROADMAP:

Increase Yield by 10% Absolute / Develop Modified Pulping Process.

BENEFITS TO INDUSTRY:

Significant cost reduction in chemical pulp product from low wood consumption and/or high production rate with present kraft mill capacity.

PROJECT OBJECTIVE:

The objective of this project is to significantly improve the strength properties of higher yield chemical pulps to the level of current, low yield, kraft pulp. Initial work will center on the suitable processes which do not require significant capital investment.

DELIVERABLES:

(1) **Complete the experiments on modification of one-liquor (no split sulfidity) cooking:** the goal of this research is to develop modified cooking conditions that do not require any significant amount of capital investment when applied in current mill equipment.

(2) **Start to develop multi-stage pulping processes using split-sulfidity liquors per 3-year research plan:** Using split-sulfidity liquors should allow higher yield gain, and give the possibility of improving pulp strength.

(3) **Continue to develop suitable process conditions for Soda-Catalyst pulping to achieve high yield and strength:** This part of research will use alkali concentration to alter carbohydrate degradation and extraction rate.

(4) **Start the research on high kappa number followed with oxygen delignification:** This part of research will focus on improvement of the strength properties of this kind of pulp.

Average Overall PAC Rating ____________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

Project Title:	Selective Determination of Lignin Linkages in Wood and Pulp
Project Number:	New
PAC:	Chemical Pulping and Bleaching, Forest Biology
Project Duration:	Three years, starting in FY 2000
Project Faculty/Senior Staff:	Gary Peter, Don Dimmel
Staff:	Elizabeth Althen
Project Funding:	
Proposed Budget:	$100,000 FYR 2000

RESEARCH LINE - ROADMAP

Environmental Performance – (a) Develop economically viable pulping technology to produce kraft equivalent pulp which ensures no odor at mill boundaries and (b) reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.
Improved Forest Productivity – Increase the yield of kraft-pulp equivalent fiber by 10%.

BENEFITS TO INDUSTRY

Accurate knowledge of residual lignin structure prior to and after various bleaching stages will provide the scientific basis needed to make significant advances in pulping and bleaching technologies. Present methods of characterizing lignin rely mainly on isolating (with modification) a faction of the lignin present. Reagents that are specific to *in situ* lignin-lignin and lignin-carbohydrate linkages are required to determine the amounts and spatial distribution of key linkages of residual lignin in the fiber. Sensitive, specific reagents will provide unique fundamental information about lignin structure and, thus, accelerate the development of (1) more rapid, milder pulping reactions that increase productivity and pulp strength with lower applied energies, (2) bleaching systems that target specific linkages, resulting in improved selectivity, lower costs and processes that limit water usage and organic discharges, and (3) the detection of trees with lignin structures better suited for pulping and bleaching.

PROJECT OBJECTIVES

Develop and characterize antibody reagents that rapidly identify specific lignin-lignin and lignin-carbohydrate linkages. We will use this antibody technology to (1) quantify the level of such linkages and attempt to correlate their location and structural features with lignin reactivity and (2) develop a high-through put screening method that will aid in the discovery of novel chemistries for lignin removal and of natural tree variants with more easily removed lignin. Limited studies have shown that antibodies, which are proteins, can be developed to react with specific linkages of lignin or carbohydrates. Presently, we have polyclonal antibodies that react with select condensed and uncondensed lignins in pines. These antibodies can be used to rapidly map the spatial aspects of condensed versus uncondensed lignin that are removed and redeposited during the various pulping and bleaching treatments.

DELIVERABLES

We will generate a set of antibodies that bind specifically with distinct lignin linkages. The research will consist of:

1. producing various synthetic lignin model compounds, both soluble and insoluble,
2. characterizing the specificity of existing antibodies with these synthetic lignins,
3. generating new antibodies with defined specificity to lignins and lignin carbohydrate complexes, and
4. using purified antibodies to investigate the structure and organization of residual lignins after modified pulping and bleaching reactions

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Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

Project Title: Trees with Easily Pulped Lignin through New Genetic Selection Methods
Project Number: New
PAC: Chemical Pulping and Bleaching PAC & Forest Biology PAC
Project Duration: 3 years (Initiate FY 2000).
Project Staff:
  Faculty/Senior Staff: John MacKay, Don Dimmel
  Staff: Elizabeth Althen
Project Funding:
  Allocated as Matching Funds: USDA funds of $24,000; IPST exploratory funds of $10,000 (1998, 1999)
  Proposed Budget: $100,000 yearly (FY 2000).

RESEARCH LINE - ROADMAP:

Improved Productivity - Improve the fiber productivity of North American lands so that they are competitive in the world pulpwood market. (Genetically improved trees)
Environmental Performance – (a) Develop economically viable pulping technology to produce kraft equivalent pulp which ensures no odor at mill boundaries and (b) reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.

BENEFITS TO INDUSTRY:

The proposed research is aimed at developing trees that containing easily extracted lignin and/or less lignin. Trees containing modified lignin will allow pulping to be conducted more rapidly or under milder conditions, leading to increased productivity, stronger pulps (because of less fiber damage), lower energy and bleaching costs, less bleaching by-products, and possibly processes that rely less on sulfur.

PROJECT OBJECTIVES:

The objectives are first, to develop and use methods of producing trees with modified lignin and/or less lignin that do not require gene transfer technology. Without gene transfer the cost to develop and produce the trees will be low and, rapid implementation would be possible through traditional tree improvement methods. Secondly, we will investigate lignin structure and reactivity in pulping and bleaching to determine the potential benefits to industry.

DELIVERABLES:

1. The research will continue and expand the genetic and chemical (pulping and bleaching) study of loblolly pine trees that are deficient in cinnamyl alcohol dehydrogenase (CAD), a key enzyme in lignin synthesis. We have already shown that trees that are completely deficient in CAD enzyme are easily delignified by alkali alone. Specifically, we propose to:
   - Identify and characterize diverse loblolly pines that are partially CAD-deficient.
   - Evaluate the potential benefits for pulping and bleaching of trees with complete and partial CAD-deficiency, emphasizing kraft, kraft/AQ, and soda/AQ pulping and standard DEDED bleaching.
   - Investigate the relationship between partial and complete CAD-deficiency, lignin structure, and lignin reactivity to better understand the chemical basis of delignification during pulping in CAD-deficient trees.
2. A second area will be aimed at identifying other potential methods for genetic modification of lignin synthesis that could decrease the lignin content of wood and, thereby, increase the cellulose content. This research is longer term in nature and relies, in part, on developments being reported in other research groups.
3. Selective breeding programs, aimed at amplification of the novel lignin component, will be initiated with North Carolina State University.

Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY
FY 1999 – 2,000

Project Title:	Fundamentals of Bleaching Mixed Office Waste
Project Number:	New
PAC:	Chemical Pulping and Bleaching
Project Duration	3 years (Initiate FY 2000)
Division:	Chemical and Biological Sciences
Project Staff	
Faculty/Senior Staff:	Arthur J. Ragauskas, Lucian Lucia
Staff:	Lenong Allison
Project Funding:	
Allocated as Matching Funds:	N/A
Proposed Budget:	$ 75,000

RESEARCH LINE/ROADMAP:

Recycling

Reduce and/or control contaminants (e.g., stickies, dyes, toners) in recycled-fiber pulp using break-through technologies to allow complete interchange of recycled pulp with virgin pulp of similar fiber make up at economical cost.

- Develop new separation processes
- Develop techniques to modify contaminants

BENEFITS TO INDUSTRY:

The proposed research will provide a fundamental understanding of how chemical bleaching agents destroy color bodies in Mixed Office Waste (MOW). These results will provide a basis from which new, improved bleaching sequences for MOW could be developed and also facilitate optimization of current bleaching sequences. In addition, the detrimental impact of mechanical pulp in MOW streams will be studied and new chemistries will be developed to minimize the effect of this furnish

PROJECT OBJECTIVE:

The goal of this 3-year project is to develop a fundamental understanding of the oxidative and reductive chemical reactions involved in bleaching MOW. A special emphasis will be placed on determining how differing bleaching chemicals/sequences influence the final brightness and color of the bleached pulp. The fundamental factors contributing to improved MOW bleaching for an oxidative – reductive sequence over a reductive – oxidative sequence will be established. The chemical reactions involving high-yield fibers in bleaching MOW will be determined and this data will be employed to minimize color formation from this fiber source.

DELIVERABLES FOR FY 99 – 2000:

1. Literature report summarizing the available technologies for bleaching MOW.
2. Study the oxidative degradation of the five most common dyes with ozone, chlorine dioxide, hydrogen peroxide and FAS.

Average Overall PAC Rating ________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY
FY 1999 – 2,000

Project Title:	Fundamentals of Fiber Modification
Project Number:	New
PAC:	Chemical Pulping and Bleaching
Project Duration	4 years (Initiate FY 2000)
Division:	Chemical and Biological Sciences
Project Staff	
Faculty/Senior Staff:	Arthur J. Ragauskas
Staff:	Lenong Allison
Project Funding:	
Allocated as Matching Funds:	N/A
Proposed Budget:	$ 75,000

RESEARCH LINE/ROADMAP:

1. **Increase the yield of kraft-pulp equivalent fiber by ten percentage points.**
   - Develop techniques to modify fiber sources
     - For chemical and high yield pulping
   - Develop modified/new pulping/bleaching processes
     - Chemical
     - Hi yield mechanical strength
   - Use of post treatments to give kraft properties
     - Chemical treatments
     - Mechanical treatments
   - Modification of structure or composition of products.

PROJECT BENEFITS:
The application of enzymatic systems to high lignin content fibers provides several new opportunities to modify the physical properties of pulp fibers. In brief, this project will be targeted at developing several new bio-treatments that improve strength properties, pulp refining requirements, and/or modify water retention properties.

PROJECT OBJECTIVE:
The objectives of this project are to explore the application of chemical and biochemical treatments to modify the physical properties of high lignin content pulps. The use of novel enzymatic and/or chemical treatments on mechanical and liner grade kraft pulps will be studied to modify important post-processing properties including water retention, fiber-to-fiber bonding, general web consolidation, wet-pressing and freeness. Changes in fiber properties will be studied in terms of basic fiber chemistry properties including acid group content, hemicellulose structure, and surface fiber chemistry.

DELIVERABLES FOR FY 99 – 2000:
1. Literature report summarizing state-of-the-art chemical and biochemical technologies available to modify physical properties of 'high lignin content pulp.'
2. Evaluate the effects of laccase and laccase/mediator-mediator treatments on the physical properties of SW TMP and liner grade kraft pulps.
3. Examine the chemical interactions occurring between manganese peroxidase and SW TMP and liner grade kraft pulps.

Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

DUES-FUNDED PROJECT SUMMARY

Project Title:	Low-Capital Bleach Plants
Project Number:	New
PAC:	Chemical Pulping and Bleaching
Project Duration:	3 years
Project Staff:	
Faculty/Senior Staff:	T.J. McDonough, C.E. Courchene
Staff:	B. Carter, A. Shaket, M. Turner
Project Funding:	
Allocated as Matching Funds:	
Proposed Budget:	$100,000 yearly

RESEARCH LINE/ROADMAP:
Improved Capital Effectiveness: 8. Develop technologies to allow cost effective expansion of fiber capacity.

BENEFITS TO INDUSTRY:
The ability to install full chemical pulp bleaching capacity with very low capital requirements would be of great value to the industry. It would provide avenues for low-cost expansion of bleached pulp capacity, low-cost greenfield bleaching capacity, and would be capable of retrofitting to replace aging bleach plants with minimum capital expenditure.

PROJECT OBJECTIVES:
Develop technologies for efficient, short retention time, bleaching stages capable of being assembled into an effective sequence for bleaching kraft pulps to high brightness. Identify suitable conditions for fast chlorine dioxide delignification and brightening stages as well as low pressure, rapid alkaline extraction and peroxide stages. Assess and investigate opportunities for identifying alternative bleaching technologies that offer the possibility of unusually rapid delignification and/or brightening. Devise technically feasible means of coupling the stages to form effective bleaching sequences, and optimize the sequences with respect to bleaching conditions and chemical charges.

DELIVERABLES:
1. Survey of the literature to consolidate and analyze existing information on rapid delignification and brightening technology, as well as all available relevant information on bleaching kinetics and opportunities for catalysis of bleaching.

2. Conditions for running and linking fast chlorine dioxide delignification and brightening stages as well as low pressure, rapid alkaline extraction and peroxide stages

3. Alternative technologies for rapid bleaching stages, based on the use of novel bleaching agents, catalysts, or both.

Average Overall PAC Rating ____________________

Project Recommendation ☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

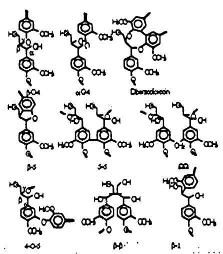
Fundamentals of Bleaching Chemistry
F015

Mid-Year Review

Art J. Ragauskas

F015: Project Objective

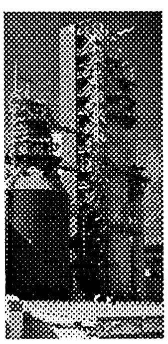
- Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences.



F015: Project Goals and Staff

Goal
- Improve bleaching sequences

Staff
- A. Ragauskas
- L. Lucia
- L. Allison
- K. Hwang



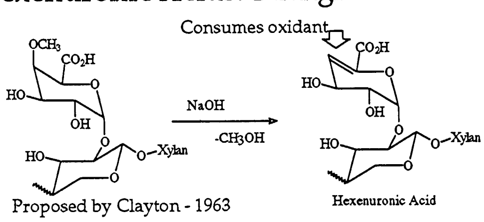
F015: Current Research Focus

- Hydrogen peroxide
- Biobleaching ✓
- Hemicellulose ✓
- Oxygen ✓

Hemicelluloses

Hexenuronic Acids

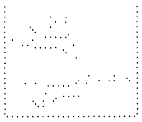
Hexenuronic Acids: Background



Proposed by Clayton - 1963
Studied:

- Johansson & Samuelson - 1977
- Simkovic - 1986
- Teleman ... - 1995

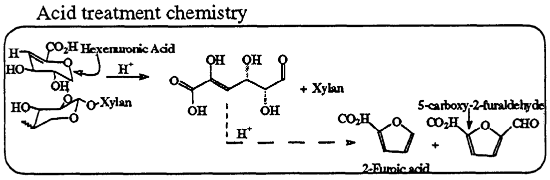
Hexenuronic Acids: Background



- Consumes D & Z
- Inert to P & O
- Sensitive to acid
- **Related to % xylan in pulp**
- **HW kraft: 30-55% of apparent kappa #**
- **SW kraft: 0 - 18%**
- **Binds metals**
- **AQ influences % HexA**
- **PS does not influence % HexA**

Hexenuronic Acids: Background

Acid treatment chemistry



Hexenuronic Acids: Research Goals

Long Term

- Determine impact of HexA.
- Develop technologies that will minimize their effects.

FY 1998-99

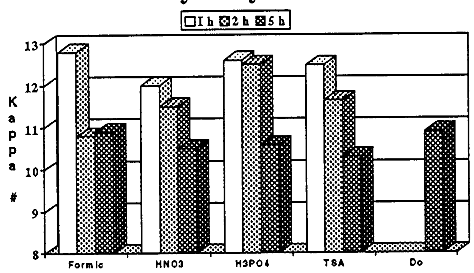
- Examine the effect of alternative acidic treatments to remove HexA$_{completed}$
- Determine the effects of HexA removal on yield, pulp bleachability$_{completed}$

HexA: Alternative Acids

Experimental Design

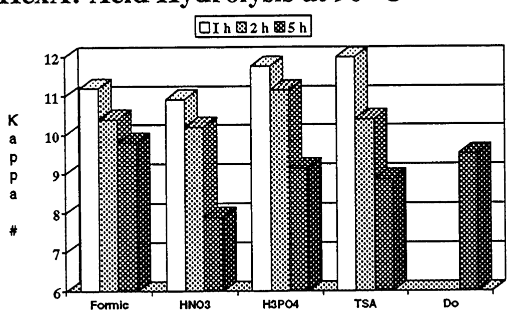
- Commercial southern hardwood kraft pulp
- 3% csc, initial pH: 3.0
- Hydrolysis time: 1,2, 5 h
- Hydrolysis temperature 80, 90, and 95° C
- Acids Employed: Formic Acid/Sodium Formate (buffered)
  - Nitric acid
  - Phosphoric acid
  - p-toluenesulfonic acid...........
  - Do effluent (note initial pH 2.2)

HexA: Acid Hydrolysis at 80° C

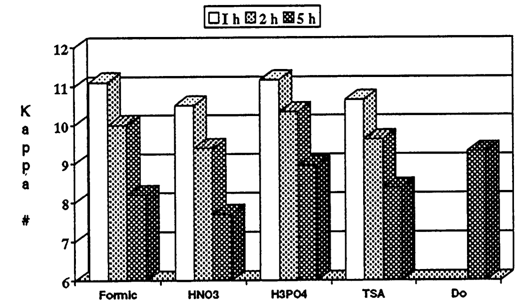


Brownstock kappa #: 13.5

HexA: Acid Hydrolysis at 90° C

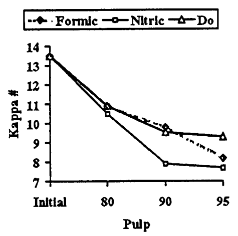


HexA: Acid Hydrolysis at 95° C



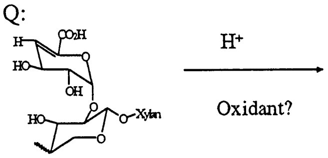
HexA: Summary of Acid Work

- Do wash is an effective treatment for HexA
- At 95°C need 5 h for max. effect >> For this pulp!
- 20 - 28% loss in viscosity (95 C)



HexA: Oxidative reinforced acid treatment of HW Kraft

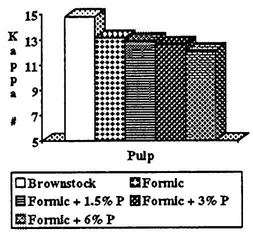
Q:



HexA: Preliminary investigation into use of acidic peroxide

Experimental Conditions

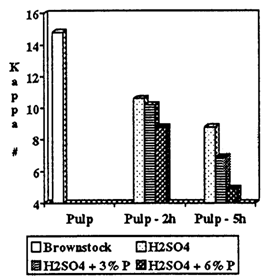
- HW kraft pulp
- Formic acid/Sodium formate (pH 3.0)
- 1 h at 95°C
- 10% csc



HexA: Preliminary investigation into use of acidic peroxide

Experimental Conditions

- HW kraft pulp
- H_2SO_4 pH initial: 3.5
- 2 & 5 h at 93°C
- 10% csc



HexA: Full Sequence HW Kraft Bleaching Studies

Experimental Design

I. Study DEDED vs ADEDED

A-stage: Formic Acid/Sodium Format 3 h

D_0 0.20 kf, 3.5% csc, 45 min, 50°C

D1: 0.6% Charge, 10% csc, 3h , 75°C

D2: 0.1, 0.2, 0.4, 0.6% charge

II. Study ODED vs OADED

D_0 0.20 kf, 3.5% csc

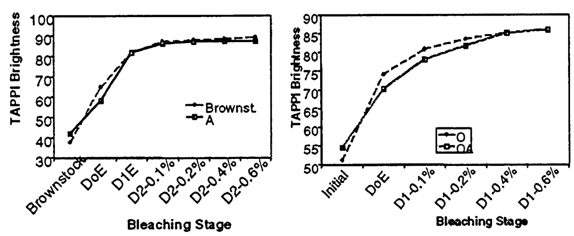
D1: 0.1, 0.2, 0.4, 0.6% charge

HexA: Full Sequence HW Kraft Bleaching Studies

Experimental Results

Pulp	Kappa #	Viscosity/cP	Yield %
Brownstock	11.4	24.4	
Brownstock(A)	5.6	22.8	98.2
O	8.5	21.8	
OA	2.8	19.9	98.0

HexA: Full Sequence HW Kraft Bleaching Studies



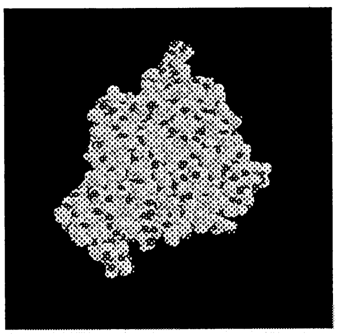
HexA: Conclusions

- Exact acid not overly important for HexA removal
- Temp. is important for HexA removal
- Acidic peroxide stage may be effective for HexA removal
- HexA removal is beneficial for Do and subsequent stages
- No 'noticeable effect' of A-stage on yield

BIOBLEACHING

Laccase

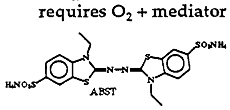
Laccase

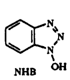


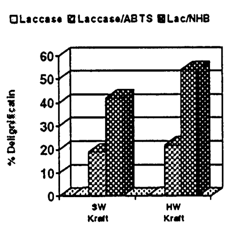
Laccase
- Oxoreductase enzyme
- Reduces O_2 to H_2O & concomitantly oxidizes
- Catalysis occurs due to 4 copper atoms/active site
- Active sites on surface
- Large protein: 36 - 120 kDa
- In nature: polymerization & depolymerization of lignin

Laccase - Review

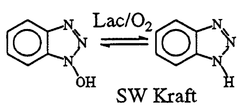
- Laccase catalyzed delignification requires O_2 + mediator



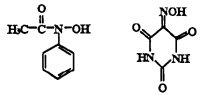




Laccase: Mediator Chemistry



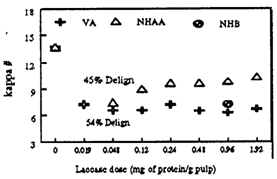
New Mediators



NHAA

Violuric Acid

SW Kraft



Laccase/VA yields improved delignification at 12% charge of enzyme wrt laccase/NHB

Laccase: Research Goals

Long Term

- Develop new methods of improving kraft bleaching operations employing enzymatic technologies

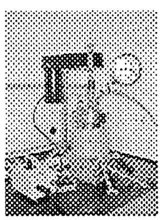
FY 1998 - 98

- Determine influence of metals on LMS treatment
- Determine pulp yield after LMS

Laccase: Role of Metals

Laccase-Mediator Conditions

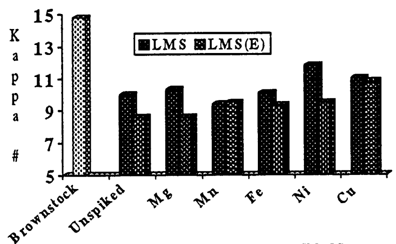
HW and SW kraft pulps
Temp.: 50-54°C
Pressure 120 psi
Time: overnight
Laccase dose: 190 LAMU/gr od pulp
Violuric Acid: 3% charge
Added 0.1% charge of $MgSO_4$ or molar equivalent of $MnSO_4$, $CuSO_4$, $FeSO_4$, $NiSO_4$



Extraction Stage

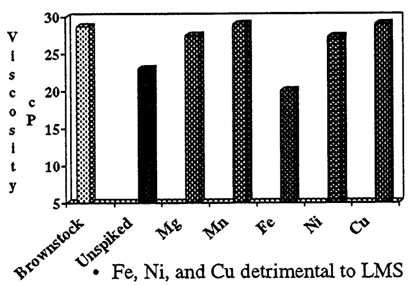
2% NaOH, 3% csc, 70°C, 2h

Laccase: Role of Metals in LMS of HW kraft



- Fe, Ni, and Cu detrimental to LMS stage
- Mg and Mn not detrimental to delignification
- Yield unspiked: LMS 99.6%, LMS(E): 99.3%

Laccase: Role of Metals in LMS of HW kraft



- Fe, Ni, and Cu detrimental to LMS stage
- Mg and Mn not detrimental to delignification

Laccase: Conclusions

- Yield results for LMS continue to be promising
- LMS stage exhibits different metal sensitivity than P, Z
- or O
- LMS stage not sensitivity to viscosity losses caused by Mn

Related Research Issues

- High Efficiency ClO_2 Delignification - DOE
- Improved Peroxide Bleaching - GA Consortium
  - inventory of NPEs in GA wood resources
- Dr. D.H. Kim: Zeolite catalyst for P-stage
- Mill Designed Biobleaching Technologies - DOE*

Student Research

Troy Runge
  - Bleaching chemistry of alkaline extraction
- Kaaren Haynes
  - Fiber properties of Laccase/mediator bleached pulps
- Micheal Zawadzki
  - Bleaching chemistry contributing to brightness ceilings
- Fadi Chakar
  - Chemistry of Laccase/mediator delignification
- John Werner - MSc
  - NPE - black liquor complexes

Exploratory Studies

Chemistry of Oxalic Acid Generation

Oxalic Acid Generation from Do

- Generation of OxA from Do from lignin principally
- Chemical pathways of formation know only in general
- OxA impacts operations and products
- Exploratory studies directed at chemistry of OxA formation & OxA interaction with other lignin fragments

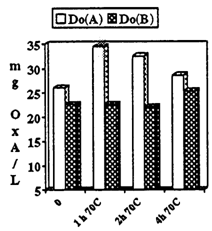
Oxalic Acid Generation Post-Do (SW Sulfite)

Do effluents were collected stored at O°C prior to analysis

Samples were heated, aliquots taken, and OxA analyzed by CEP

Do(A):0.27 kf

Do(B):0.28 kf



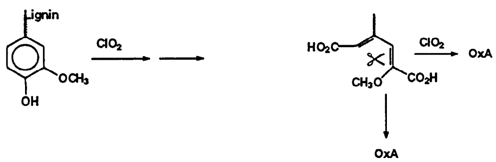
Ulmgren and Radestrom, STFi

Oxalic Acid Generation Post-Do

- Do (kf:0.25) effluent from a OD SW kraft pulp

[OxA] in effluents (mg/L)

Oxalic Acid Generation Post-Do



-slow hydrolysis is occurring

Importance>> mill balance and control of OxA

OxA Studies: Next

- CIE analysis is variable.. Suspect sample preparation needs refinement
- Explore factors contributing to differences in OxA generation (D & Z)
- Study dynamics of OxA solubility with bleach plant effluents

Acknowledgments

L. Allison, T. Runge, K. Haynes, M. Zawadzki, F. Chakar, C. Li, J. Werner, P. Agrawal, D.H. Kim

Member Companies IPST

Project F015 Sub-Objective:

Fundamentals of Oxygen Delignification

Lucian A. Lucia
Ki-Oh Hwang

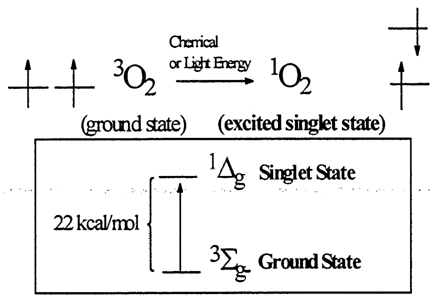
Oxygen Delignification Objectives

- To improve the selectivity and efficiency of the process;
  - ⇨ Generate active oxygen species;
  - ⇨ Study their impact on pulp;
- To develop a fundamental understanding of the interaction of active oxygen species with pulp;
  - ⇨ Use pre- and post-O_2 pulp
  - ⇨ Chemical characteristics of pulp

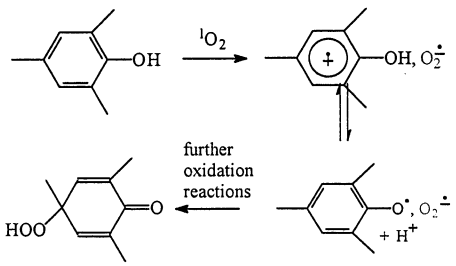
Summary of 1998-99 Proposed Goals

- Determine the effect of Singlet Oxygen on Pulps
- Evaluate inducing self-sensitized delignification of kraft pulps
- Attempt to generate singlet oxygen
- Compare photochemical and chemical generation of singlet oxygen
- Investigate PARR Reactor custom design for oxygen delignification kinetics

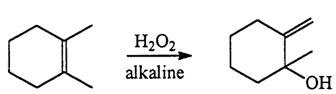
Generation of Singlet Oxygen



Chemical Reactivity of $^1O_2$ Toward Lignin-like Substrates



Implication of $^1O_2$ in H_2O_2 Bleaching Reactions

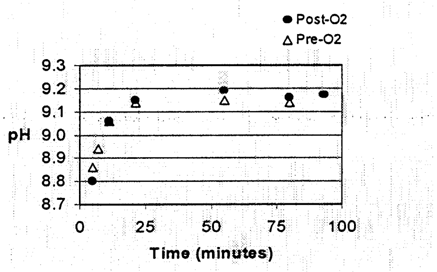


17%

Singlet Oxygen Product

Agnemo, R.; Gellerstedt, G.; Lindsfors, E.-L. "Reactions of 1,2-dimethylcyclohexenwith Alkaline Hydrogen Peroxide." Acta Chem. Scand. B 33 (1979), 155-156

pH of SW Kraft Pulp as a Result of Alkali Leaching



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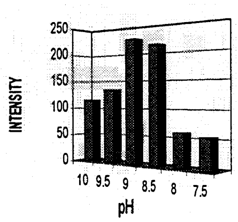
Activity of $^1O_2$ as a Function of pH



- Definite trend is observed
- Interestingly, our system does show noticeable differences
- At higher pHs, differences not pronounced

Thompson, K. "The Role of Singlet Oxygen in the Bleaching of Cotton." Ph.D. Thesis (1996). Georgia Tech

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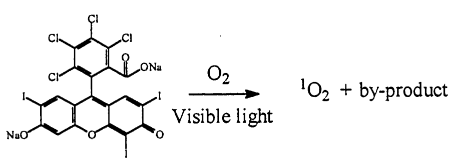
Photogeneration of Singlet Oxygen



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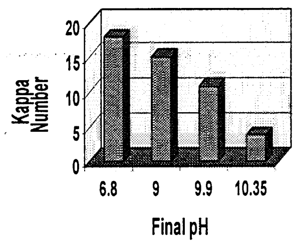
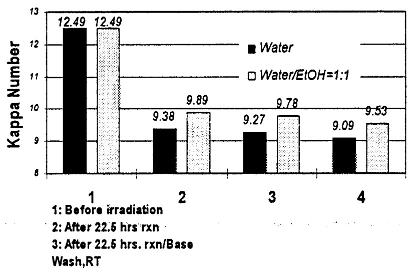
$^1O_2$-Reactions: Increased Delignification for higher pHs

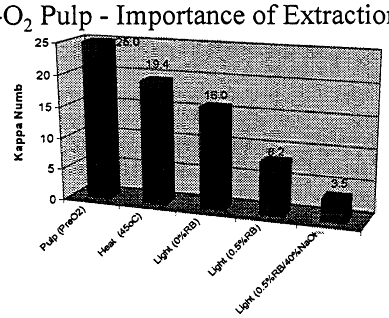


- Pre-O_2 Kraft SW
- $Kappa_0 = 25$
- Rose Bengal (0.5%)
- Fluorescent Lamps (22 hours)
- Dual Effect of pH: Lignin Extraction and $^1O_2$ Lifetime

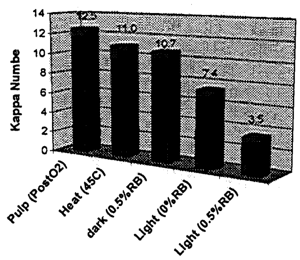
Longer Singlet Oxygen Lifetime in Ethanol - No Effect



Preliminary Experiments for $^1O_2$- Treated Pre-O_2 Pulp - Importance of Extraction



Preliminary Experiments for $^1O_2$-Treated Post-O_2 Pulp



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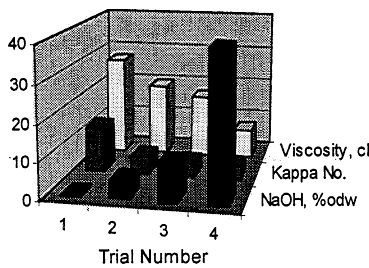
Optimizing Base Concentration in $^1O_2$ Reaction with Post-O_2 Kraft Pulp



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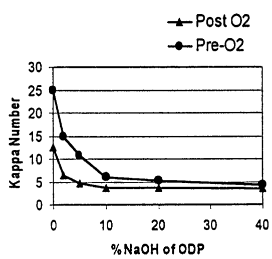
Enhanced Delignification From Increased Base Concentration



- Base Concentration influence on $^1O_2$ lifetime, but also lignin extraction
- Point of diminishing returns
- Same changes for both pulps

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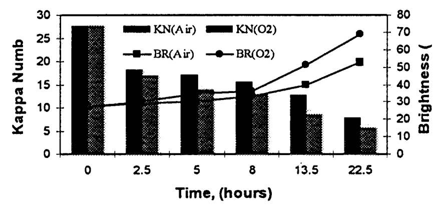
Optimizing Kappa and Brightness by Control of Oxygen and Protectors in Pre-O_2 Pulp

(10% NaOH, 0.5% RB, 0.5% MgSO4, 2% Cn.)



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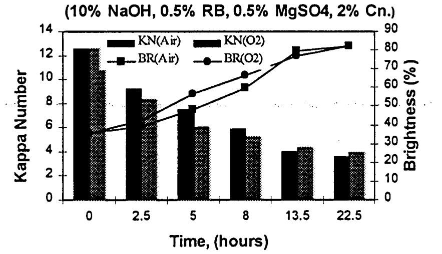
Optimizing Kappa and Brightness by Control of Oxygen and Protectors in Post-O_2 Pulp

(10% NaOH, 0.5% RB, 0.5% MgSO4, 2% Cn.)



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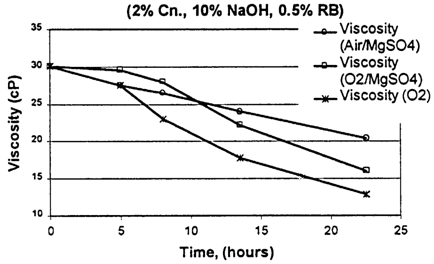
Viscosity Changes for Pre-O_2 Pulp

(2% Cn., 10% NaOH, 0.5% RB)



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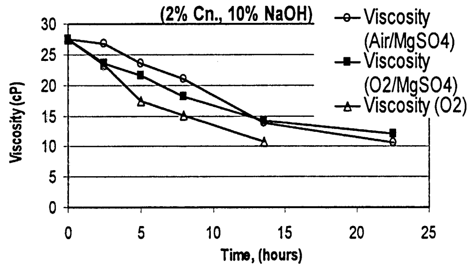
Viscosity Changes for Post-O_2 Pulp



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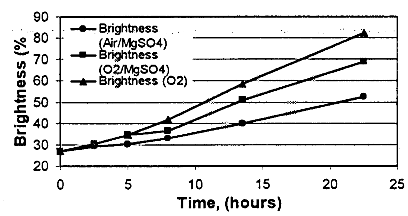
Absence of Protector: Effect on Pre-O_2 Pulp Brightness

(2% Cn., 10% NaOH, 0.5% RB)



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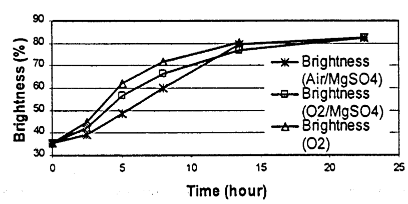
Absence of Protector: Effect on Post-O_2 Pulp Brightness

(2% Cn., 10% NaOH)



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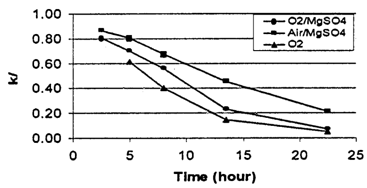
Decrease of k/s Over Time for $^1O_2$ Treated Pre-O_2 Pulp

(10% NaOH, 2% Cn)



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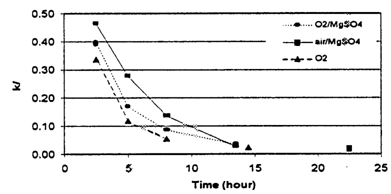
Decrease of k/s Over Time for $^1O_2$ Treated Post-O_2 Pulp

(10% NaOH, 2% Cn.)



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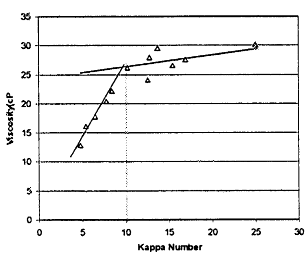
Selectivity Changes vs. Kappa Number of Pre-O2 Pulp



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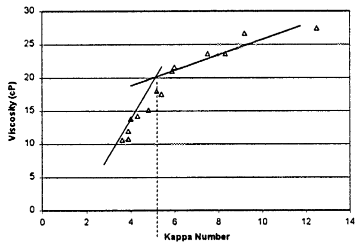
Selectivity Changes vs. Kappa Number of Post-O2 Pulp



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Classical Chemical Generation of Singlet Oxygen

$$^{\ominus}OCl + H_2O_2 \longrightarrow HOCl + HO_2^{\ominus}$$

$$HO_2^{\ominus} + HOCl \longrightarrow HO_2Cl + HO^{\ominus}$$

$$HO_2Cl + HO^{\ominus} \longrightarrow {}^{\ominus}O_2Cl + H_2O$$

$$^{\ominus}O_2Cl + H_2O \longrightarrow \boxed{{}^1O_2} + Cl^{\ominus}$$

Singlet Oxygen

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Chemical Structures in $^1O_2$-Treated (Chemical) Extracted Lignin

	mmol/g isolated lignin	
NMR	Brown Stock	Singlet Oxygen-Treated
Aliphatic OH	1.38	1.15
Condensed phenolic OH	0.82	0.79
Guaiacyl phenolic OH	0.94	0.88
Carboxylic acid OH	0.28	0.43

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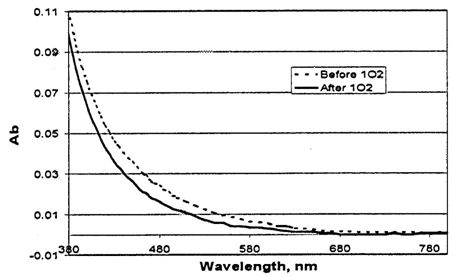
$^1O_2$-Treated Pulps Absorb Less in Visible



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Summary

- Singlet oxygen was generated both photochemically and chemically
- It behaved as a more active delignification agent than ground state oxygen
- Pulp brightness gains were observed
- Protectors were helpful in sustaining viscosity and increasing selectivity

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Future Work

- Further investigate the factors which influence the singlet oxygen-mediated bleaching response of pulps
- Pursue patentability of the bleaching technology
- Investigate higher intensitylamp sources (more light, less heat) for optimum response

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Acknowledgements

Dr. Ki-Oh Hwang
Wood Chemistry Group

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Improved Selectivity in Ozone Bleaching

- USDA Funded at $128,436 for October 1996-98
- Personnel: Don Dimmel, Cathy Welder (Postdoc), Elizabeth Althen (Senior Technician)
- Objective: To determine the relative importance of the reaction pathways by which ozone degrades carbohydrates. Clarification of the mechanism will facilitate the development of improved ozone selectivity and, thus, improved pulp properties.
- Compliments F015 research objectives

Research Goals

- Determine the extent cellulose is degraded by:
  - ozone directly
  - radicals derived from ozone (i.e., hydroxyl radical)
  - reactive hydroperoxides (ROOH) and hydrotrioxides (ROOOH) from lignin and carbohydrate intermediates
- Define selectivity factors by examining:
  - cellulose molecular weight changes
  - cellulose sites of oxidation
  - extent of lignin degradation in cellulose/lignin mixtures

Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Ozone transport
  - Ozone must move from a gaseous state to a water interface and then react at a solid matrix
  - If ozone encounters lignin-depleted regions, the only reactants available are carbohydrates
  - Without efficient mixing there will be regions in the pulp containing no O_3 and others where the O_3 concentration exceeds the lignin demand
  - Bad transport leads to more O_3-induced carbohydrate damage

Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Relative rates of direct ozone reaction

Compound	Rate Constant $(Msec)^{-1}$
$PhCH=CH_2$	3×10^5
$HO\text{-}Ph\text{-}CH_3$	3×10^4
Glucose	0.5
Saccharose	0.1

Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Ozone transport (relates to reactant availability)
- Relative rates of direct ozone reaction
- Relative rates of secondary radical reactions
  - from ozone decomposition

$$O_3 + HOH \longrightarrow O_2 + 2HO^{\circ}$$

$$O_3 + HOH \longrightarrow 2HO_2^{\circ}$$

$$O_3 + M^{n+} + H^{+} \longrightarrow O_2 + M^{(n+1)+} + HO^{\circ}$$

Hydroxyl Radical Reactions

- Hydroxyl radical is extremely reactive:

$$RH + HO\cdot \longrightarrow R\cdot + HOH$$

$$O_2 + R\cdot \longrightarrow ROO\cdot$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

- Relative rates of lignin/carbohydrate model rxs

Compound	Rate constant $(M{\cdot}s)^{-1}$
Veratrylglycol	1.5×10^{10}
Veratrylglycol-β-guaiacyl ether	1.7×10^{10}
Methyl- β-D-glucopyranoside	3.2×10^{9}
Methyl- β-D-xylopyranoside	2.6×10^{9}

Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Ozone transport (relates to reactant availability)
- Relative rates of direct ozone reaction
- Relative rates of secondary radical reactions
  - from ozone decomposition
  - from hydrotrioxide decomposition

$$R\text{-}O\text{-}O\text{-}OH \longrightarrow R\text{-}O\text{-}O\bullet + \bullet OH \quad \text{or} \quad R\text{-}O\bullet + \bullet O\text{-}O$$

  - from ozone-phenol reactions

$$Ar\text{-}OH + O_3 \longrightarrow Ar\text{-}O\bullet + O_2 + \bullet OH$$

Chemistry of Ozone-Cellulose Reactions

- Examining model systems:
  - water soluble cellulose dimer
  - fluffed cotton linters
  - lignin-spiked fluffed cotton linters
  - amorphous cellulose
- Examining the importance of:
  - direct ozone attack
  - radical reactions derived from O_3 decomposition
  - radical reactions derived from O_3-lignin reactions

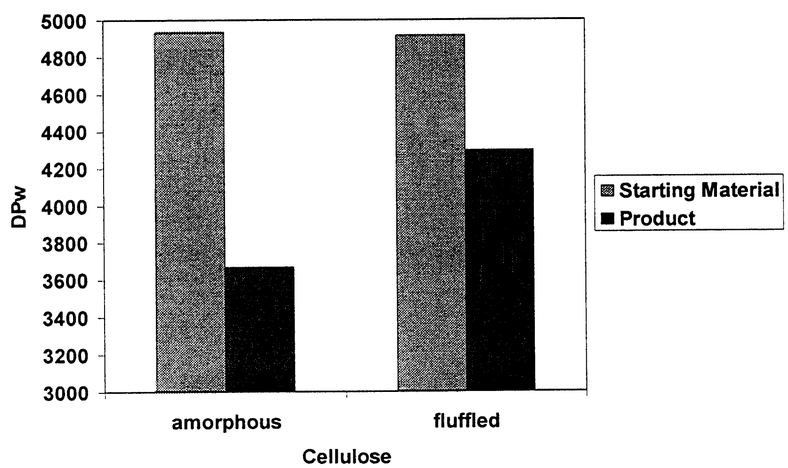
O_3-Cellulose Dimer Reactions

Rx time	Recovered Dimer	1,5-Anhydroglucitol	Glucose
2 min	66%	2%	1%
10 min	30%	trace	trace
2 h	0%	none	trace

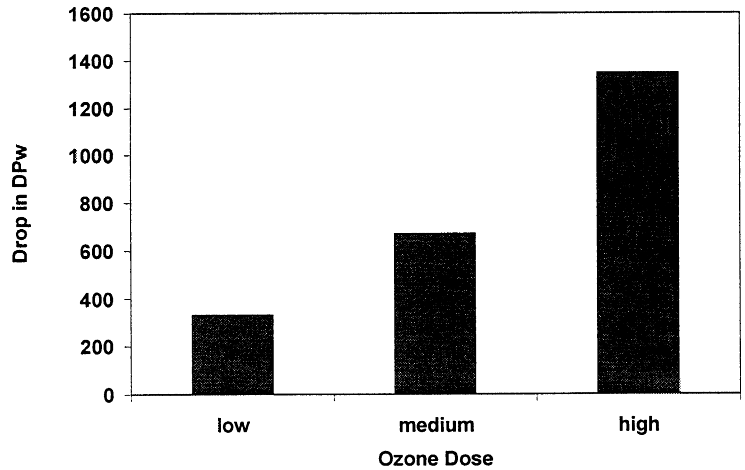
Data indicates that there is a complex set of unselective ozone reactions with this water soluble cellulose dimer

Cellulose Structure & Reactivity

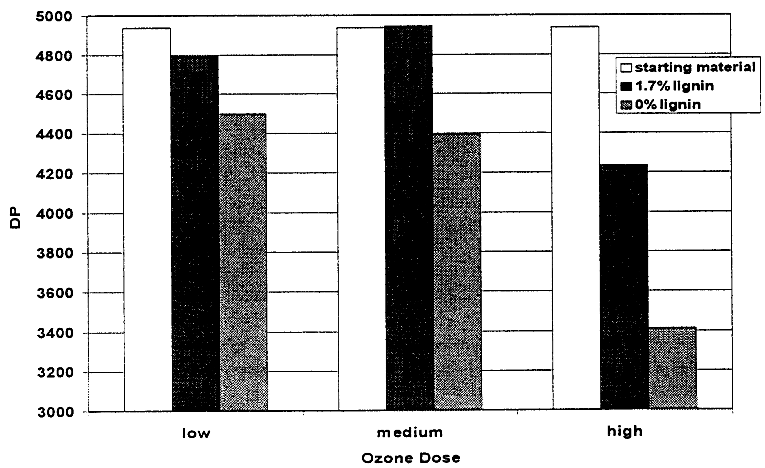
DP Drop with O_3 Application



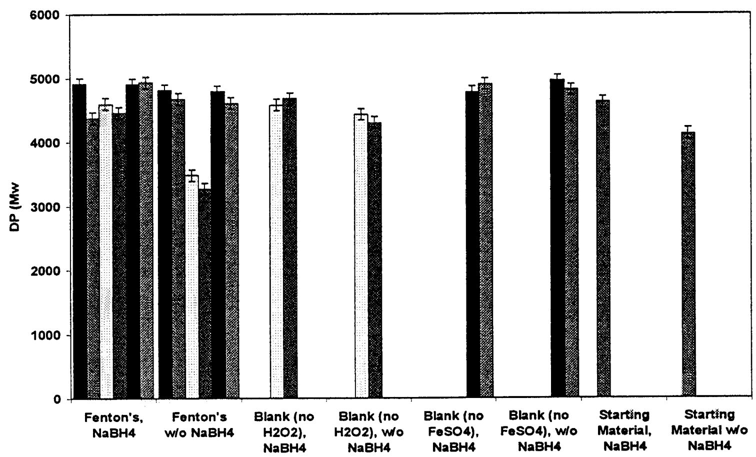
Ozone Dose is an Important Factor in Cotton Linters Case



Protecting Effect of Lignin



Fenton's Reagent Reactions
(H_2O_2 + Fe^{+2} --> HO·)



Conclusions

- Little cellulose direct chain cleavage occurred with low-dose ozonation stages of cotton linters or a lignin-cotton linters mixture
- Soluble dimer ozonations gave an unusual result - no selectivity
- Amorphous cellulose was more reactive than fluffed cotton linters
- Ozone dose is an important variable
- Lignin provides a protecting effect
- Fenton's reagent gave variable results

Chemistry of Ozone-Cellulose Rxs Future Directions

- Evaluate differences between ozone reactions of:
  - pulp
  - fluffed cotton linters containing absorbed lignin
  - amorphous cellulose precipitated in the presence of lignin
- Examine different levels of spiked lignin; analyze the effect of phenolic content of the lignin

Chemistry of Ozone-Cellulose Rxs Future Directions

- Prepare (if possible) a lignin carbohydrate complex (LCC) of amorphous cellulose and a lignin dimer, and study the ozone-degradation of the LCC under different conditions
- Perform select ozone reactions at different pH, temperature, and additive levels
- Summarize the 2-year study in a final report to IPST member companies and to the USDA

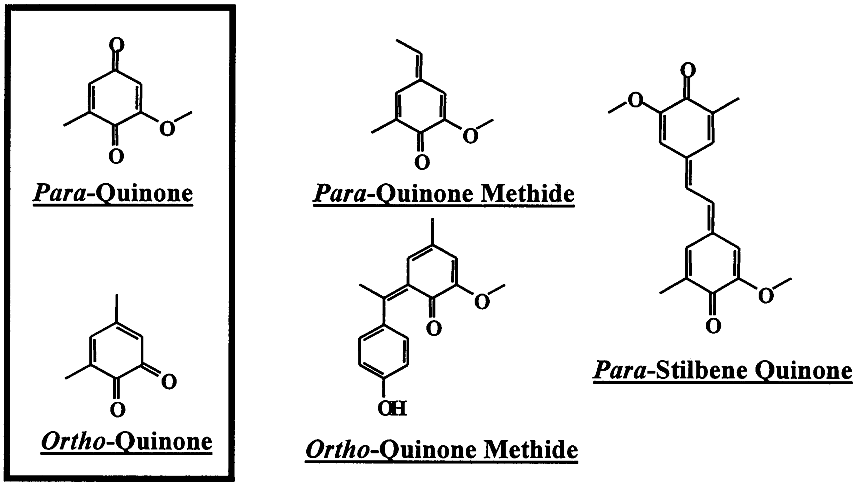
Quinone Chromophores in Bleached Kraft Pulps

Michael Zawadzki
Supervisor: Arthur Ragauskas

Overview

- **Chromophores in Kraft Pulps**
- **Trimethylphosphite Derivatization of Quinones**
- **Results:**
  - **Quinone Contents: DE*D Pulps**
  - **Correlation Between Quinone Content and Brightness Values**
- **Bleaching Chemistry**

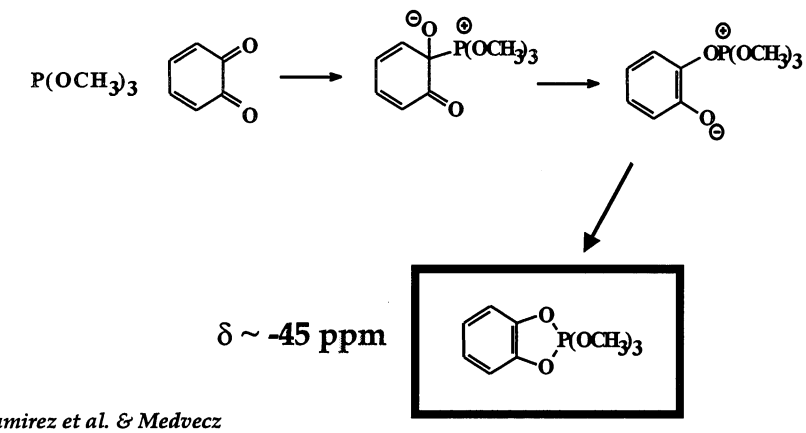
Lignin Chromophores in Kraft Pulp



Trimethylphosphite Derivatization of Quinones

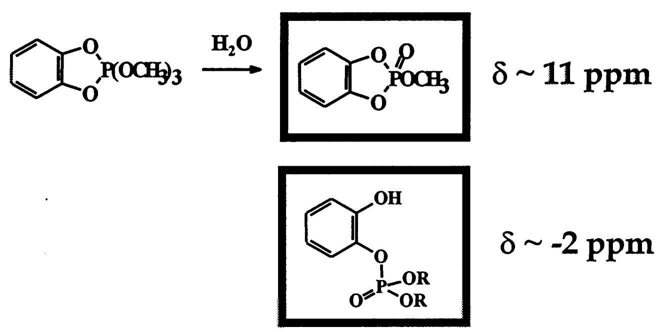
- **Developed a ^{31}P-NMR Based Analytical Procedure for the Quantification of Quinones in Isolated Lignins**
- **Based on Mechanical Pulp Studies by Lebo *et al.* (IPST) & Argyropoulos *et al.***
- **And Model Compound Studies by Medvecz (IPST) & Ramirez *et al.***

Trimethylphosphite Chemistry:
Reaction with Ortho-Quinone Structures



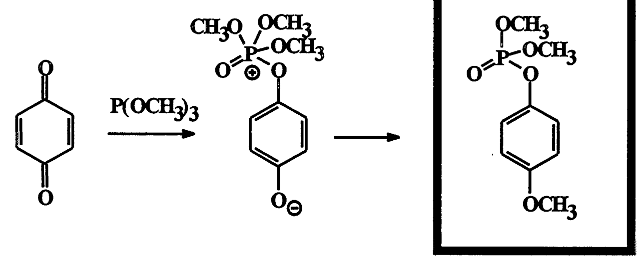
Ramirez et al. & Medvecz

Trimethylphosphite Chemistry:
Dioxaphospholene Hydrolysis



Ramirez et al.

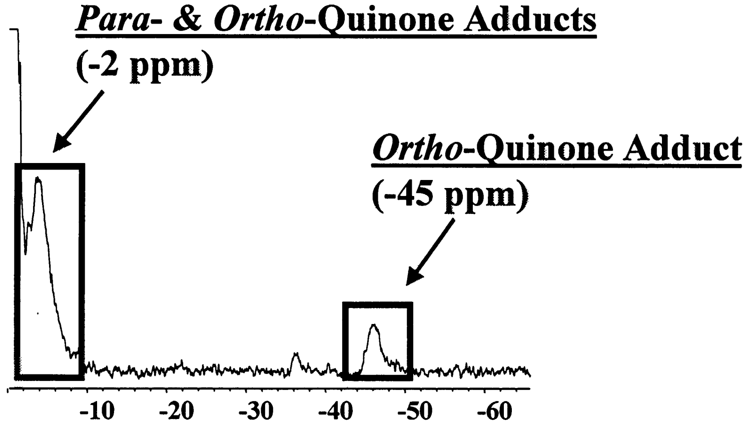
Trimethylphosphite Chemistry:
Reaction with Para-Quinone Structures



δ ~ -2 ppm

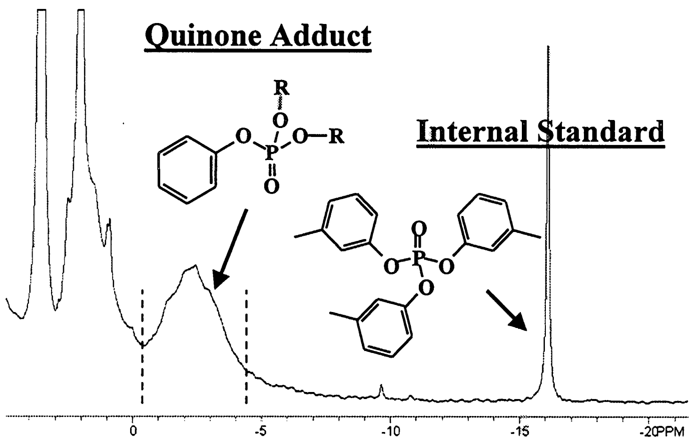
Ramirez et al. & Medvecz

^{31}P-NMR Spectrum:
Trimethylphosphite Treated Effluent Lignin



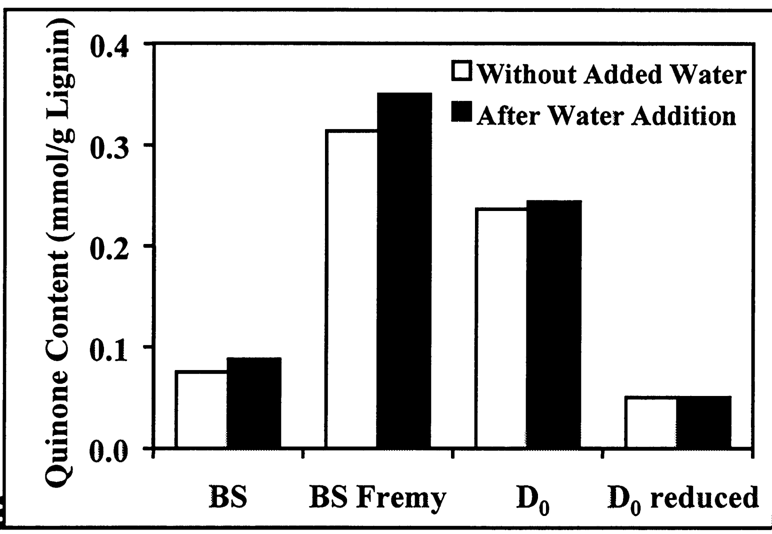
^{31}P-NMR Spectrum:

D_0 Lignin (1) Trimethylphosphite Treated (2) Hydrolysis



Residual Lignin Quinone Contents:

Brownstock, Fremy, D_0 & D_0 Dithionite Reduced



Pulps Studied

- **Residual Lignins were Isolated from BS, Alkaline Extraction and D Stage Pulps:**

DE*D

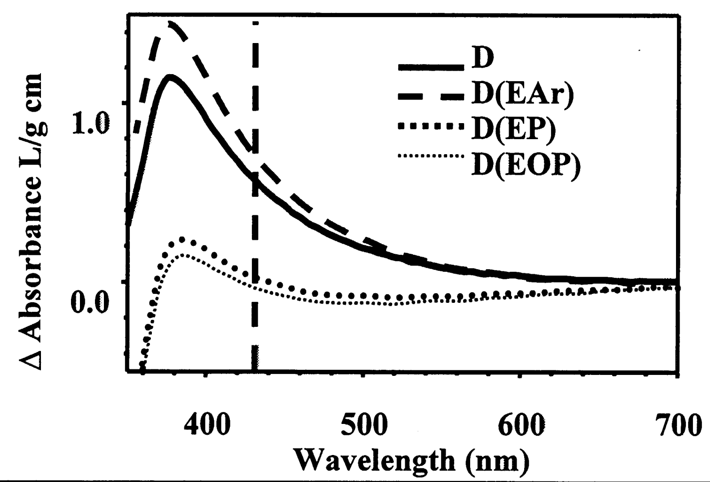
where, E* = EAr, E, EO, EP, EOP

(EAr means Alkaline Extraction with Air Excluded)

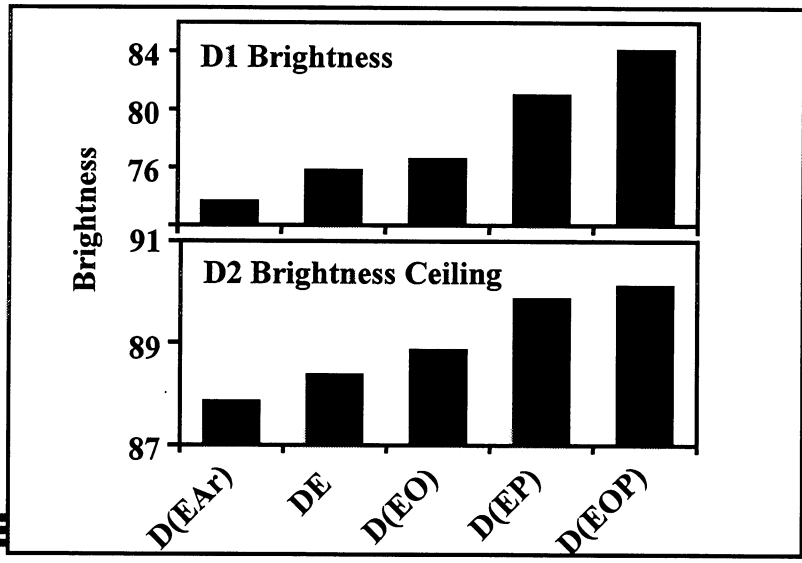
- **Brightness Properties were Measured**
- **Quinone Content was Measured**

Visible Absorbance Difference Spectra:

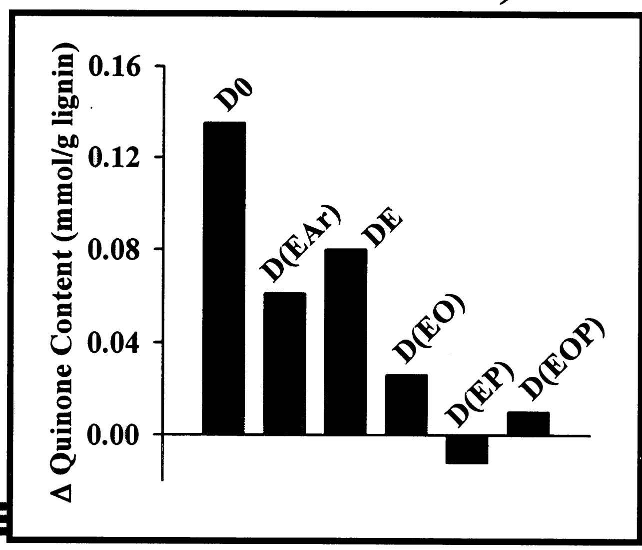
(DE* - BS Residual Lignin Value)



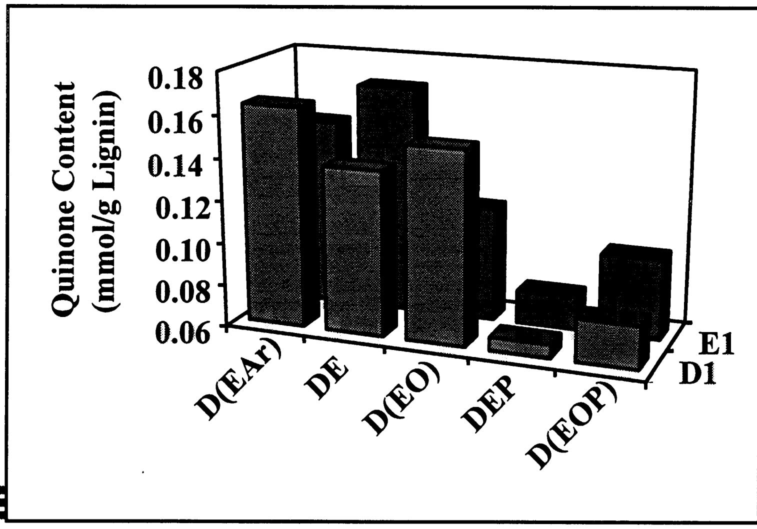
D1 & D2 Brightness Values



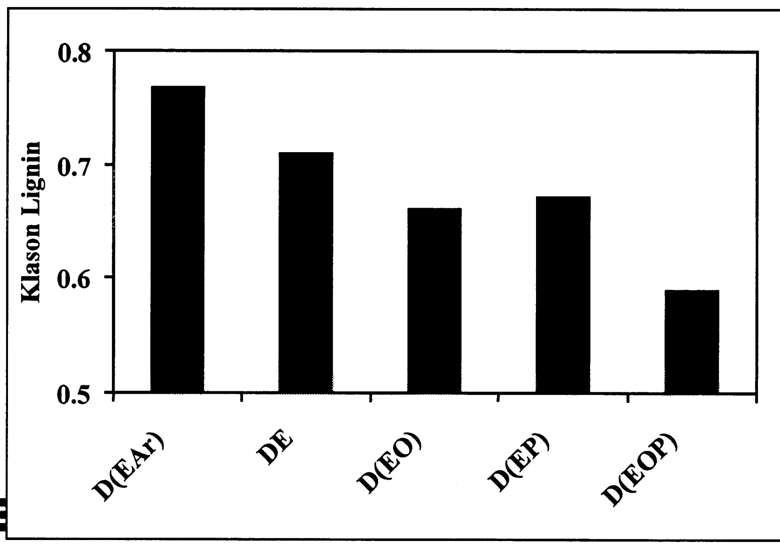
Residual Lignin Quinone Contents (Brownstock Value Subtracted)



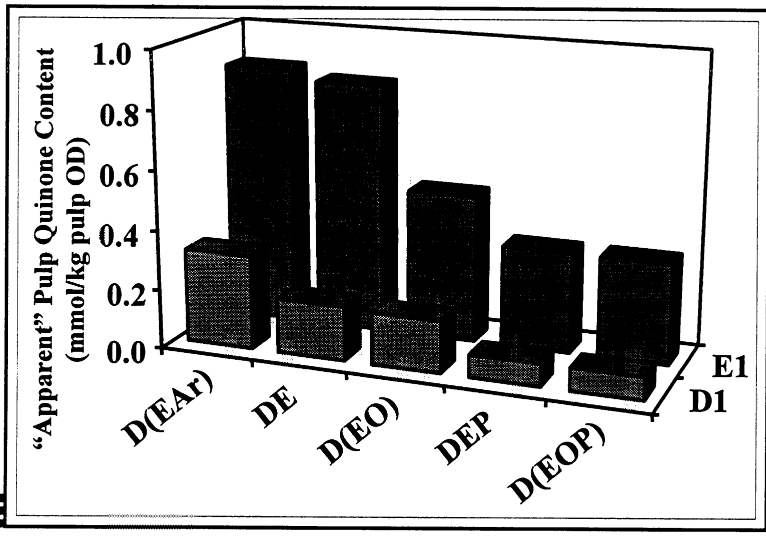
Quinone Contents: E1 & D1 Residual Lignins



E1 Stage Klason Lignin Contents



“Apparent” Pulp Quinone Contents: E1 & D1 Stages



Kubelka-Munk Equation

$$\frac{B}{100} = 1 + \frac{k}{s} - \sqrt{2\left(\frac{k}{s}\right) + \left(\frac{k}{s}\right)^2}$$

B = Brightness, k = absorption, s = scattering

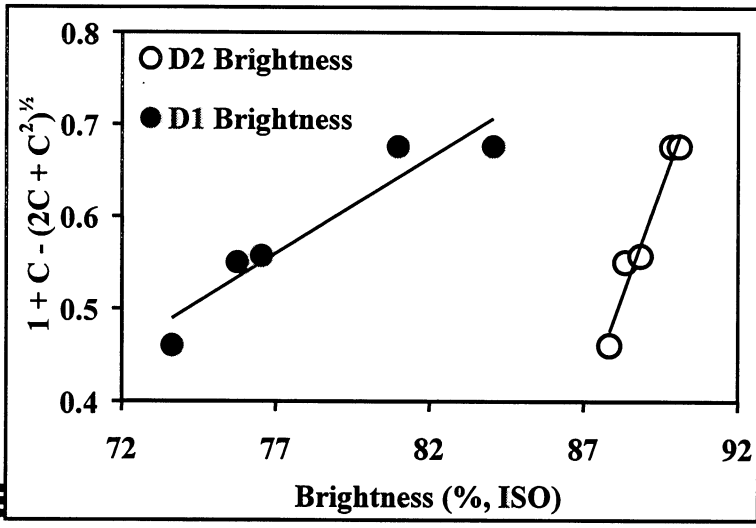
$$\frac{k}{s} = \left(\frac{\phi}{s}\right) \times C$$

ϕ = constant, C = chromophore content

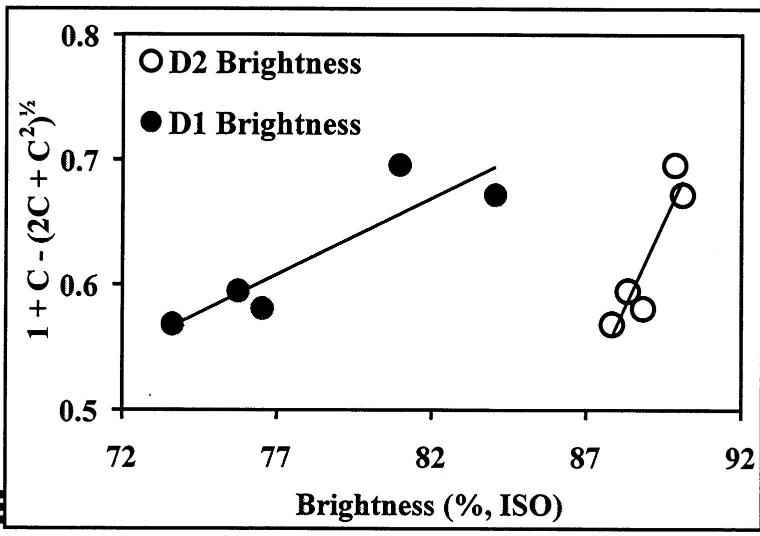
$$\frac{k}{s} = \phi_1 \times C \text{ or } \frac{k}{s} \propto C$$

$$B \propto 1 + C - \sqrt{2\ C\ +\ C \times C}$$

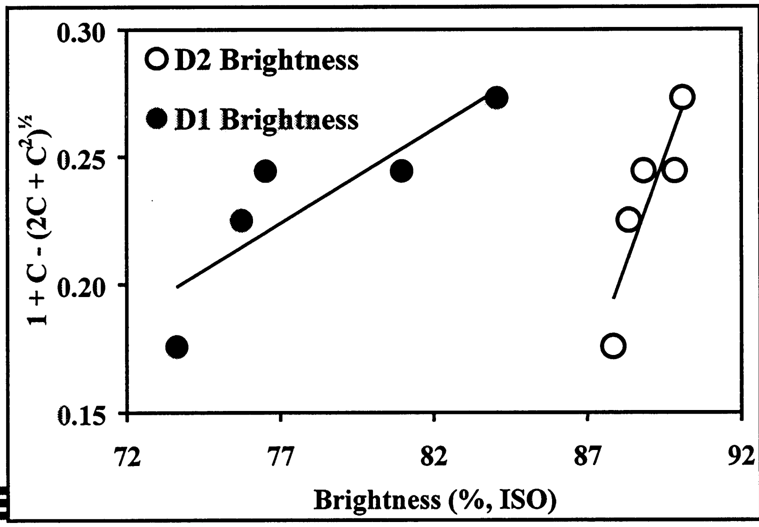
D1 "Apparent" Pulp Quinone Contents Correlated with D1 & D2 Brightness



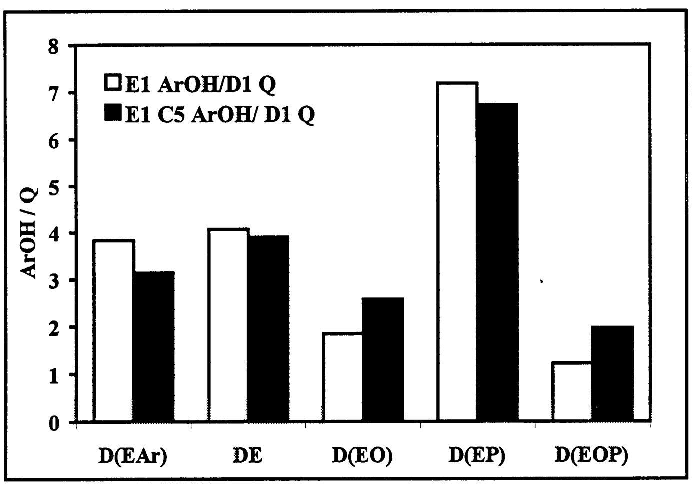
D1 Quinone Contents Correlated with D1 & D2 Brightness



D1 Klason Contents Correlated with D1 & D2 Brightness



Conversion of E1 Phenolics to D1 Chromophoric Quinones



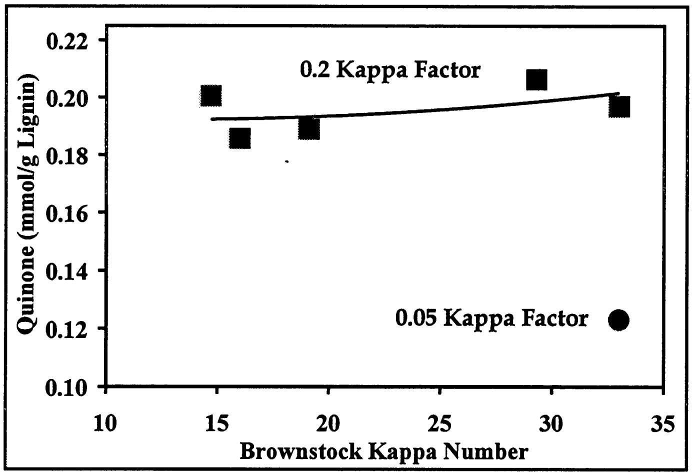
Conclusions, Part (1):

- Trimethylphosphite/^{31}P-NMR has been Developed as a New Tool to Study Chromophores in Lignin
- Quinone Content Correlates with Pulp Brightness and Brightness Ceiling Values
- Hydrogen Peroxide Destroys Quinones and Quinone Precursors

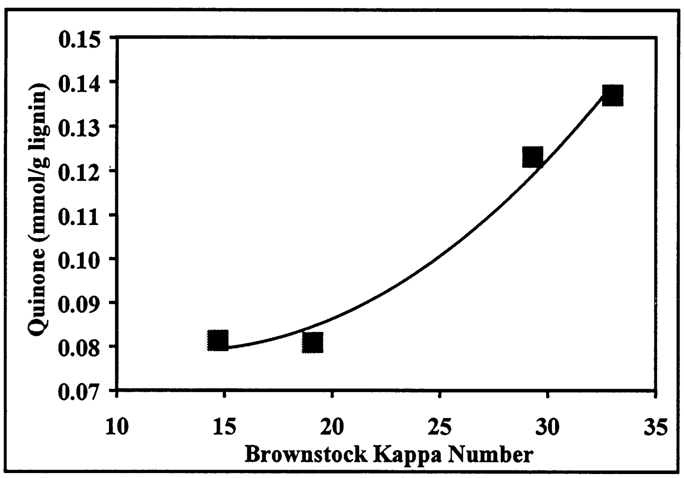
Results Part (2): D_0 & D(EO) Pulps

- Residual Lignins were Isolated from D_0 and Alkaline Extraction Stage Pulps
- Initial Brownstock Kappa Number was Varied

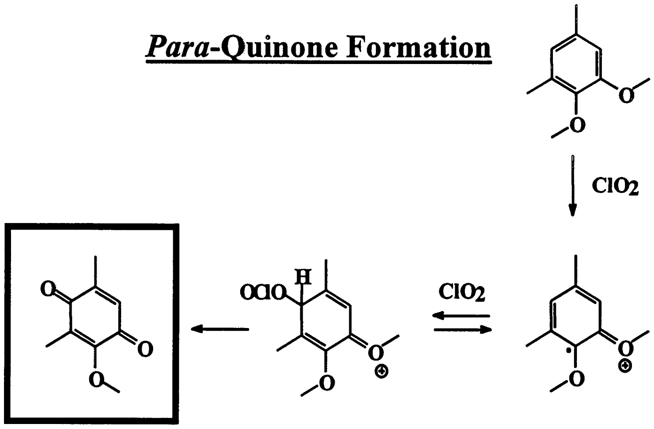
Quinone Content of D_0 Residual Lignins



Quinone Contents of D(EO) Residual Lignins

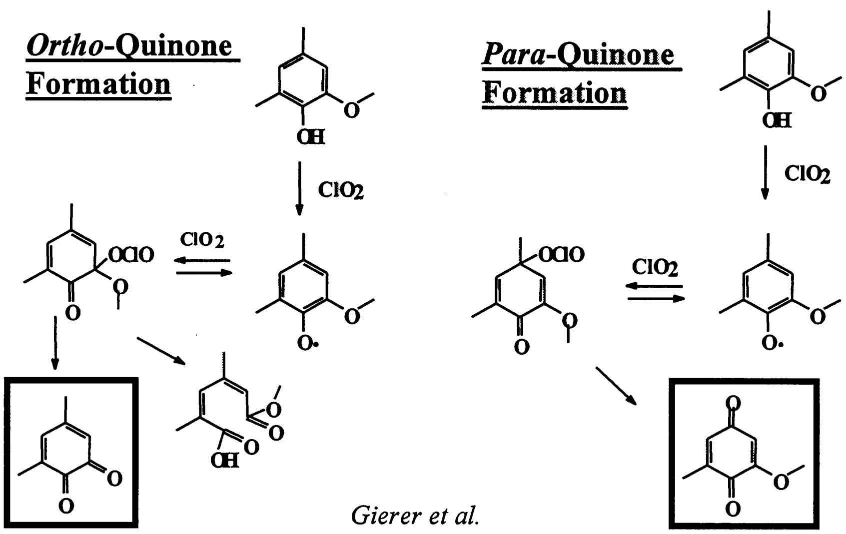


Chlorine Dioxide Bleaching Chemistry



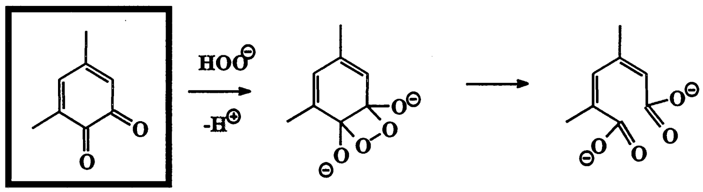
Gierer et al.

Chlorine Dioxide Bleaching Chemistry



Gierer et al.

Hydrogen Peroxide Chemistry



Gierer et al.

Conclusions

- **These Studies Validate Bleaching Model Compound Studies in Pulp**
- **Chlorine Dioxide Causes Colored Lignin-Quinone Structures to Form**

Also,

- **Trimethylphosphite/^{31}P-NMR method has Recently been Repeated by:**
  Gellerstedt (STFI) & Argyropoulos (Paprican)

Acknowledgements:

- **IPST Member Companies**
- **T. Runge, A. Ragauskas, T. McDonough, D. Dimmel, L. Lucia**

Guest Presentation by Peter Pfromm Associate Professor, Chemical Recovery and Corrosion Division, Purpose:

- 1. We are looking for help in locating a pilot scale test site for a process to remove metals/trans. metals and chloride from D-stage effluent.
- 2. A request to consider recommending a new project for Consortium funding.

Project 4160
(DOE funded, no IPST matching funds)

<u>Recycling of Bleach Filtrates using Electrodialysis</u>

Shih-Perng Tsai
(Argonne National Laboratory)
P. H. Pfromm
(DOE Agenda 2020, 8-1996 to 8-1999, ~$200,000/year, $50,000/year to IPST)

The Issue

- Low effluent bleached kraft pulp production
  - ➔need to recycle bleach effluent
- Acidic bleach effluent recycle introduces metal ions, calcium, chloride.

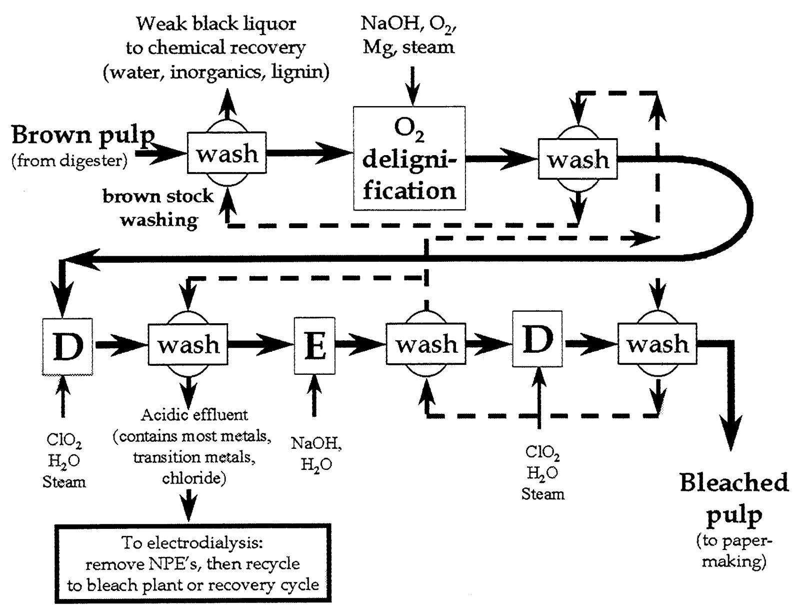
The Approach

- Remove NPE's from bleach effluent before recycling.
- Challenges:
  - ➔dissolved organics
  - ➔particulate matter
- Choose a technology that addresses anions (chloride) and cations (metals, calcium..)

Bleach effluent electrodialysis:

- Expected results:
  - ➔Simple process that can be retrofitted to existing installations, pilot-scale test data
- Impact on the industry:
  - ➔decrease chloride, NPE problems from bleach effluent recycle
  - ➔No chemicals needed
  - ➔Tolerant towards small particulates
  - ➔Enable bleach plant recycle

Process flowchart



Bleach Filtrate Electrodialysis: Advantages

- Continuous process, no regeneration
- Open flow channels (tolerates particulate matter)
- Remove Cl^- selectively over $SO_4^{=}$, simultaneous to metals/trans. metals, Ca^{++}

Bleach Filtrate Electrodialysis: Challenges

- Fouling?
- Membrane area?
- Removal efficiency, selectivity?

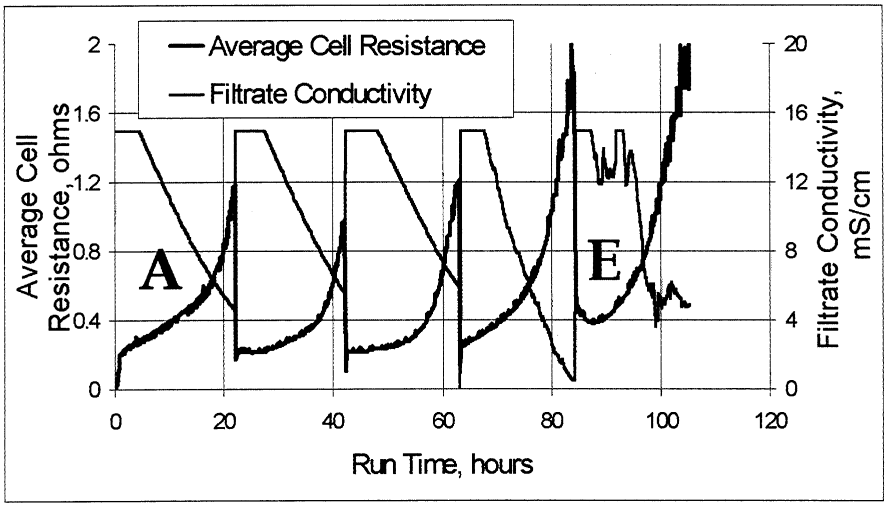
Bleach Filtrate Electrodialysis: Year 1 Summary

- Acidic effluents from three mills (IPST).
- Successful electrodialysis (lab scale) with two effluents, no pre-treatment
- Estimate for scaleup done
- Conclusion: perform long -term tests to show no-fouling, and prepare for pilot scale

Bleach Filtrate Electrodialysis: Year 2 Summary

- Acidic D stage effluent from a new mill (Mill D) obtained for long-term tests
- Sequential batch runs with no membrane cleaning
- Analyze (IPST, ANL)
- Conclusion Year 2: no significant fouling, ready for pilot test

Bleach filtrate electrodialysis, Year 2: long-term process performance



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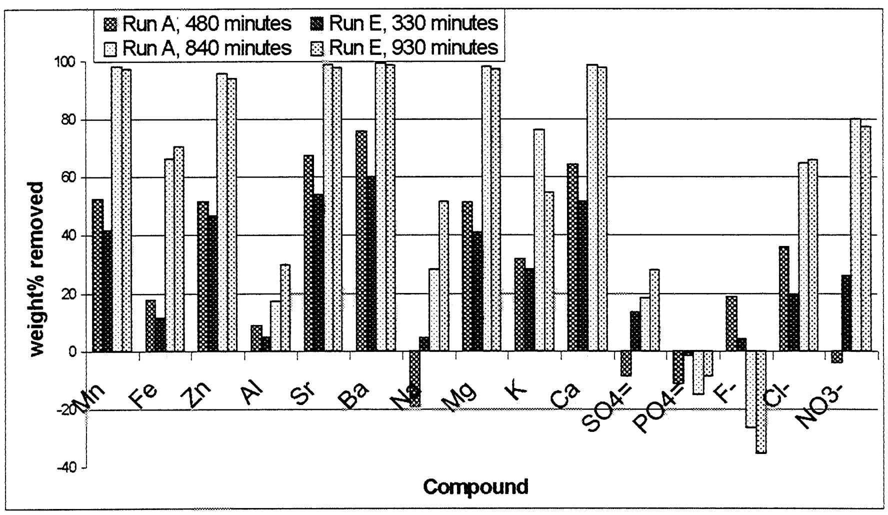
Removal by species: compare 0 and 100 hrs



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Concluding Remarks

- Long-term laboratory performance OK.
- High removal levels for important NPE's, and Chloride.

Path Forward, Year 3

- Search for pilot scale test site
- Can PAC help to find a site?

New planned project

Ultrafiltration of bleach effluent: new approaches for partial closure

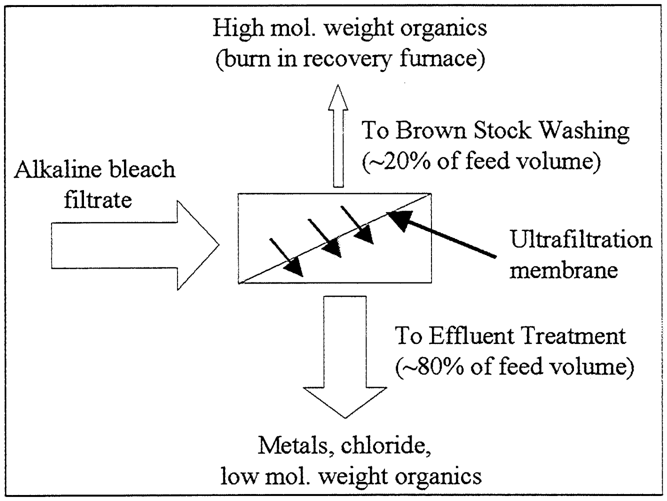
Current sponsor: Eka Chemicals

Dr. Patrick Bryant, Eka
Peter Pfromm

The issue

- Compliance of bleach plant effluents (COD, color, AOX) from existing bleach plants is or will be an issue.
- Radical changes in bleaching technology, or total closure are costly.
  - ➔An "intermediate" lower cost solution is needed.

Approach



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Ultrafiltration: been there, done that, did not work...

- This is not end-of-pipe, but a "fractionation" by mol. weight.
- The stage cut is relatively low (less conc. polarization, fouling).
- Membranes have made progress. Tubulars are tolerant to particles, experience on pilot and full scale in Scandinavia is good.

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Expected results ultrafiltration of E-stage effluent

- Laboratory work to determine specific separation properties of ultrafiltration for BP effluent (concurrent to pilot tests).
- Pilot scale data for hardwood and softwood mills with and without O_2 delignification.
- Full scale implementation.

Impact on the industry, ultrafiltration of BP effluent

- Compliance can be achieved without fundamental changes in bleaching technology.
- Chlorides and other inorganics are not recycled to chemical recovery.

Funding and resources for ultrafiltration of BP effluent

- Eka donates use of a pilot scale UF plant during the project (value $150k).
- Cash (Eka): $20k donation to start, $50k/year, 2 years (pays for post-doc), $50k/year in-kind (analytical, personnel).
- Need additional funding:
  - ➔DOE funding (Agenda 2020) seems not successful: Dues co-funding?

Proposal to PAC: IPST Consortium funding if no DOE money is available?

- This project becomes P. Pfromm's PAC project, total of $100,000 from IPST per year for two years (analytical, Pfromm's time, technician support, pilot test travel+supplies)
- NOTE: Results must be OK to publish without delay.

Path forward, ultrafiltration of BP effluent

- Currently searching for Post Doc, have $20k from Eka for 1998.
- DOE funding may not be likely. Recovery PAC was asked to recommend for consortium funding.
- A request for the Pulping&Bleaching PAC: Could you recommend this work to RAC for consortium funding?

Modeling the Fate of Metal Ions During Brown Stock Washing With Bleach Filtrate Recycle

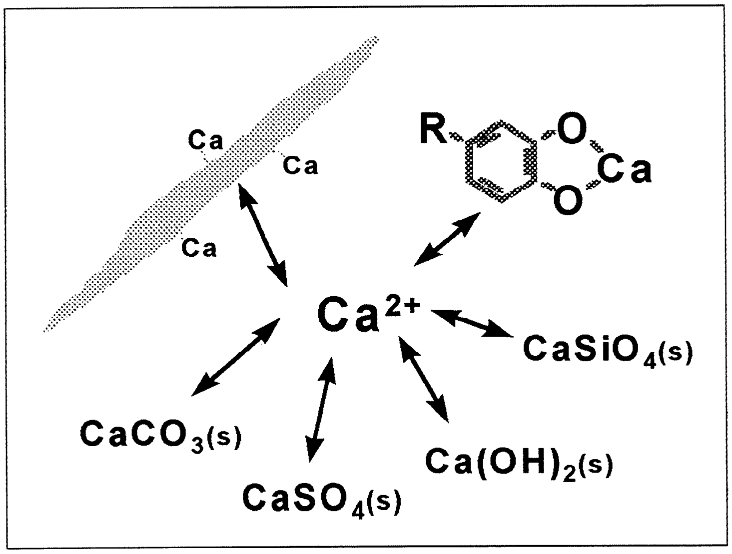
Jim Frederick Wolfgang Schmidl, Alan Rudie
The Institute of Paper and Science and Technology

November 4, 1998

Background

- To reduction of water use in pulp and paper mills, we must recycle water
  - **evaporator condensate,**
  - **bleach plant filtrates**
  - **whitewater**
- With recycle, inorganic and organic materials accumulate
- They can interfere with process operation

Metal ions interact with other species



Two washing scenarios were simulated

- Base case: water as the wash liquor input to the second stage
- Recycle case: alkaline filtrate from ECF bleaching is recycled as the wash liquor

Input streams based on mill data

- ***Unwashed brownstock slurry***:
  - 12.5% consistency
  - 20% dissolved solids in liquor
  - 90°C
- ***Wash liquor (DF = 3.0)***
  - Base case: water, 60°C
  - Recycle case: alkaline filtrate, 0.5% solids content, 60°C
- ***Pulp consistencies:*** 1% in vats, 12.5% in mats

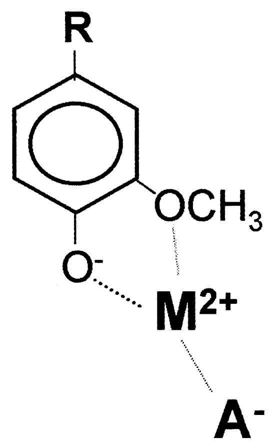
An advanced chemical equilibrium simulator was used

- Chemical equilibrium simulator: ESP (OLI Systems, Inc.)
  - advanced chemical equilibrium simulator
  - predicts ion activities to >10 molal
  - extensive inorganic data base
  - treats dissolved species, precipitation, and adsorption simultaneously
  - includes process simulation capability

An equilibrium model for organometal complexation was developed

Assumptions:

- Dissolved lignin binds multivalent metals at phenolic hydroxyl sites
- The stability constants for metals with carbohydrates and carboxylic acids on lignin are too small to be important.



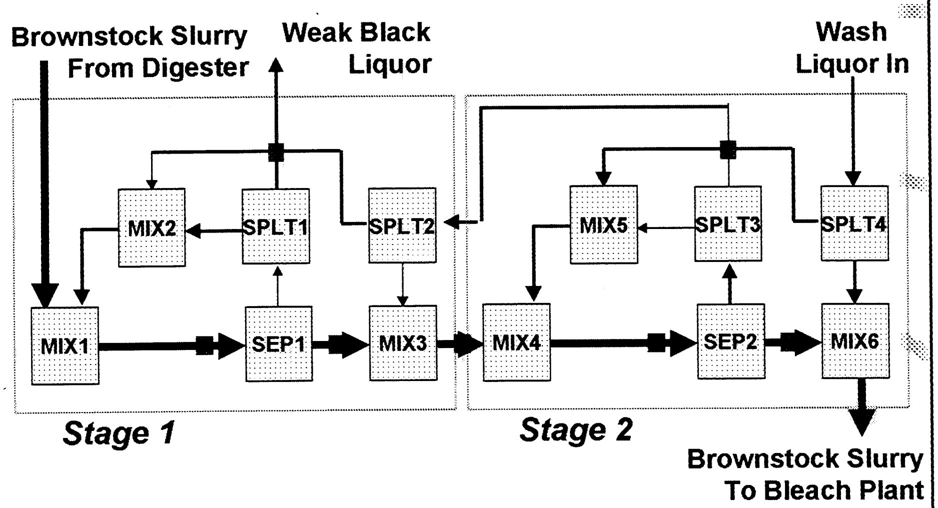
Constants for the ion exchange model were obtained

Adsorption model

- M^{+} + H-Pulp = M-Pulp + H^{+},
- M^{2+} + 2H-Pulp = $M\text{-}Pulp_2$ + $2H^{+}$

Additional constraint: electrical neutrality of fibers

2-Stage Brownstock Washer Model



Soluble inorganic calcium species

(as Ca, g/BDT Pulp)

	Unwashed Brownstock	Black Liquor	Washed Brownstock
Ca^{2+}	0.17	0.36	0.49
$CaOH^{+}$	8.1×10^{-5}	0.98	0.17
$CaHCO^{3+}$	3.6×10^{-5}	7.1×10^{-5}	4.2×10^{-4}
CaC_2O_4	0.28	0.47	0.36
$CaCO_3$	0.77	1.55	1.83
$CaSO_4$	0.01	0.02	0.03

Total Ca input: 1395 g/BDT Pulp

Soluble inorganic manganese species

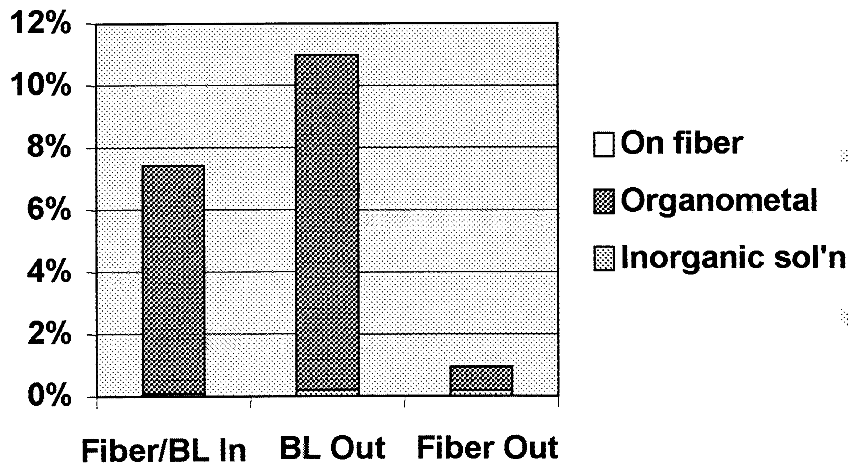
(Data as Mn, g/BDT Pulp)

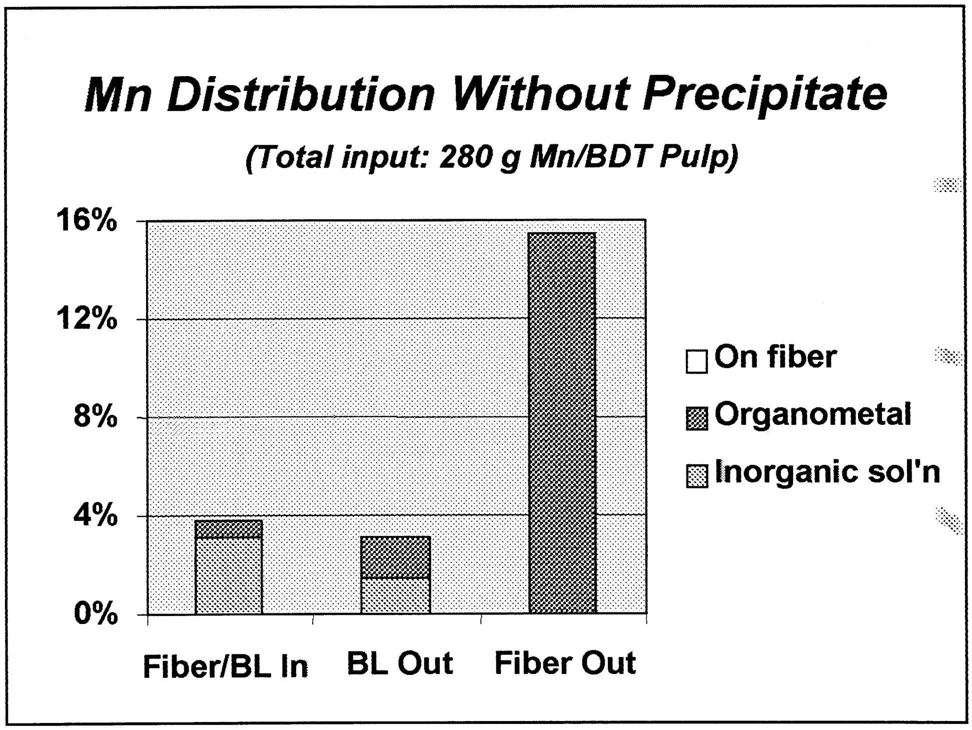
	Unwashed Brownstock	Black Liquor	Washed Brownstock
Mn^{2+}	6.1×10^{-6}	1.7×10^{-5}	4.9×10^{-4}
$MnOH^{+}$	3.2×10^{-3}	0.01	0.04
$Mn(OH)_2$	0.04	0.06	0.05
$Mn(OH)_3^{-}$	1.1	0.89	0.03
$Mn(OH)_4^{2-}$	7.6	3.1	4.3×10^{-3}
MnC_2O_4	3.9×10^{-4}	1.6×10^{-3}	0.09

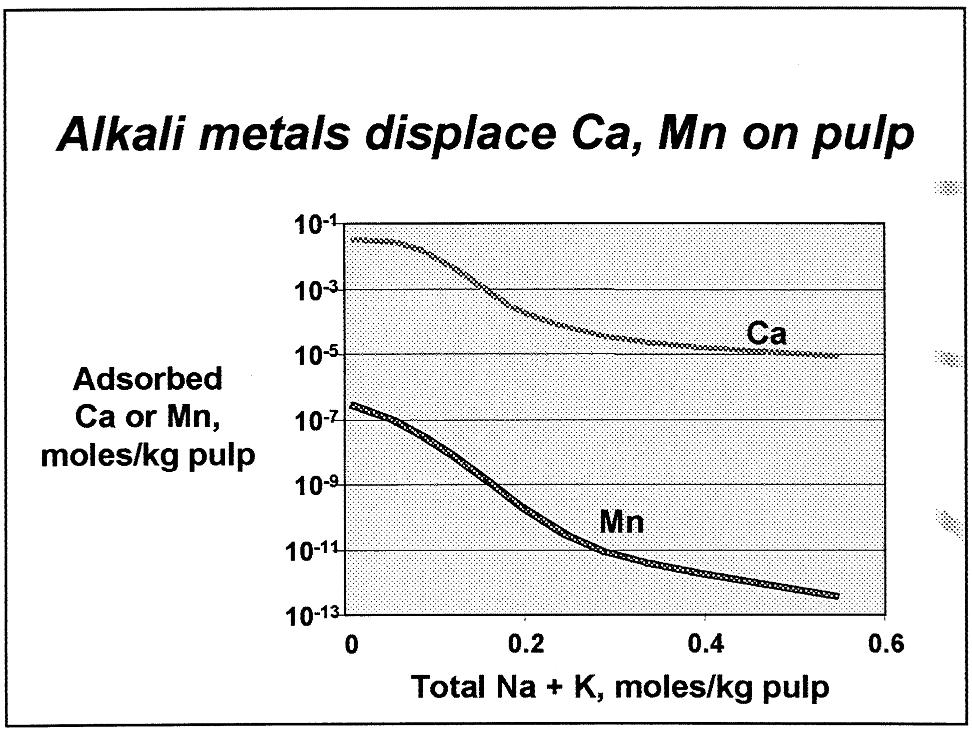
Total Mn input: 280 g/BDT Pulp

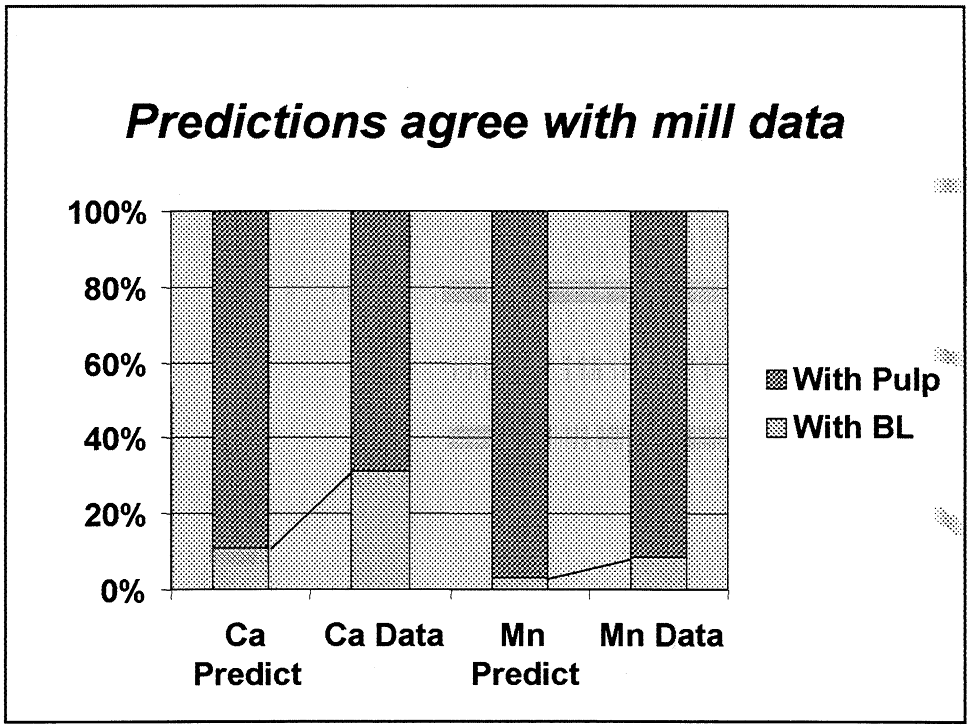
Ca Distribution Without Precipitate

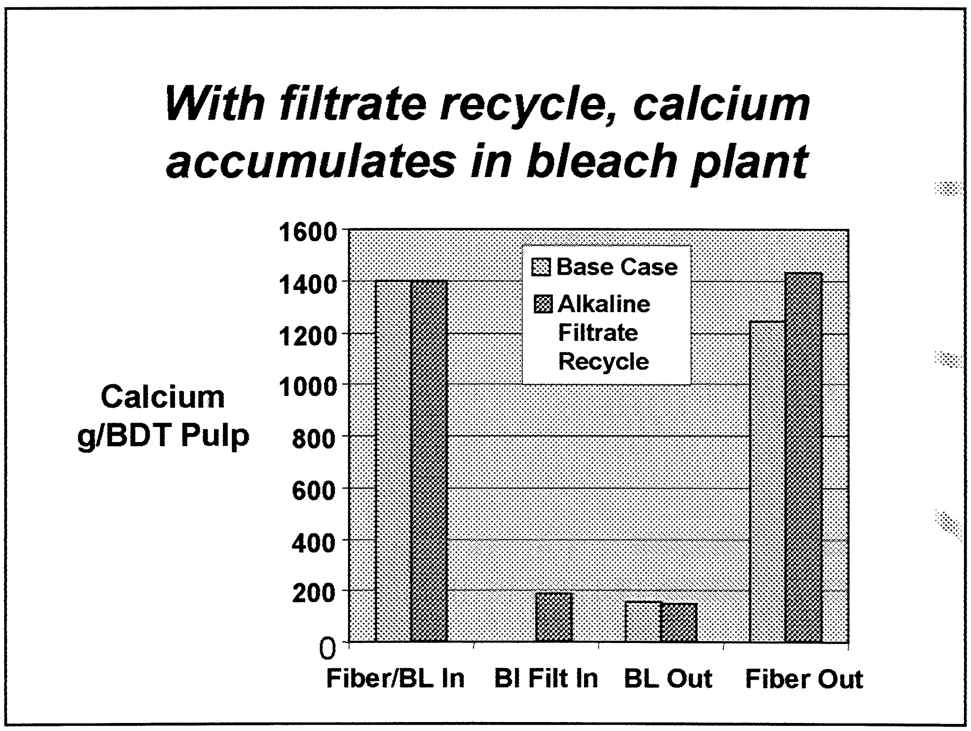
(Total input: 1395 g Ca/BDT Pulp)



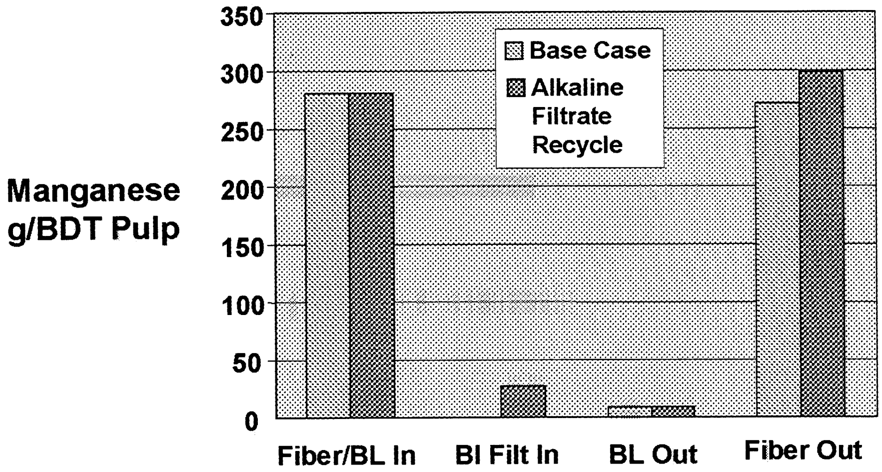

Mn Distribution Without Precipitate
(Total input: 280 g Mn/BDT Pulp)
16%
12%
8%
4%
0%
Fiber/BL In
BL Out
Fiber Out
On fiber
Organometal
Inorganic sol'n


Alkali metals displace Ca, Mn on pulp
Adsorbed Ca or Mn, moles/kg pulp
10-1
10-3
10-5
10-7
10-9
10-11
10-13
Ca
Mn
0
0.2
0.4
0.6
Total Na + K, moles/kg pulp

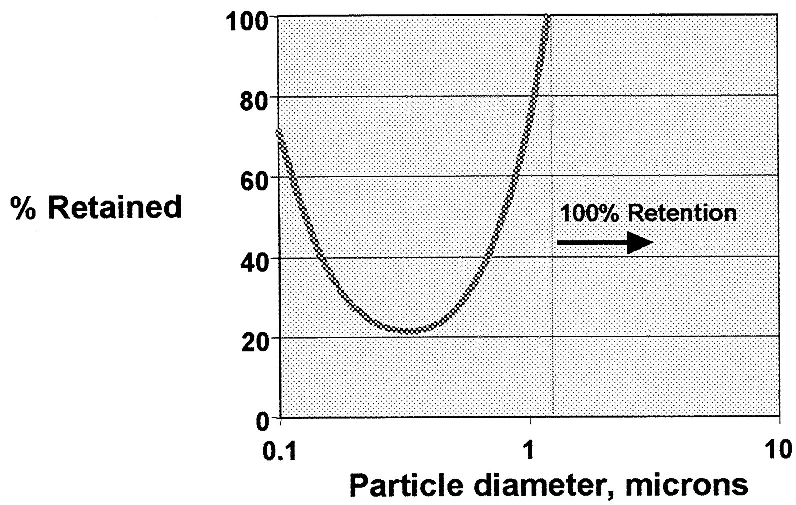

Predictions agree with mill data
100%
80%
60%
40%
20%
0%
Ca Predict
Ca Data
Mn Predict
Mn Data
With Pulp
With BL


With filtrate recycle, calcium accumulates in bleach plant
Calcium g/BDT Pulp
1600
1400
1200
1000
800
600
400
200
0
Base Case
Alkaline Filtrate Recycle
Fiber/BL In
Bl Filt In
BL Out
Fiber Out

With filtrate recycle, manganese also accumulates in bleach plant



Fine particles are retained by fiber mat



Conclusions

- The binding capacity of dissolved organic matter and pulp fibers is small compared with total metals input.
- Most of the metals that are insoluble as hydroxides, carbonates, sulfates, or sulfides will remain mainly as precipitates throughout brownstock washing

Conclusions

- Metals recycled to the brownstock washers with bleach filtrate, they will be returned to the bleach plant.
- These conclusions depend upon the inorganic precipitates remaining with the fibers. This assumption needs to be tested.

Acknowledgments

This work was supported by

- DOE/OIT under contract no. DE-FC07-96ID13441
- Member companies of the Institute of Paper Science and Technology

Jennifer Koenig performed many of the calculations for this study

Calcium is mainly inorganic precipitate

(Data are as Ca, g/BDT Pulp)

	Unwashed Brownstock	Black Liquor	Washed Brownstock
Inorganic, in sol'n	0.95	2.9	2.5
Organometal	103	150	10.2
Adsorbed on fiber	4.7×10^{-7}		0.32
Inorganic precip.	1293		1229
Total	1395	153	1241

Manganese is mainly inorg. precipitate

(Data are as Mn, g/BDT Pulp)

	Unwashed Brownstock	Black Liquor	Washed Brownstock
Soluble inorganic	8.8	4.0	0.12
Organometal	1.8	4.8	43.3
Adsorbed on fiber			3.1×10^{-4}
Inorganic precip.	269		227
Total	280	8.8	271

Lignin Variability

Brian Boyer (Ph.D. 1998)

Alan Rudie

Time Domain Variation
(Batch to Batch)

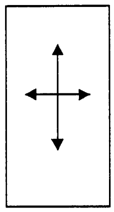
- Wood supply
  - species mix
  - density changes
  - moisture content
- White liquor charge and strength

Fiber-to-fiber and Within Batch Variation

- Viscosity and strength
- Bleachability
- Chemical consumption

Causes

Radial and vertical temperature and liquor profiles

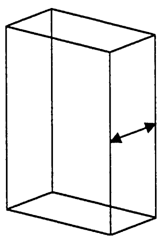


Measurement

Hanging basket method

Fiber to Fiber Variation Causes

- •Chip thickness
- •Species
- •Chemical Penetration



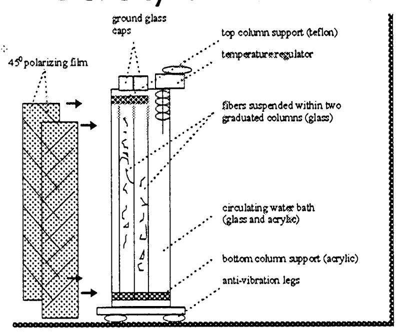
IPST Project

- Ph.D. Research: Brian Boyer, July, 1998
- Targeted at continuous digesters
- methods
  - density gradient column
  - single fiber FT-IR (failed)

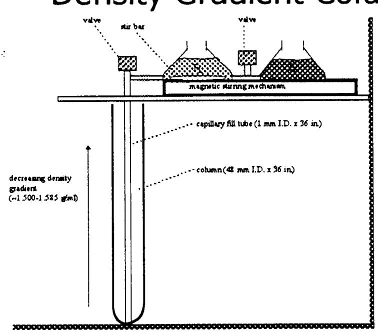
Kraft Cooks

- M/K batch digester
- 10 mm hand cut, or 2.5 mm veneer chips
- 2 hours pre-steaming
- 6:1 l/w ratio
- 40 gpl EA (24% EA), 30% sulfidity
- 150° to 170° C
- 60 minutes to, 240 minutes at temperature

Density Gradient Column



Density Gradient Column



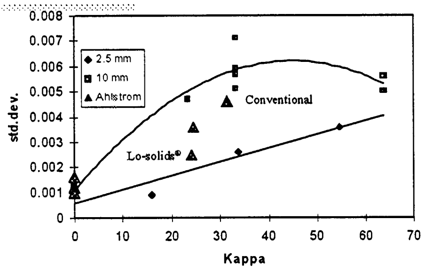
Density Gradient Column

- Carbohydrate: 1.546 g/ml
- Lignin: 1.272 g/ml
- Solvents:
  - $CHCL_3$
  - C_2Cl_4
- Method: Mix C_2Cl_4 into $CHCl_3$ as add mixture to the bottom of a glass column.

Tasks

- Density measurement - certified glass beads
- Imaging - cross polars and red filter
- Image analysis - Optimus
- Data analysis - mean, standard deviation and Composite Normal Distributions

Summary Data

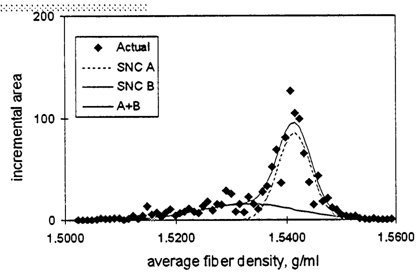


Density Gradient Column

Composite Normal Model:

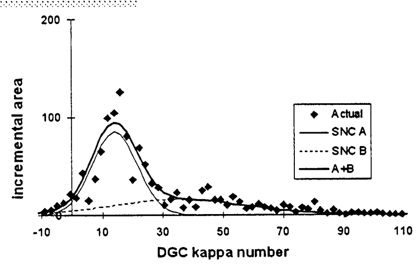
$$F(x) = \frac{1}{\sqrt{2\pi}}\left[\frac{f_A}{S_A}\exp\left\{-\frac{1}{2}\left(\frac{x-\overline{x}_A}{s_A}\right)^2\right\} + \frac{f_B}{S_B}\exp\left\{-\frac{1}{2}\left(\frac{x-\overline{x}_B}{s_B}\right)^2\right\}\right]$$

33 Kappa Pulp from 10 mm thick chips.



Fiber distribution as Kappa number

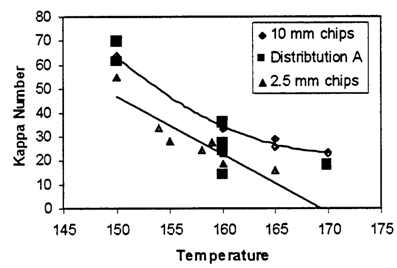
33 kappa number 10 mm chip pulp



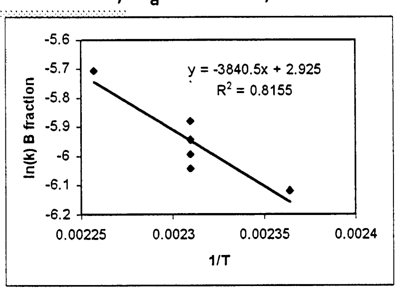
Distribution A and B

- Is Distribution A from the chemical reaction rate portion of the wood chips?
- Is distribution B from the mass transfer controlled portion of the wood chips?
- What can Distribution A and B tell us about the process?

Kappa from distribution A is between Kappa for 2.5 mm and 10 mm chips



Arrhenius Activation Energy of fraction B, E_a = 32 KJ/°mole



Conclusions

- The density gradient column was suitable for measuring the variation in lignin content of kraft pulps.
- The lignin distribution can be modeled as the sum of two normal distributions.
- The lower kappa distribution for 10 mm thick chips is not reaction rate limited.
- The higher Kappa distribution is diffusion limited.

Closed Mill
Metal Binding

Alan Rudie

Project F017 November, 1998

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The Problem!

- Mills have problems with scale formation and transition metal decomposition of peroxide based bleach chemicals.
- Increased recycle of process water to minimize water use and wastewater discharge increases the build up of the non-process metal.

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Task Objective

- Evaluate metal binding behavior relative to pH and competition with other metals.
- Develop a predictive model suitable for use in trace metal equilibrium calculation.

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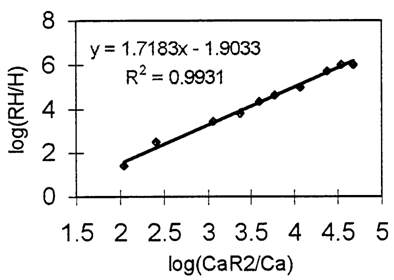
Method: Selectivity Coefficient

$$\frac{[NaR]}{[Na^+][R^-]} = K_{Na}$$

$$\frac{[CaR_2]}{[Ca^{2+}][R^-]^2} = K_{Ca}$$

$$\frac{[CaR_2][R^-]^2[Na^+]^2}{[NaR]^2[R^-]^2[Ca^{2+}]} = \frac{K_{Ca}}{K_{Na}^2} = K_{Na}^{Ca}$$

Log(CaR_2/Ca^{++}) vs Log(RH/H+)



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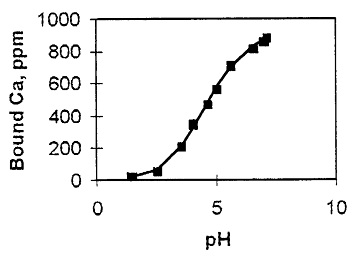
Selectivity Coefficient vs Data



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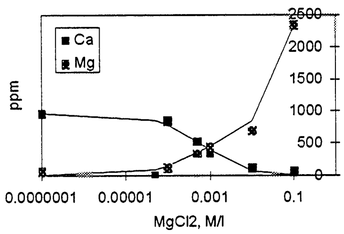
Status as of March, 1998

- Had determined room temperature selectivity coefficients for most cation pairs.
- Had incorporated activity coefficients into the calculation procedure.
- Had worked out a free water/bound water correction.

Ca/Mg, With Adj., Act. & Water

acids = 0.00063 meq/kg, k = 3



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Progress

- Completed the selectivity coefficient matrix.
- (TIP & F017) Completed data sets at 25, 45, & 65° for Ca vs H, Na, Mg, Ba and Mn.
- (TIP & F017) Completed data sets at 25, 45, & 65° for Mg vs H, Na, Ba and Mn.
- Gibbs energy relationships for Ca with acid and Ca with Na and Mg with Na.

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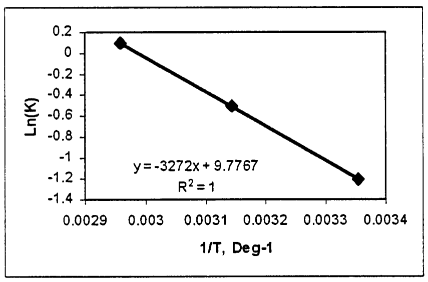
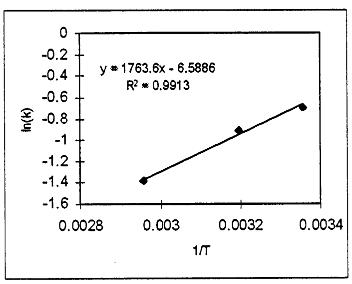
Gibbs Free Energy

- $\Delta G = -RT\ln(K) = \Delta H - T\Delta S$
- Therefore a plot of ln(K) vs 1/T should give a straight line with slope = $-\Delta H/R$ and intercept = $-\Delta S/R$
- Enthalpy is also dependant on changes in heat capacity which is usually small unless there is a change in state.

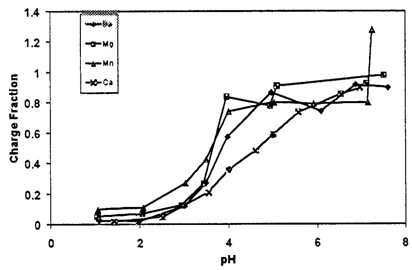
Mg^{++} vs Na^{+} (F017)



Ca^{++} vs H^{+} : Linerboard HW



A comparison of divalent metals.



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Plans: F017

- Complete the data analysis for selectivity coefficient, ΔH and ΔS for bleachable grade SW.
- Characterize metal removal with acids. There appear to be greater differences between metals and pulps than thought.
- Characterize fully bleached pulps.

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Related Student Work:

- Masters & Ph.D. research, Giselle Ow Yang: XANES and EXAFS of tightly bound iron (96).
- Masters Independent Study, Ana Puckett: Laboratory bleaching filtrate recycle experiments to evaluate metals accumulation between D_0 and BSW and D_1 and E.

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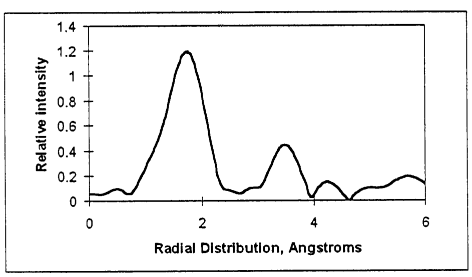
Related Work: Continued

- Georgia Consortium funding has been approved ($57,500 annually), Project PP98-MP4.
- Georgia Consortium project PP98-MP1: Paper machine closure (Woitkovich).
- DOE: (Frederick): Equilibrium model development.

Results: Giselle Ow Yang and Georgia TIP[3] PP98-MP4

- The analysis of the iron EXAFS spectrum indicates the binding site is probably a guaiacyl group.
- The Ca and Mn EXAFS results have been obtained.
- Efforts to synthesis Fe-Guaiacol and Fe-Vanillin complexes are ongoing.

Ca, Radial Distribution Function



Mn EXAFS

- Radial positions (preliminary): 1.9Å, 2.8Å, & 3.8Å.
- Comparison Ca: 1.75Å, 3.50Å, and 4.23Å.
- These do not appear to be the same binding site!

Giselle Ow Yang: Plans

- Using FEFF7 to model possible Ca and Mn binding sites.
- Continuing synthetic effort to isolate Fe-vanillin type site.
- Beginning project to remove "intractable" iron and evaluate influence on bleaching.

DOE Metal binding by black liquor solids

- Approach: Competition for binding sites using UV-VIS or Fluorescent indicators.
- $[MI]/([M^+][I^-]) = K$.
- Know [MI] and [I] from the indicator added and the UV-Vis spectrum.
- Calculate $[M^+]$.
- $[MBl] = M_T - [M^+] - [MI]$

Status

- Many indicators are not pure (ie-don't know [I] and/or [MI]).
- Need $K_I < K_{Bl}$
- Additional problems at pH>10 due to limited $Ca(OH)_2$ solubility.
- **Black liquor appears to have one binding site for every 2 to 3 monomers, $K \sim 10^3$-10^5**

DOE - Next

- Look at competitive binding to pulp to establish equilibrium.
  - $K=(CaP_2)[Na^+]^2/([Ca^{++}](NaP)^2)$
  - can determine bound Ca and Na by analysis
  - know total Na^+ and Ca^+
  - assume Na^+ does not bond with BL
- $[CaBl] = Ca_T - CaP - [Ca^{++}]$

Acknowledgments

- Narendra Patel, Alan Ball and Fern Peterson.
- Chemical PAC and Member Companies for project support.
- Clark Woitkovich (Georgia TIP[3]) for funding the high lignin pulp effort.
- Jim Frederick (DOE Agenda 2020) for funding the black liquor work.

Project F013

Environmentally Compatible Production of Bleached Chemical Pulp

TJM981104

1

Contributors To Project F013

- Aric Bacon
- Jean-Christophe Baromes
- Tim Bonner
- Blair Carter
- Chuck Courchene
- Craig Jackson
- Brendan Lee
- Tom McDonough
- Art Ragauskas
- Alex Shaket
- Mark Turner
- Andreau White

TJM981104

2

Research Goals

- Effects of modern delignification methods on refining behavior and fiber properties
- Find predictors of ease of delignification by oxygen and DE sequences (with DOE-funded Project 4120 - part of $36K matching)
- Evaluate and develop QP as alternative to O
- Assist in implementation of Rapid D_0
- Evaluate and compare (D/Z) sequences

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Related External Funding

- Proj. 4120 - DOE/Auburn effort on pulping and bleachability - $36K matching
- Proj. 4159 - Agenda 2020 funded project on ClO_2 delignification - no matching in FY 99
- Proj. 4201 - Agenda 2020 funded work on Rapid D_0 plus Simplified Bleaching as routes to low-capital plants - $15K matching

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Related Student Work

- Aric Bacon (Ph.D.) - Effects of delignification methods on fiber properties
- Carter Johnson (M.S.) - Effects of organics buildup in closed bleach plants
- Timothy Jacoby (M.S.) - Ultraselective ASAQ pulping as an alternative to kraft
- Cesar Goncalves (External Ph.D.) - Fate and effects of metals in closed bleach plants

TJM981104

5

Chelation and Peroxide as an Alternative to Brownstock Oxygen

TJM981104

6

Rationale

- Most of the peroxide delignification work reported in the literature has been done to evaluate and optimize peroxide as a stage following oxygen and/or ozone
- Advances in chelation technology have extended the degree of delignification achievable with peroxide
- Catalysis by transition metals or their complexes offers an additional opportunity

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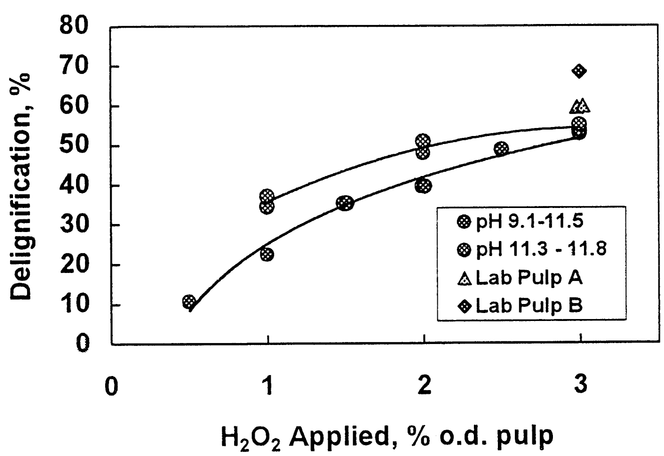
QP Delignification vs. H_2O_2 Charge



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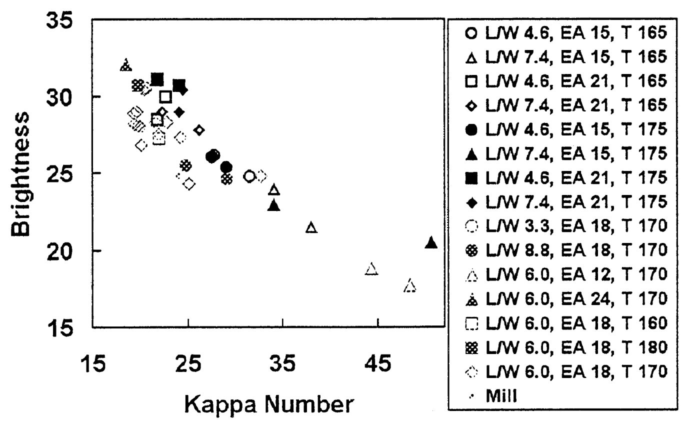
Brightness After QP (3%H_2O_2) For Lab and Mill SP Kraft Pulps



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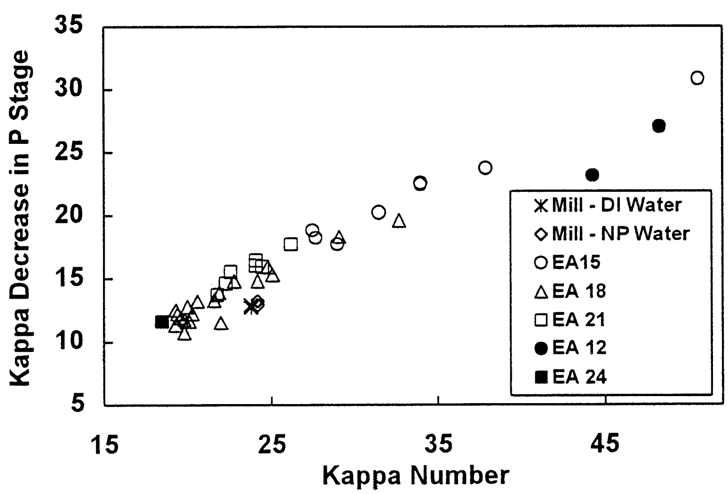
9

Kappa Drop in QP (3%H_2O_2) For Lab and Mill SP Kraft Pulps



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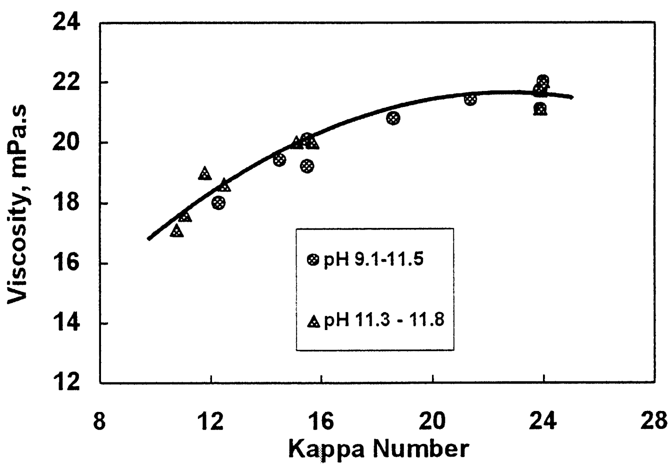
QP Selectivity



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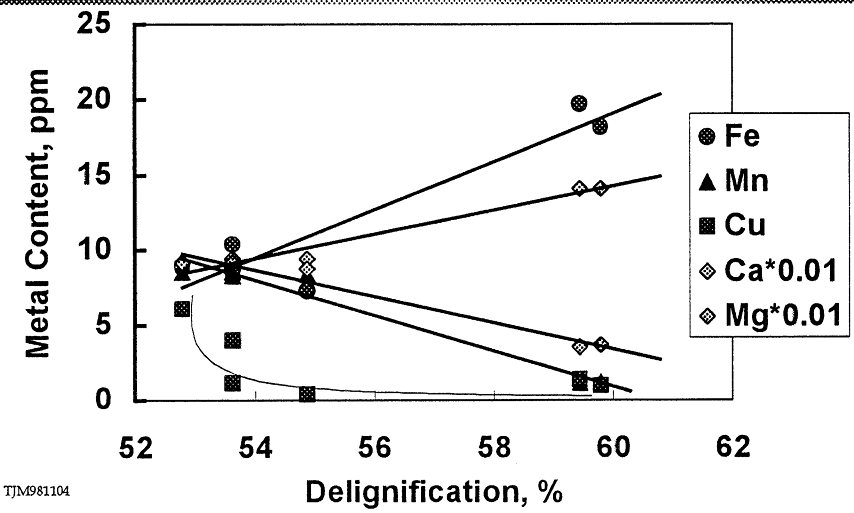
Metals in QP Delignified Pulps



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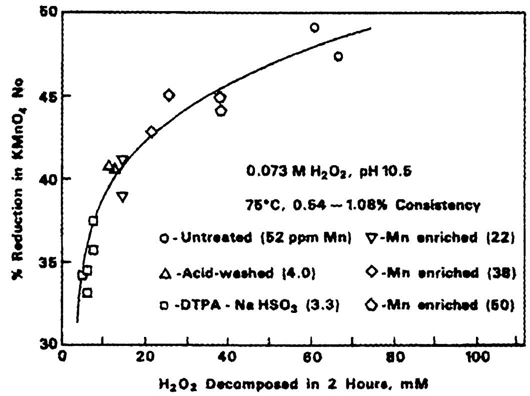
Beneficial H_2O_2 Decomposition (Previous Work)



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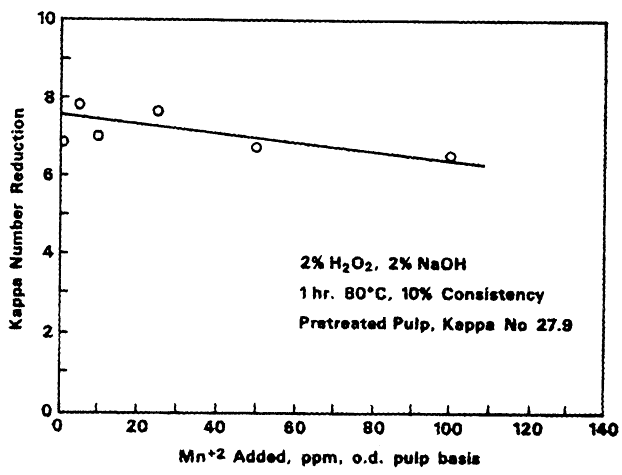
Mn Affects Delignification Little (Previous Work)



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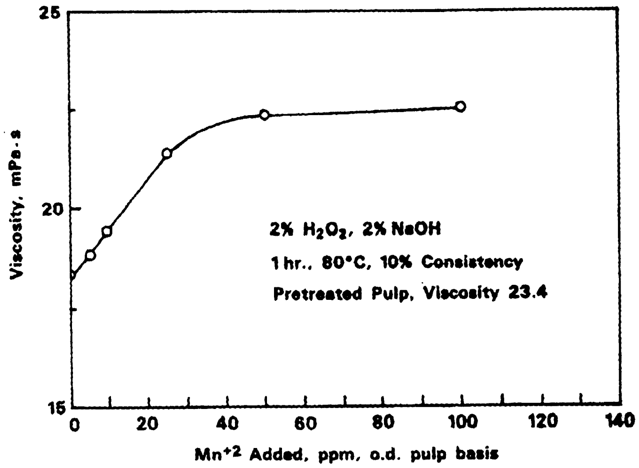
Mn Increases Viscosity After QP (Previous Work)



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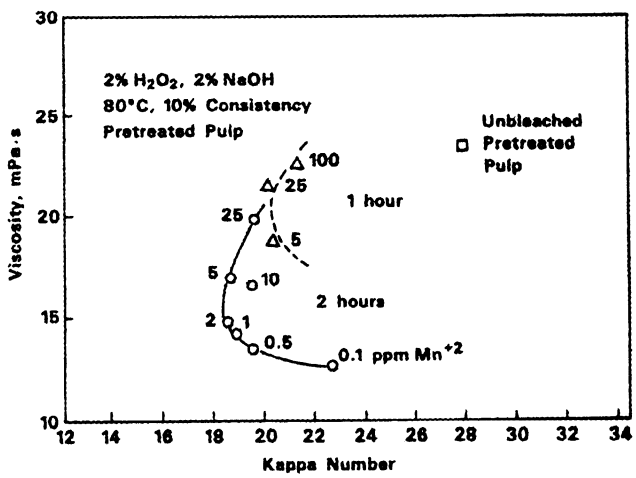
Mn Improves Selectivity (Previous Work)



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Effects of Pulping Parameters on DE Bleachability

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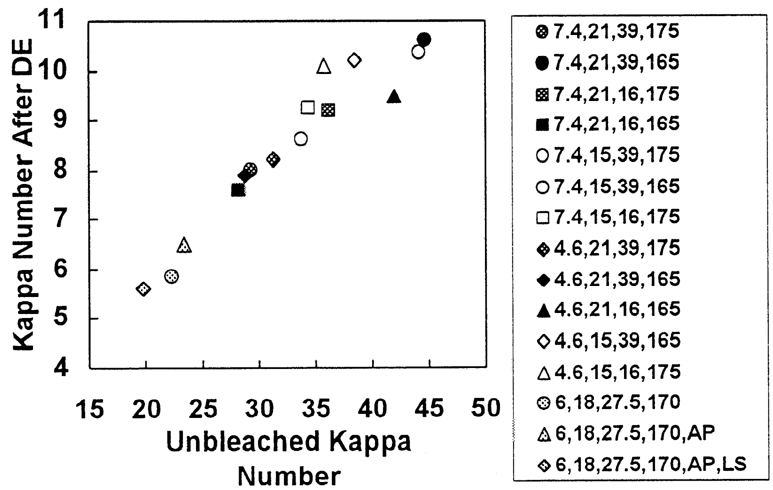
DE Delignification vs. Unbl. Kappa and Pulping Parameters



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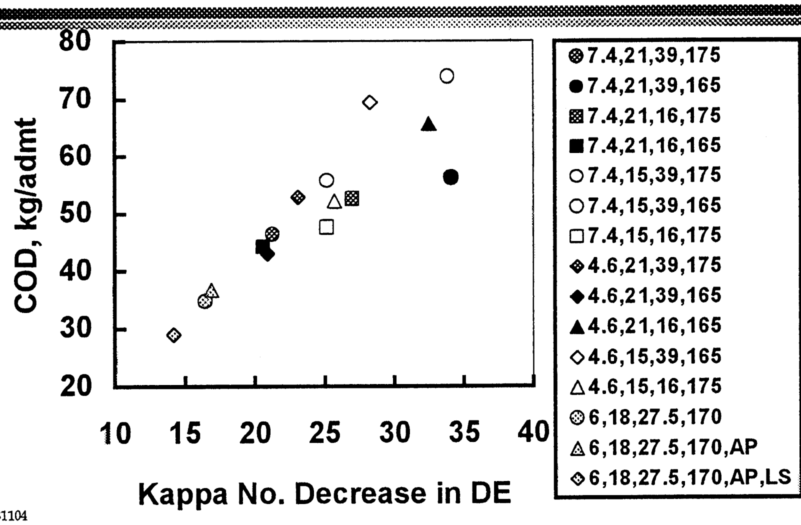
DE COD vs. Unbl. Kappa and Pulping Parameters



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(D/Z) Bleaching

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(D/Z) Conditions

- Assumed 1 kg O_3 = 4.44 kg Cl_2 and 1 kg ClO_2 = 2.63 kg Cl_2
- Carryover of 1% BL solids into (D/Z) and carryover of 10% (D/Z) filtrate into (EPO)
- (D/Z) 15/30 min, 50°C, exit pH 2.5, kappa factor 0.20 on washed kappa no., mixing 20 sec after injection then 20 sec every 5 min.
- EPO: 0.4% H_2O_2, 35/0 psig O_2 for 15/30 min.

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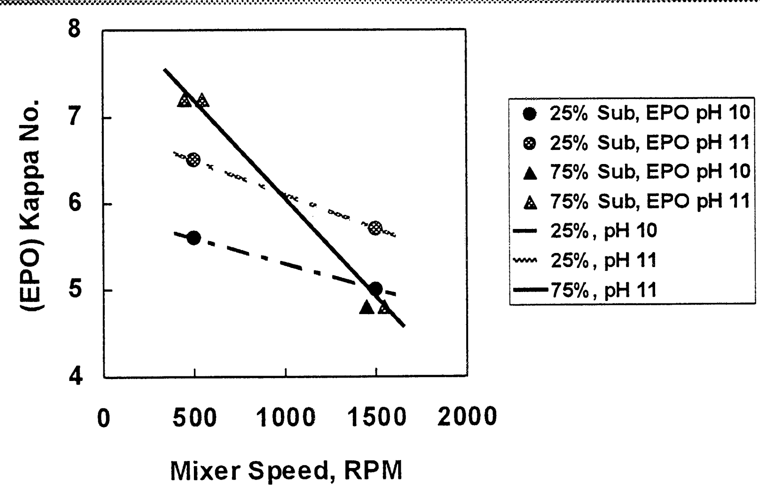
(D/Z)(EPO) Kappa No. vs. Speed, Subststitution, and pH



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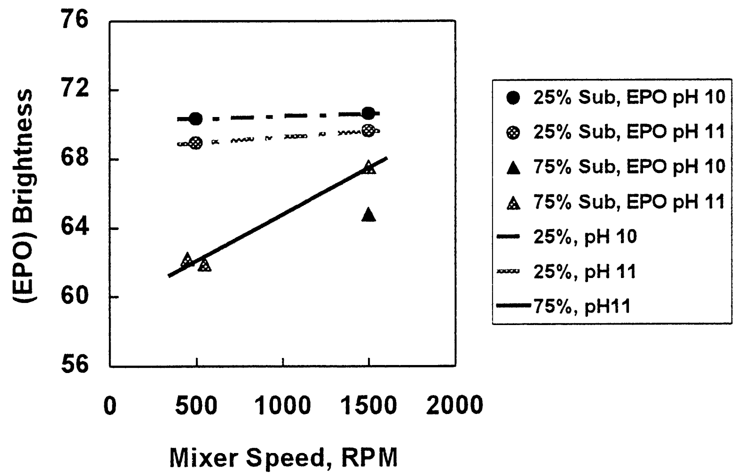
(D/Z)(EPO) Brightness vs. Speed, Substitution, and pH



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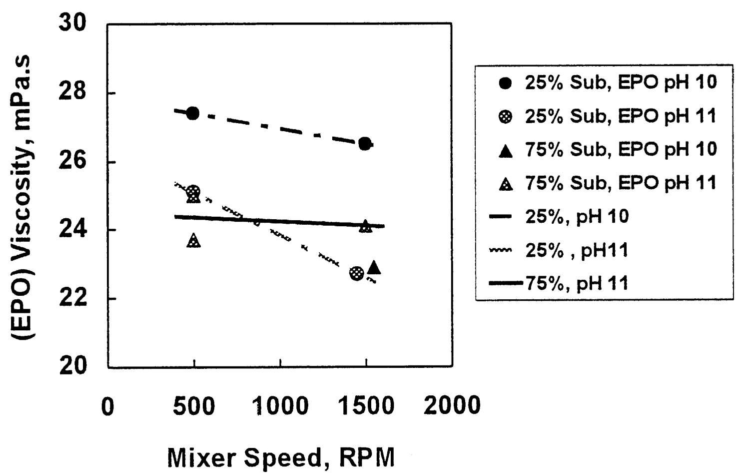
(D/Z)(EPO) Viscosity vs. Speed, Substitution, and pH



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F013 - Effect of Pulping and Bleaching Processes on Pulp and Fiber Properties

- **Pulping and Bleaching**

Tom McDonough
Chuck Courchene
Blair Carter
Tim Bonner

- **Paper Physics (F024)**

John Waterhouse
Hiroki Nanko
Miranda Bliss

F013 and F024 Project Objectives

- F013 - To evaluate the effects of delignification processes and ECF bleaching on fiber properties, paper properties, and refining behavior
- F024 -Determine how changes in fiber structure and the means to produce them, are related to improved paper machine productivity, paper quality, and reduced energy consumption.

Shorter Term Objectives

1. Establish methods for producing selected changes in fiber structure.
2. Establish methods to measure and characterize these changes in fiber structure.
3. Determine the relative impact of these changes on drainage, water removal, and paper properties.
4. Determine how selected pulp variables influence these changes in fiber structure.
5. Determine the extent to which these changes can be produced in production refiners.

Project Deliverables

1. Tools for improved pulp characterization.
2. Characterization of delignification and bleaching processes for optimum fiber and paper properties.
3. Methodology for determining a pulp's response to refining.
4. Strategies for reducing energy consumption and improving paper-machine productivity.

F013 - Effect of Pulping and Bleaching Processes on Pulp and Fiber Properties

- Experimental plan, pulping and bleaching - Prepare lab kraft pulps from common wood source. Oxygen delignify pulps to different final kappa nos. Bleach pulps with both CED and DED sequences.
- Experimental plan, paper physics - Prepare pulps with common cation exposure. Refine samples in PFI mill to 3000 revolutions. Measure pulp samples for fines content, WRV, wet zero span, handsheet properties, internal and external structural changes.

F013 - Pulping and Oxygen Delignification

- Kraft Pulping - S. Pine mill chips
  - Kappa 110 - 17,5% AA, 30% sulfidity, 400 H-factor
  - Kappa 28 - 18.5% AA, 30% sulfidity, 1250 H-factor
  - Kappa 17 - 25% AA, 25% sulfidity, 1250 H-factor
- Oxygen Delignified Pulps from Kappa 28 kraft
  - 10% cons., 100°C, 90 psig O_2, 0.05% Mg^{+2}
  - 20.4 Kappa - 0.8% NaOH
  - 15.7 Kappa - 1.45% NaOH
  - 12.1 Kappa - 2.30% NaOH
  - 10.7 Kappa - 2.70% NaOH

F013 - Bleaching Conditions

- CED and DED Bleaching
  - C or D - 0.2 KF, 3% cons., 45°C, 30 min.
  - E - 10% cons., 70°C, 60 min., 55% act. Cl_2 NaOH
  - D - 1.2 % ClO_2, 10% cons., 70°C, 180 min.

F013 - Samples for Testing

Pulp samples		Kappa no.	CED	DED
Kraft	+	110	no	no
Kraft	+	28.1		
Kraft	+	17.1	*	*
Kraft 28 – O_2	+	20.4	+	+
Kraft 28 – O_2	+	15.7	+	*
Kraft 28 – O_2	+	12.1	*	*
Kraft 28 – O_2	+	10.7	*	+

F013 - Brightness after Bleaching

Pulp samples		CED	DED
Kraft	110		
Kraft	28.1		
Kraft	17.1	86.9	84.7
Kraft 28 – O_2	20.4	88.3	81.2
Kraft 28 – O_2	15.7	88.6	83.1
Kraft 28 – O_2	12.1	90.8	84.1
Kraft 28 – O_2	10.7	89.9	85.8

F013 - COOH Content of Pulps

Pulp samples		Brownstock	CED	DED
Kraft	110	0.175 meq/g	-	-
Kraft	28.1	0.077		
Kraft	17.1	0.049		
Kraft 28 – O_2	20.4	0.081	0.046	0.041
Kraft 28 – O_2	15.7	0.078	0.036	
Kraft 28 – O_2	12.1	0.072		
Kraft 28 – O_2	10.7	0.067		0.043

F013 - Calcium content

Pulp samples		Brownstock	CED	DED
Kraft	110	4360 ppm		
Kraft	28.1	1680		
Kraft	17.1	903		
Kraft 28 – O_2	20.4	1720	663	755
Kraft 28 – O_2	15.7	1610	613	
Kraft 28 – O_2	12.1	1425		
Kraft 28 – O_2	10.7	1420		717

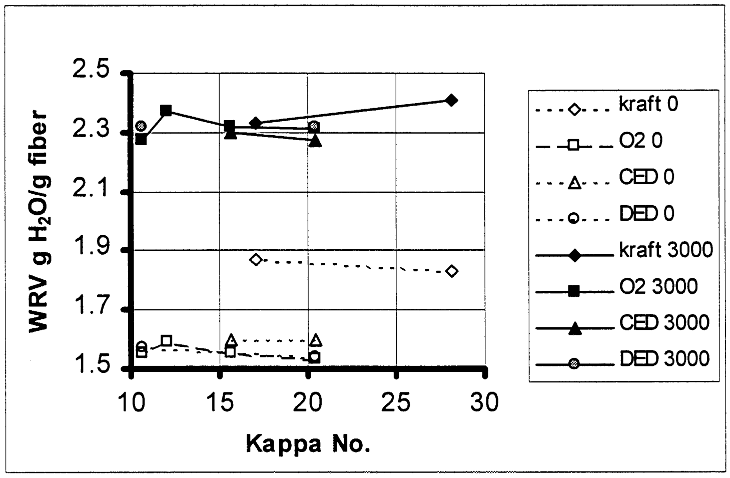
F013 -PFI Refining - CSF 0 revs/3000revs

Pulp samples		Brownstock	CED	DED
Kraft	110	751/669		
Kraft	28.1	743/400		
Kraft	17.1	727/342		
Kraft 28 – O_2	20.4	753/364	728/341	728/366
Kraft 28 – O_2	15.7	740/338	733/320	
Kraft 28 – O_2	12.1	732/296		
Kraft 28 – O_2	10.7	755/347		736/244

F013 - WRV - 0 revs/3000 revs

Pulp samples		Brownstock	CED	DED
Kraft	110	1.70/2.17		
Kraft	28.1	1.83/2.41		
Kraft	17.1	1.87/2.33		
Kraft 28 – O_2	20.4	1.53/2.31	1.60/2.27	1.64/2.32
Kraft 28 – O_2	15.7	1.55/2.32	1.60/2.30	
Kraft 28 – O_2	12.1	1.59/2.37		
Kraft 28 – O_2	10.7	1.55/2.27		1.63/2.32

Variation of WRV with KAPPA No.



F013 - Wet (never-dried) Zero Span Tensile Index - 0 revs/3000 revs

Pulp samples		Brownstock	CED	DED
Kraft	110	102/116		
Kraft	28.1	124/119		
Kraft	17.1	110/109		
Kraft 28 – O_2	20.4	85.9/106	/101	/103
Kraft 28 – O_2	15.7	/105	/98.0	
Kraft 28 – O_2	12.1	/92.2		
Kraft 28 – O_2	10.7	70.7/91.8		/80.4

F013 - Dry Zero Span Tensile Index - 0 revs/3000 revs

Pulp samples		Brownstock	CED	DED
Kraft	110	112/121		
Kraft	28.1	133/132		
Kraft	17.1	132/137		
Kraft 28 – O_2	20.4	89.8/131	/126	/116
Kraft 28 – O_2	15.7	/124	/120	
Kraft 28 – O_2	12.1	/114		
Kraft 28 – O_2	10.7	85.5/120		/111

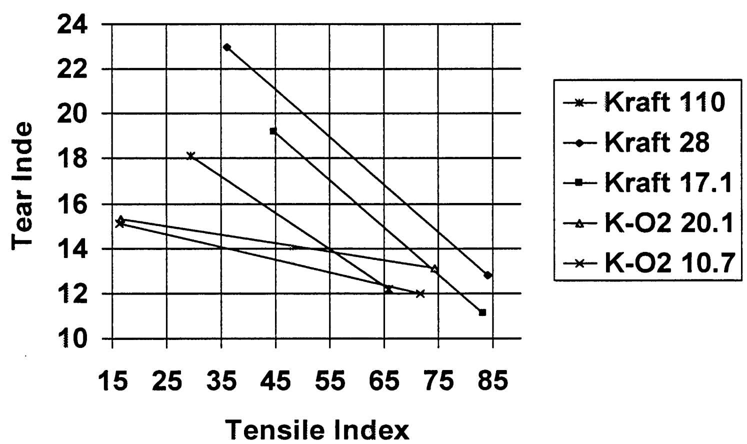
F013 - Tear Index 0 revs/3000 revs

Pulp samples		Brownstock	CED	DED
Kraft	110	18.1/12.2		
Kraft	28.1	23.0/12.8		
Kraft	17.1	19.2/11.1		
Kraft 28 – O_2	20.4	15.3/13.1		
Kraft 28 – O_2	15.7			
Kraft 28 – O_2	12.1			
Kraft 28 – O_2	10.7	15.1/12.0		

F013 - Tensile Index - 0 revs/3000 revs

Pulp samples		Brownstock	CED	DED
Kraft	110	29.4/65.8		
Kraft	28.1	36.0/84.0		
Kraft	17.1	44.8/83.1		
Kraft 28 – O_2	20.4	16.5/74.2		
Kraft 28 – O_2	15.7			
Kraft 28 – O_2	12.1			
Kraft 28 – O_2	10.7	16.3/71.5		

Tear vs. Tensile Index



F013 - Palladium and Iron Colloid Staining - 0 revs/3000 revs

Pulp samples		Pd, μg/g	Fe, μg/g
Kraft	110	313/694	12400/27700
Kraft	28.1	229/1180	16800/42100
Kraft	17.1	128/612	21100/38600
Kraft 28 – O_2	20.4	272/1370	18200/41100
Kraft 28 – O_2	15.7		
Kraft 28 – O_2	12.1		
Kraft 28 – O_2	10.7	367/1660	20100/42500

Future Work

- Finish analysis of all samples.
- Define meaningful characterizations of pulp properties.
- Identify additional delignification and bleaching processes to evaluate.

High Strength, High Yield Bleached Pulps

Dues-Funded Project - F030
(November 4, 1998)

Jian Li
Chemical Pulping and Bleaching Group

Institute of Paper Science and Technology

THE PLAN WAS

GOALS AND DELIVERABLES (July 1, 98 - July 1, 99)

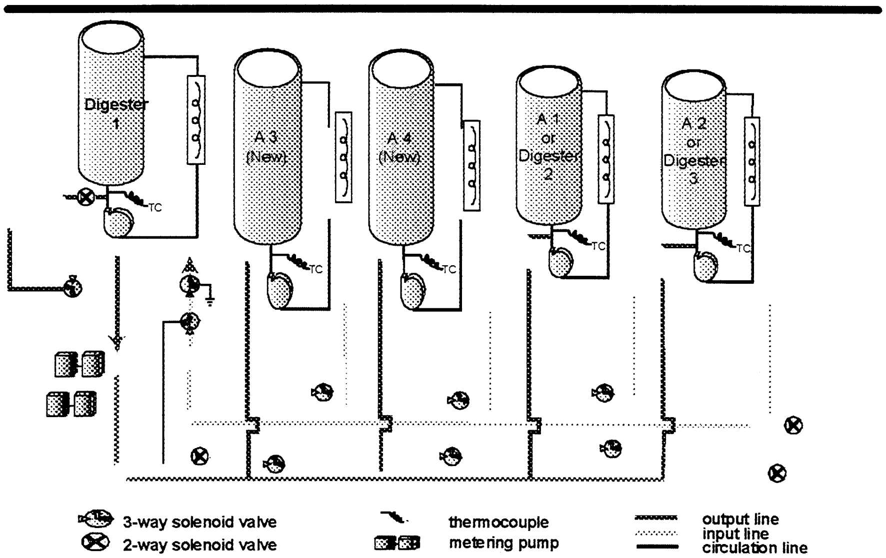
- Complete digester modification -
  - capable of simulating commercial processes:
    RDH, SuperBatch, MCC, EMCC, ITC, Lo-Solids
  - investigating new processes leading to higher yield and strength, better bleachability (collaborate with F013), etc.
- Complete reference cooks
  - conventional kraft, "AQs" and polysulfide cooks
- Initial modification of no split-sulfidity cooking
  - How to use PS and "AQs" in RDH, Lo-Solids
  - (Batch version of Lo-Solids cooking of hardwood)

THE PLAN AFTER RAC REDIRECTION

GOALS AND DELIVERABLES (July 1, 98 - July 1, 99)

- Complete digester modification
- Complete reference cooks
- Initial modification of no split-sulfidity cooking
- A review on yield - strength relationship
  - Define theoretical background on what the yield gain limits are, based on its effects on physical properties.
- A three year research plan
  - Define scientifically sound and technically feasible research approaches in the proposed research area.

PROGRESS IN BUILDING DIGESTERS



HIGH LIGHTS OF THE REPORT

Higher Yield ≈ Higher Hemicellulose

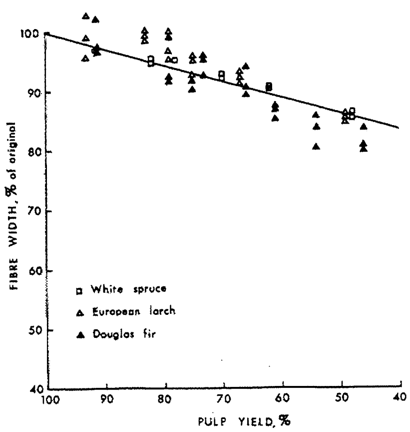
↓

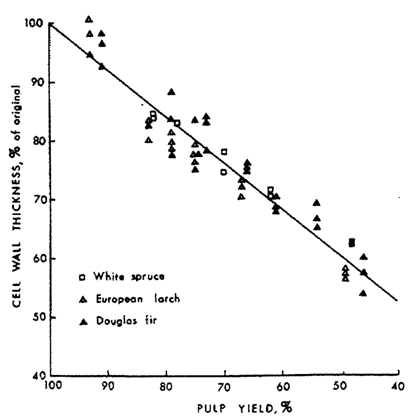
Fiber dimensions | **Bonding potential** | **Fiber strength**

↓

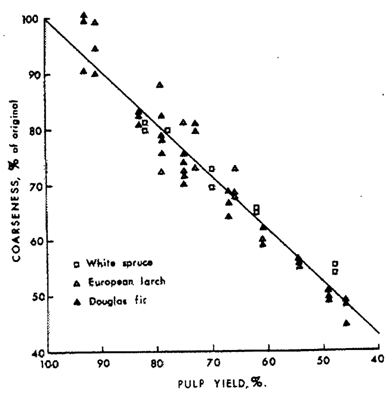
Tearing | **Tensile** | **Drainage** | **Finishing**

HIGH LIGHTS - Fiber Dimensions





HIGH LIGHTS - Fiber Dimensions

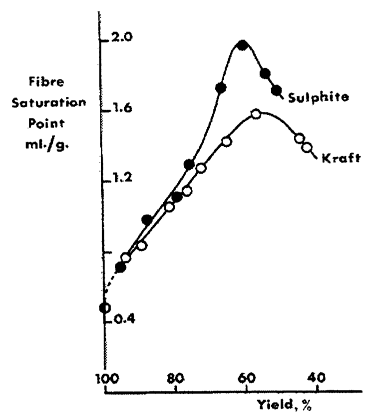


Yield increase leads to:
a) ~ no change on length,
b) transverse dimensions increase,
c) coarseness increases, e.g. 25% at 10% yield gain.

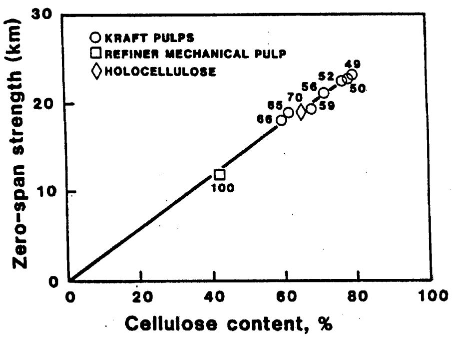
HIGH LIGHTS - Bonding Potential

Bonding potential may be enhanced due to:
a) more bondings from hemicellulose,
b) higher swelling,

may slightly reduced due to
c) higher coarseness.



HIGH LIGHTS - Fiber Strength



As yield increases, the weight-based fiber strength will be lower for pulps without severe cellulose degradation.

HIGH LIGHTS - Fiber Strength

Effect of Hemicellulose Content on Fiber Strength. (Scots pine)

Scenarios	Yield gain, %	Cellulose & Hemi % on wood	Cellulose % on pulp	% of orig. zero-span	Total yield %
Original; Low yield kraft	*0*	*35, 9*	*80*	*100*	*44*
All gain from hemicellulose	10	35, 19	65	81	54
No cellulose loss	10	39, 15	72	90	54
Max gain without strength loss	5	39, 10	80	100	49

10% yield gain would reduce fiber strength by 10-20%; max. yield gain without strength loss is about 5%.

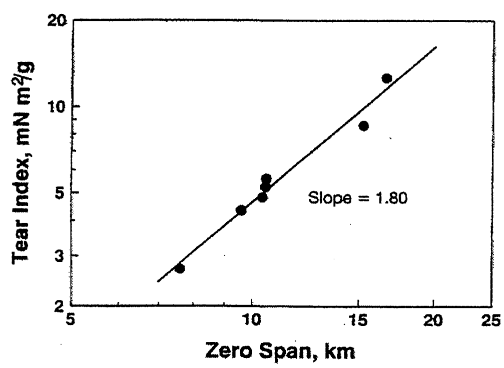
HIGH LIGHTS - Tearing Strength

Table IV. Effect of Starch Addition to Beaten Pulp

	Time beaten:				
	0 min	*2 min*	*5 min*	*10 min*	*20 min*
Without Starch					
Breaking length, m	2630	3350	4250	6010	7490
Tear factor	189	257	287	223	176
Bulk, cm^3/g	1.71	1.74	1.66	1.55	1.49
Scott bond, ft-lb × 1000	35	44	55	79	117
With 0.5% Starch					
Breaking length, m	3410	4450	5790	6770	8520
Tear factor	267	240	184	157	131
Bulk, cm^3/g	1.75	1.68	1.55	1.50	1.42
Scott bond, ft-lb × 1000	51	72	107	121	168
With 2.0% Starch					
Breaking length, m	4600	5740	6190	7560	8960
Tear factor	235	192	139	130	116
Bulk, cm^3/g	1.68	1.61	1.54	1.49	1.43
Scott bond, ft-lb × 1000	91	117	142	184	235

HIGH LIGHTS - Tearing Strength

Tearing strength = k (zero span tensile)^n
(n = 1 - 3)



Tear could be severely reduced at 10% yield gain because of higher bonding, lower zero-span.

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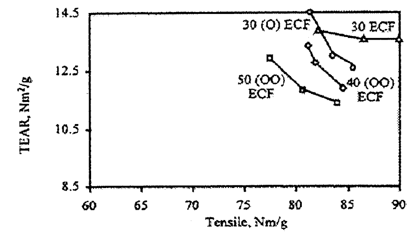
HIGH LIGHTS - Other Properties

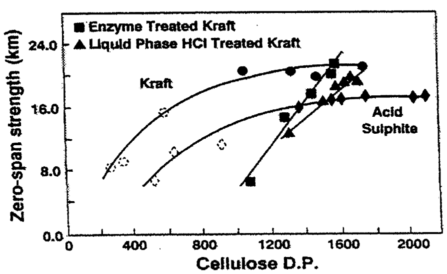
- Tensile strength may not be strongly affected since lower fiber strength may be compensated by better fiber-fiber bonding.
- Drainage may be affected, but may be easily controlled.
- Optical property and flexibility may be affected, but could be easily corrected.

POSSIBLE APPROACHES TO IMPROVE TEARING STRENGTH

- Preserve intrinsic fiber strength by avoiding any cellulose degradation
- Reduce bonding potential by reducing the amount of hemicellulose available on fiber surface: a) obtain maximum possible yield gain; b) sacrifice (=extract) the low molecular weight hemicellulose; c) better control of beating operation, i.e. no over beating.

WHY MINIMIZE VISCOSITY LOSS





Strength loss of the pulp from high kappa + oxygen delignification is likely due to severe cellulose degradation.

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MODEL FOR CELLULOSE DEGRADATION

Pulp Viscosity = f (T, t, [OH⁻])

In "G" factor Model, [OH⁻] is kept as constant :

$$\frac{1}{\eta_t} - \frac{1}{\eta_0} = a \cdot G = a \cdot \int_0^t k_r dt = a \cdot \int_0^t e^{\left[\frac{E}{R}\left(\frac{1}{373} - \frac{1}{T}\right)\right]} dt$$

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MODIFIED "G' FACTOR MODEL

$$\frac{1}{\eta_t}-\frac{1}{\eta_0}=a'\cdot\int_0^t [OH^-](t,x)\cdot e^{\left[\frac{E}{R}\left(\frac{1}{373}-\frac{1}{T}\right)\right]}dt = a'\cdot G([OH^-])$$

$[OH^-]$ is a function of time and position in chips.

HOW TO CALCULATE G(OH^-)

$$\frac{\partial C_i}{\partial t}=\frac{\partial}{\partial x}\left(D_i\frac{\partial C_i}{\partial x}\right)+R_i(x,t)$$

C_i: Concentration of Species i

D_i: Diffusion Coefficient of Species i

$R_i(x,t)$: Reaction Rate of Species i

KINETIC RATE EQUATIONS R(X,T):

- Lignin: $dL/dt = f([OH^-], [HS^-], T, L)$
- Cellulose: $dC/dt = f([OH^-], T, C)$
- Hemicellulose: $dH/dt = f([OH^-], T, H)$
- Alkali: $d[OH^-]/dt = f(dL/dt, dC/dt, dH/dt)$
- Sulfide: $d[HS^-]/dt = f(dL/dt)$

AN EXAMPLE OF KINETIC EQUATIONS

Delignification:

Initial:

$$\frac{dL}{dt} = 36.2T^{0.5}\exp\left(\frac{-4807.69}{T}\right)L$$

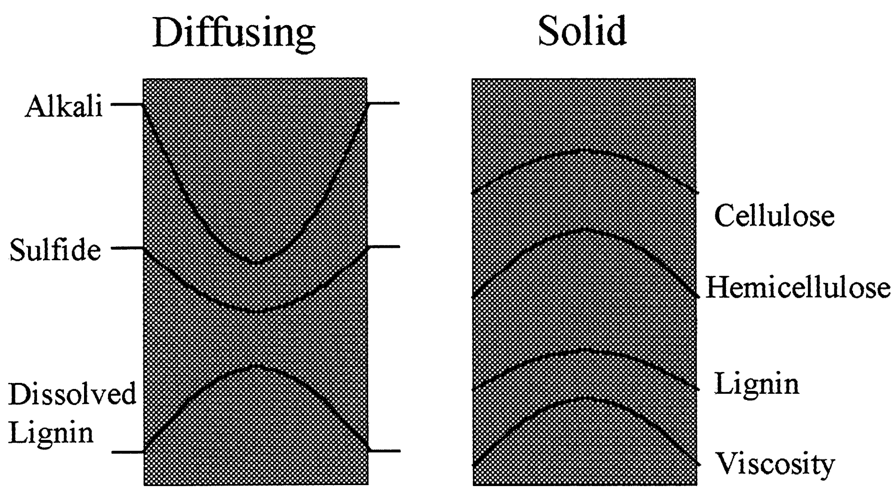
Bulk:

$$\frac{dL}{dt} = \left[\exp\left(35.19 - \frac{17200}{T}\right)[OH] + \exp\left(29.33 - \frac{14400}{T}\right)[OH]^{0.5}[HS]^{0.4}\right]L$$

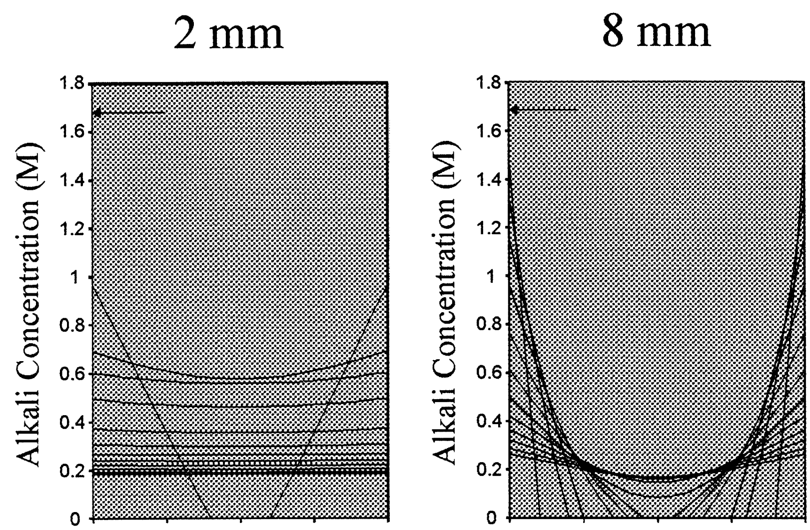
Residual:

$$\frac{dL}{dt} = \exp\left(19.64 - \frac{10804}{T}\right)[OH]^{0.7}L$$

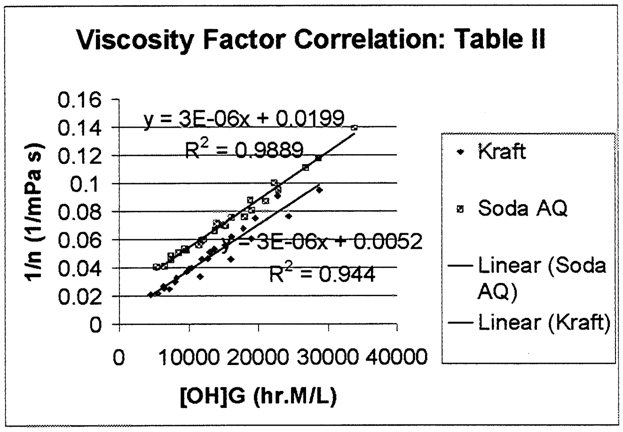
MODEL OUTPUT:



ALKALI CONCENTRATION PROFILES



G(OH⁻)-FACTOR RELATION TO VISCOSITY



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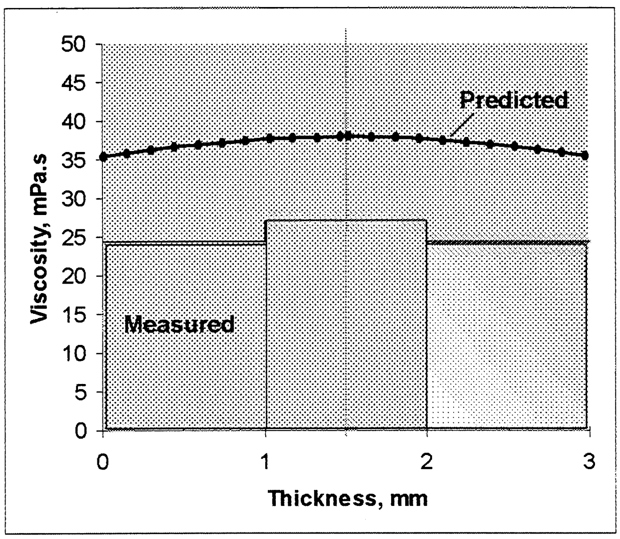
VISCOSITY: 3 MM THICK CHIPS



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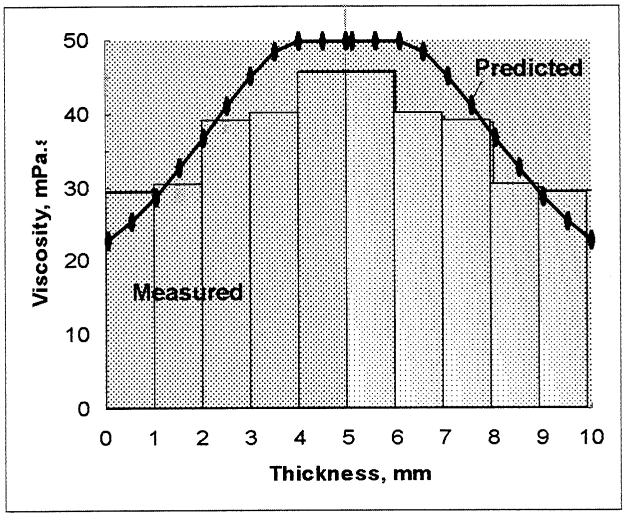
VISCOSITY: 10 MM THICK CHIPS



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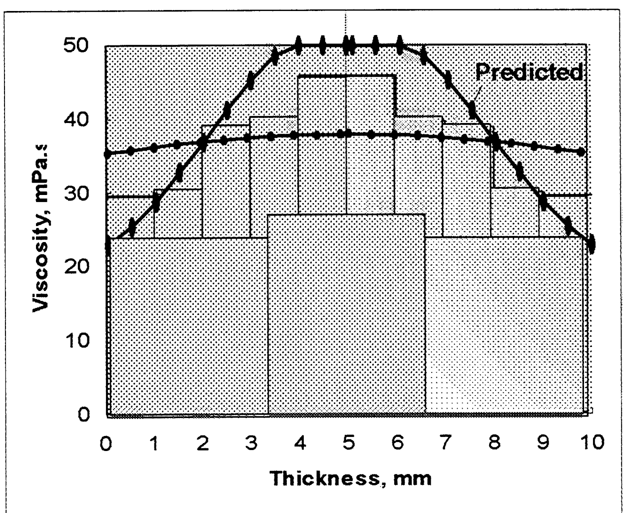
COMPARISON: 3 VS.10 MM CHIPS



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GOALS TO BE COMPLETED IN REMAINING FY

- Complete digester modification
- Complete reference cooks
- Initial modification of no split-sulfidity cooking
- A review on yield - strength relationship.
- A three year research plan

GOALS PLANED FY 2000

- Complete the experiments on modification of no split sulfidity cooking
- Start to develop multi-stage pulping processes using split-sulfidity liquors per 3-year plan
- Continue to develop suitable process conditions for Soda-Catalyst pulping to achieve high yield and strength
- Start the research on high kappa number followed with oxygen delignification

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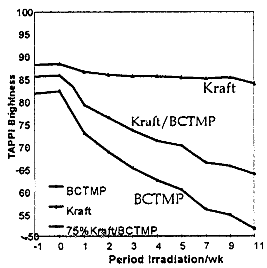
Fundamentals of Brightness F014

Mid-Year Review

Art J. Ragauskas

F014: Project Objective

Research efforts are directed at investigating the fundamental chemical reactions that are initiated when high-yield pulps are photolyzed. As our knowledge of brightness reversion increases, methods to eliminate or retard photoyellowing will be pursued.



F014: Project Goals and Staff

Goal

- **Increase the usefulness of high-yield fibers**

Staff

- **L. Allison**
- **A.J. Ragauskas**

Budget

- **$ 63,000**

F014: Current Research Focus

- Photostabilization Additives
- Application Technologies
- Photoreversion chemistry of acetylated lignin

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F014: FY 1998-99 Research Goals

- Study photoreversion of 75:25 SW Kraft - HW BCTMP handsheets with $CaCO_3$ and $TiO_{2completed}$.
- Examine role of FWA/co-additives with BCTMP to retard brightness reversion$_{completed}$.
- Examine the photostabilization chemistry of acetylated BCTMP.
- Evaluate the effects of grafting acrylic acid onto BCTMP.

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Previous Accomplishments

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Lignin Acetylation

Experimental Procedure

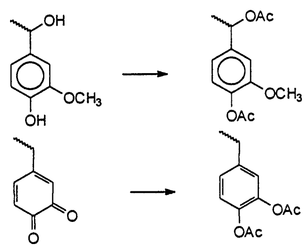
BCTMP sheet $\xrightarrow[\text{100°C, 15 minutes}]{AcOH/Ac_2O}$ Acetylated Sheet

Previously employed with TMP, GSW

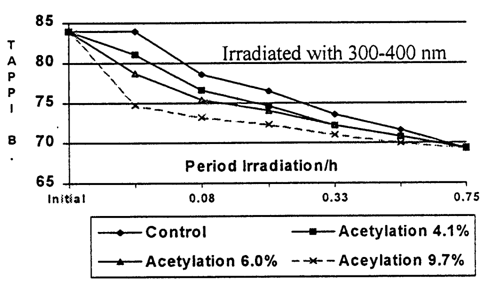
- shown to retard brightness reversion
- enhance wet strength

Alternative Approach: Lignin Acetylation

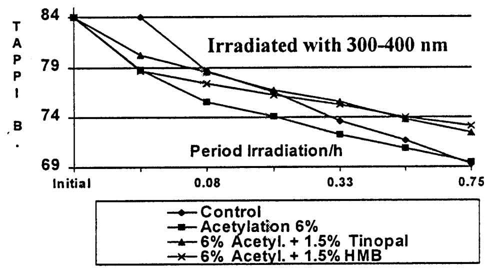
Chemistry



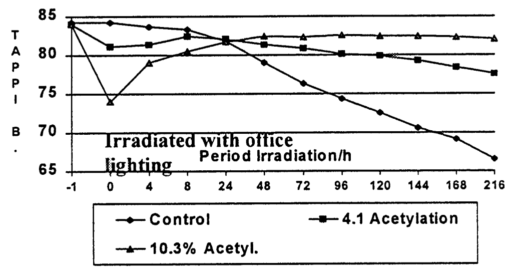
Lignin Acetylation: BCTMP Reversion Results



Lignin Acetylation: BCTMP Reversion Results



Lignin Acetylation: BCTMP Reversion Results



Summary of Lignin Acetylation: Summary

Acetylation causes significant drop in initial brightness

Acetylation reduces photoyellowing

Acetylation process works favorably with photostabilization additives:

- •OBAs, UV-absorbers
- •PEG, Polytetrahydrofuran

Equally effective for TMP SW and HW

Understanding fundamental chemistry could provide new opportunities

Performance of FWA Treated High - Yield Pulp

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Prior Results

- FWA especially Tinopal & Phorwite UW enhance initial brightness
- Provide +80 brightness for ca. 20 days continuous irradiation
  - Tappi brightness, L*a*b*, Abs.Scatt. Coeff
- Low charges of PEG improve performance of FWA
- Storage in dark or light/dark cycling does not influence FWA photostabilization effect
- FWA effect same for office light & sunlight

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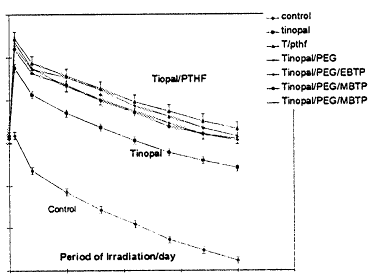
Prior FWA - Synergistic Effects

25% BCTMP/kraft
1.0% UW
1.0% PEG
3.3% PTHF
1.0% ETBP
1.0% MTBP



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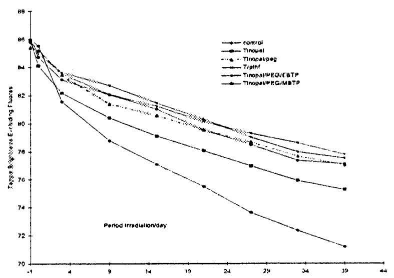
Prior FWA - Synergistic Effects



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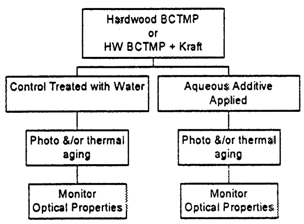
FWA /co-additive Photostabilization Results

FY 1998-99 Goals

- Study photostabilization effects of:
  - Tinopal
  - hydroxybenzophenone
  - hydroxybenzotriazole



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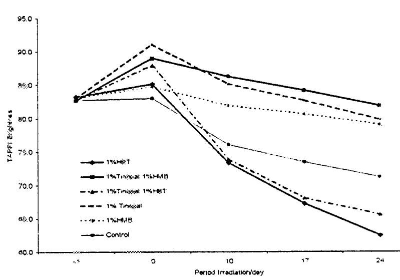
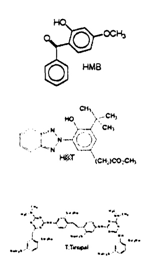
BCTMP: FWA + UV Absorber Studies





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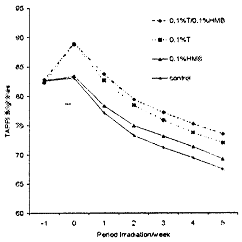
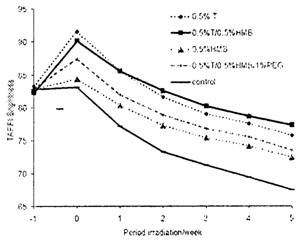
BCTMP: FWA + UV Absorber Studies





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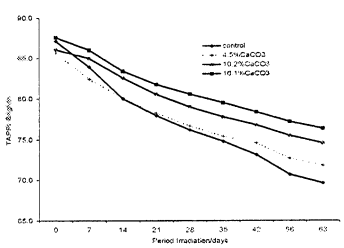
25% HW BCTMP - 75% SW Kraft : $CaCO_3$ & TiO_2



-photoreversion studies employing 0.7 - 1.7% TiO_2 exhibited no photoreversion benefits

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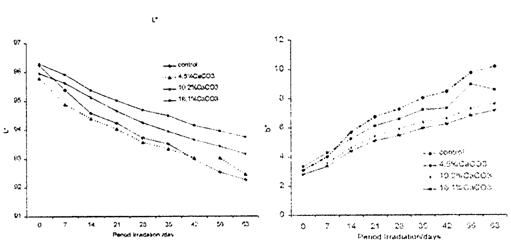
25% HW BCTMP - 75% SW Kraft : L* & b* values for $CaCO_3$



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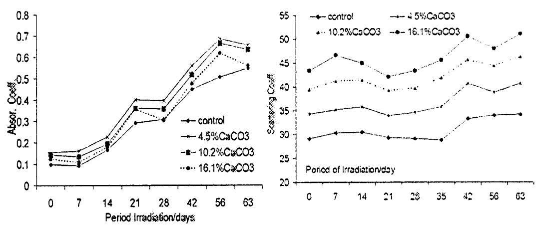
25% HW BCTMP - 75% SW Kraft : Absorption & Scattering Coeff. Values for $CaCO_3$



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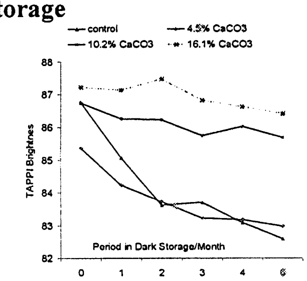
25% HW BCTMP - 75% SW Kraft : $CaCO_3$ Dark Storage



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Conclusions

FWA and $CaCO_3$ provide readily available technologies to retard photoreversion of mechanical pulps

Benzophenone derivatives extend the effect of FWAs for BCTMP

Acetylation studies initiated and will be reported at spring PAC

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Acknowledgments

L. Allison, , T. Runge, K. Haynes,
M. Zawadzki, F. Chakar, J. Werner
P. Argawal, C. Li

Member Companies IPST

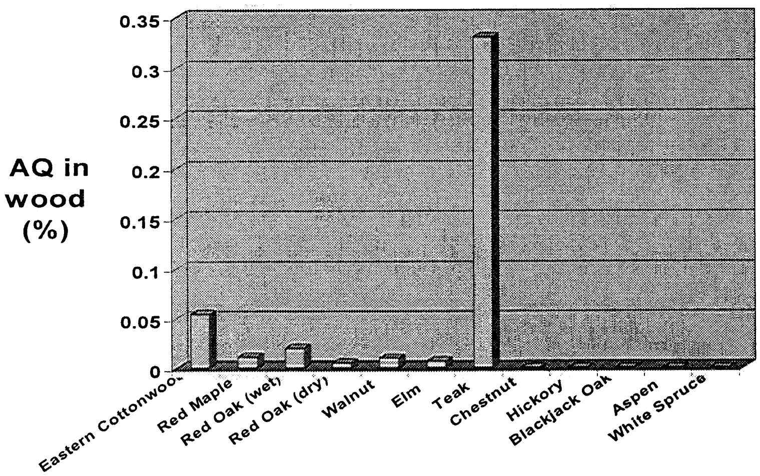
Tackling Environmental Problems

- ✦ Add effluent treatment technologies ("end of the pipe cure")
- ✦ Change the process to one that produces less discharges; i.e., bleach with O_3 instead of Cl_2
- ✦ Change the starting material (wood) to a type that produces less discharges by having:
  - Trees produce their own pulping catalyst
  - Trees with easily removed lignin, greater amounts of cellulose

Trees with Built-in Pulping Catalysts

- ✦ Funding: DOE Agenda 2020 $337K for Aug '97-99
- ✦ Personnel: Don Dimmel, Jerry Pullman, Gary Peter, Huabin Meng (Postdoc), Elizabeth Althen (Sr Tech), Karen Crews (M.S. Student)
- ✦ Objective: To develop trees that contain anthraquinone of a type and in amounts that will catalyze their own pulping. Genetic engineering strategies will be employed to enhance endogenous AQ levels for the production of valuable tree varieties.

AQ in Trees



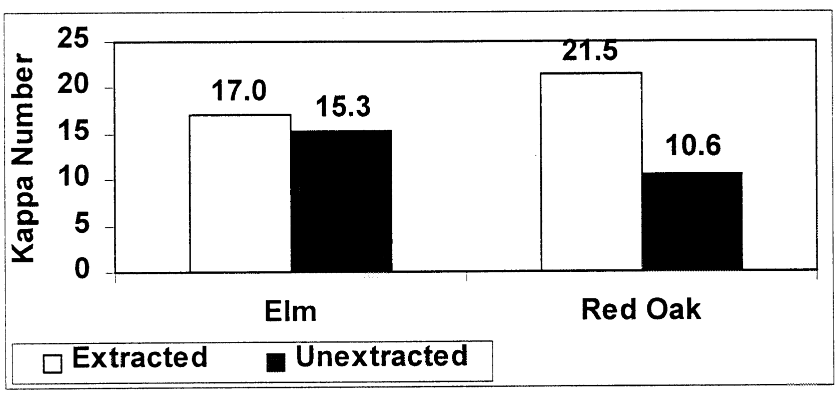
AQs in Trees

Tree	AQ types present	Percentage of AQ Components in Wood
Eastern Cottonwood	AQ	0.016
	DMAQ	0.003
	Mono-MAQ	0.035
Red Maple	AQ	0.011
Red Oak (wet)	AQ	0.020
Red Oak (Dry)	AQ	0.005
Walnut	AQ	0.010
Elm	AQ	0.007
Teak	Mono-MAQ	0.330

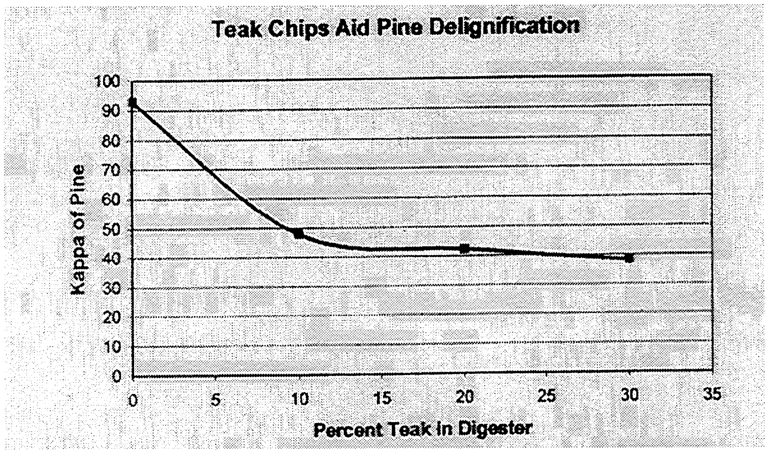
Further Cottonwood Extractions

- Have extracted two cottonwood varieties: stems, new shoots, and leaves.
- Used SIM GC/MS to aid in low level detection of various AQs
- The leaves and new shoots from an AQ-containing (young) tree showed little (no) AQ components.

Removing AQs Before Pulping Decreases Delignification Rate



Addition of Teak Chips to a Pine Cook Enhances the Delignification of Pine



AQ in Hardwoods Conclusions

- Six of ten hardwoods examined had AQ components; teak has the equivalent of 0.67% AQ.
- Cottonwood has AQ, methyl- and dimethyl-AQ in its heartwood, but none in its leaves and new shoots.
- Cottonwoods of different varieties contain significantly different levels of AQs.
- Pulping pine in the presence small amounts of teak is similar to adding AQ to a pine cook.

Studies on the Biological Side

- ✦ Want to isolate the genes that encode enzymes that catalyze AQ synthesis.
- ✦ Focus on isochorismate synthase - the first step in the biosynthesis of AQ in plants.
- ✦ Isochorismate synthase has been cloned from several prokaryotic organisms, but not from plants.

Anthraquinone Biosynthesis

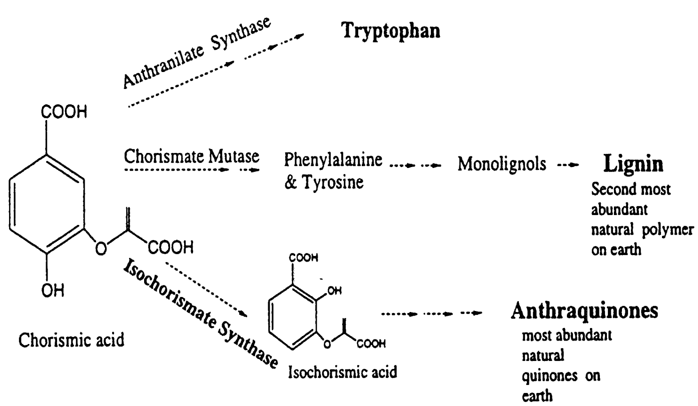
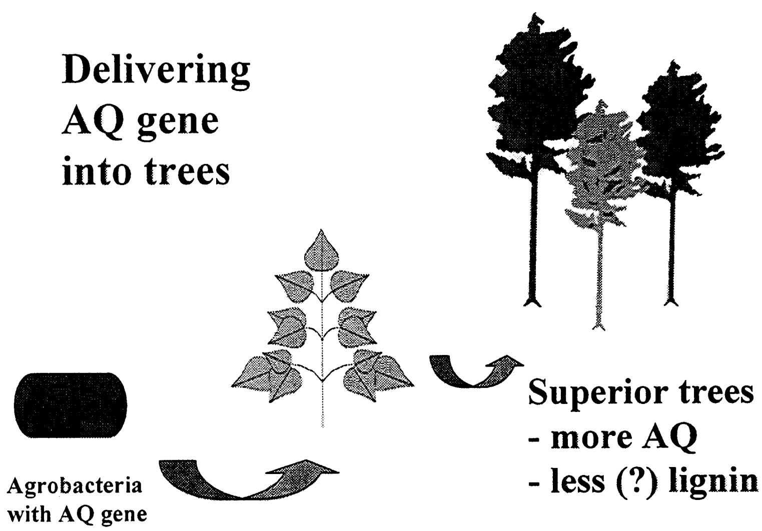


Fig. 1. The competition of anthranilate synthase, chorismate mutase and isochorismate synthase on chorismic acid for the synthesis of aromatic acids and a number of secondary metabolites.

Results from the Biological Studies

- ✦ Have isolated a full length isochorismate synthase cDNA (gene). The first AQ gene isolated from a plant.
- ✦ A binary expression vector with isochorismate synthase gene has been constructed into *Agrobacteria tumefacians*.
- ✦ Currently progressing towards delivering isochorismate synthase gene into cottonwood via *Agrobacterium* infection



Future Studies - I

- Determination of the AQ contents in:
  - turpentine condensates from mills not using AQ,
  - different cottonwood, softwood varieties, birch (which pulps easily), and western hemlock (turns red in air),
  - sections of wood from the same tree to learn the location of AQ in wood, and
  - juvenile vs mature wood varieties to establish production time for AQ in trees.

Future Studies - II

- Demonstrate a correlation between kappa drop and AQ content by pulping
  - cottonwoods containing different AQ levels and
  - extracted and unextracted cottonwoods that contain different AQ levels.

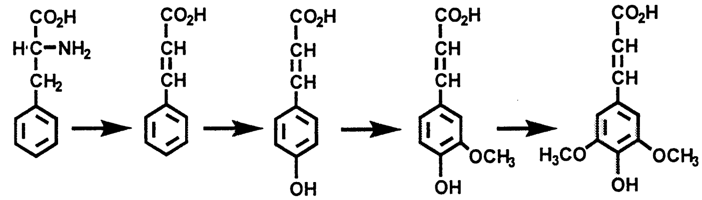
CAD-Deficient Trees

- Funding: USDA $50,000 for October 1997-99, in conjunction with NC State University
- Personnel: Elizabeth Althen (Sr Tech), Christy Parks (Summer Intern), Don Dimmel, John MacKay
- Objective: The ultimate goal is to develop trees that are easily delignified without using gene transfer technology. Our immediate goal is to understand the relationship between structure and reactivity of the lignin from CAD-deficient trees.

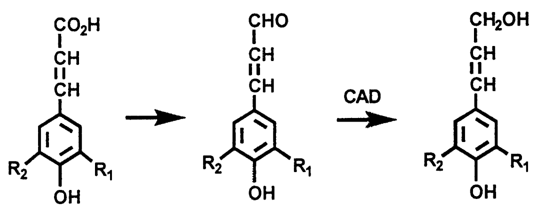
Multi-Laboratory Study

- NC State: Sederoff on tree genetics
- IPST: reactions of CAD-deficient wood
- USDA, Madison, WI: Ralph characterizing isolated CAD- lignin by NMR
- France: Lapierre characterizing CAD- wood by thioacidolysis
- Netherlands: Boon characterizing CAD- wood by pyrolysis GC-MS

Lignin Biosynthesis



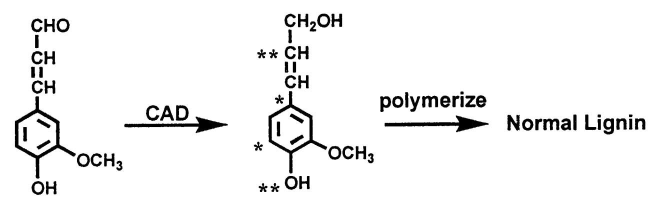
phenylalanine



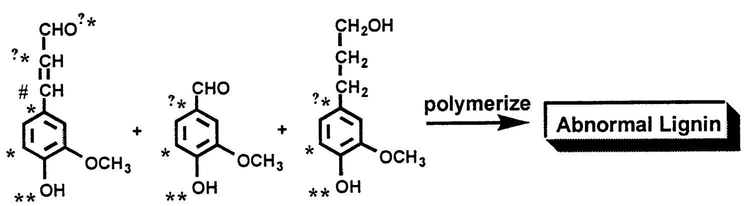
R_1 and R_2 = H and OCH_3 CAD = cinnamyl alcohol dehydrogenase

CAD-Deficient Trees

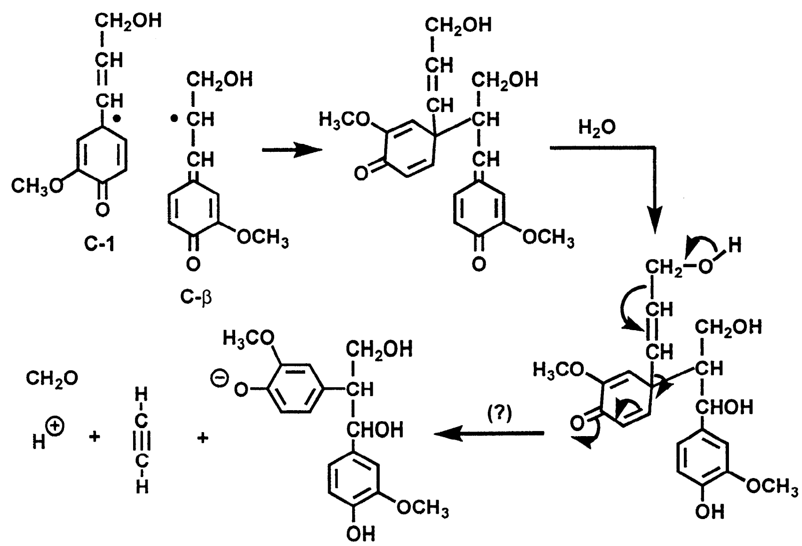
✦ Normal pine lignin biosynthesis:



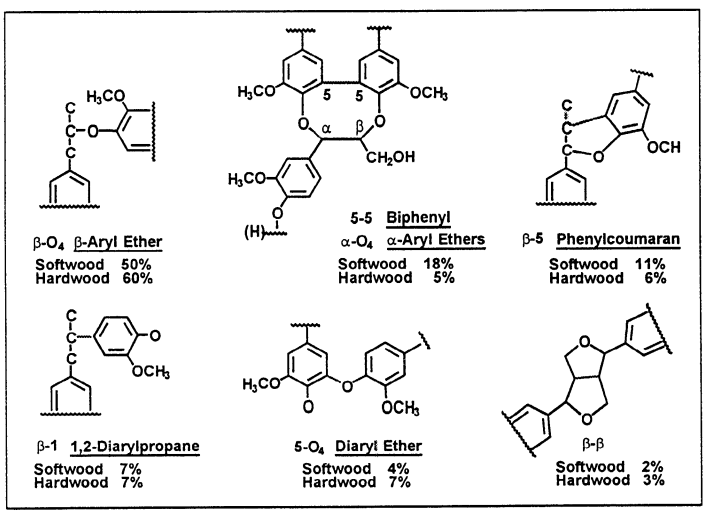
✦ CAD-deficient pine lignin biosynthesis:



Formation of C1-β Lignin Linkages



Lignin Linkage Types/Amounts



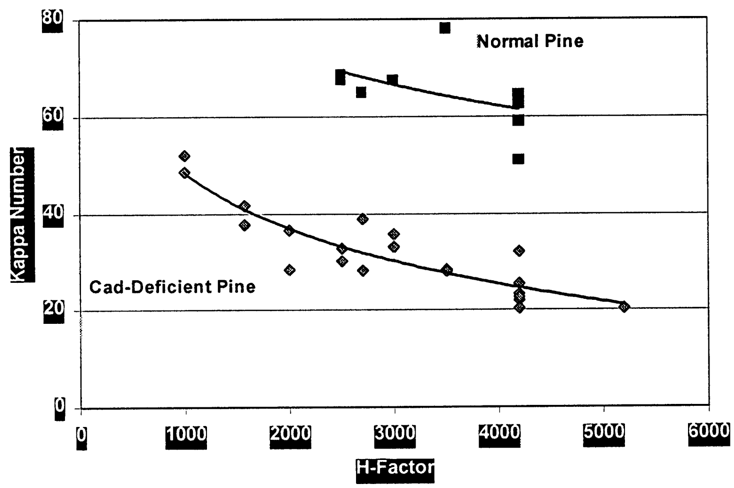
CAD-Deficient Lignin Structure

- Expect (and find) fewer β-O_4 linkages because of monomers having inactive/no C_β
- Expect (and find) more C_5 - C_5 and C_5- O_4 linkages
- Expect CAD-deficient wood would be hard to delignify, unless the lignin:
  - Has a lower molecular weight
  - Is less branched
  - Contains more ionic groups (-CHO -> -COO^-)

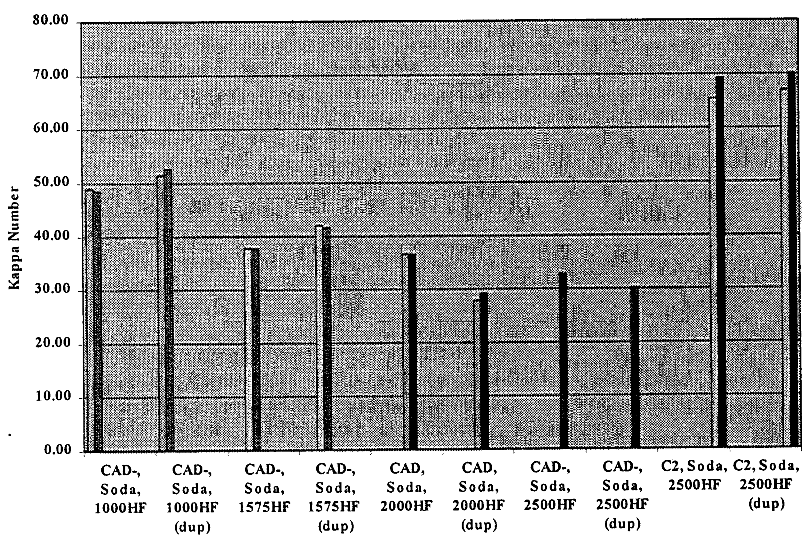
Experimental Plan

- Five sets of soda cooks, varying:
  - Wood type (CAD- and two pine controls)
  - Severity (H-factor, %NaOH)
  - Presence of additives (NaSH and AQ)
- Analyzed for:
  - Kappa number and yield
  - Yield, purity and mol. wt. of dissolved lignins
  - Molecular weights of milled wood lignins from CAD- and control pines

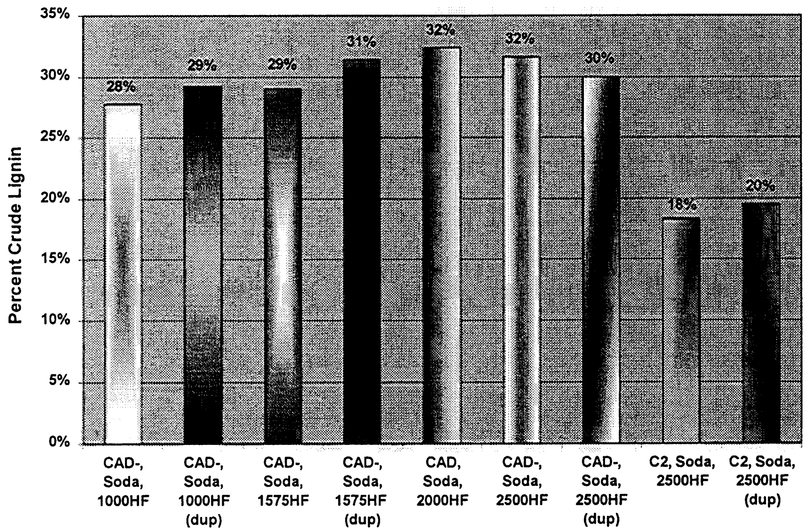
Soda Pulping of CAD-Deficient and Normal Pine Wood Chips



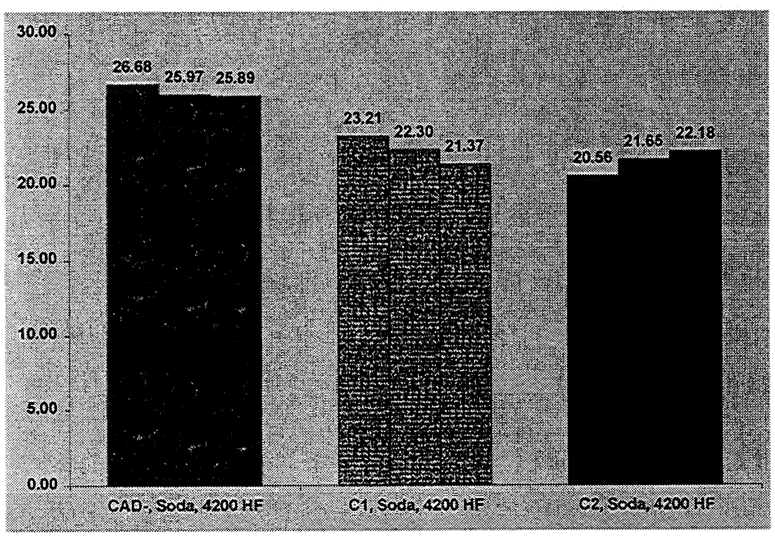
Kappa Numbers of Soda Cooks



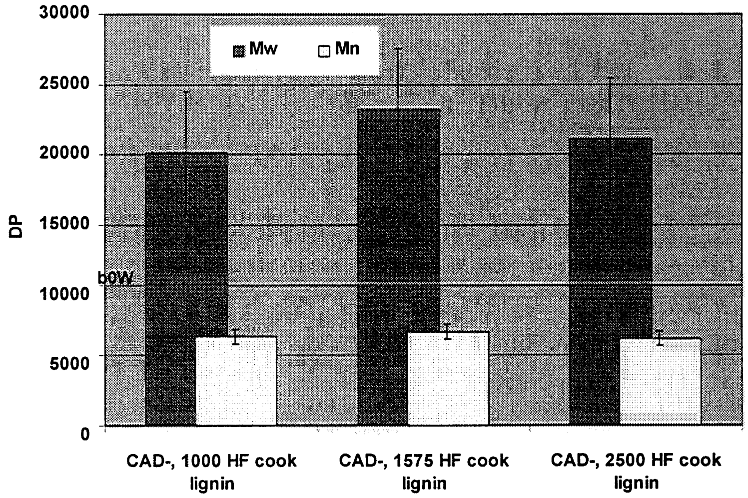
Liquor Precipitate - % of Wood



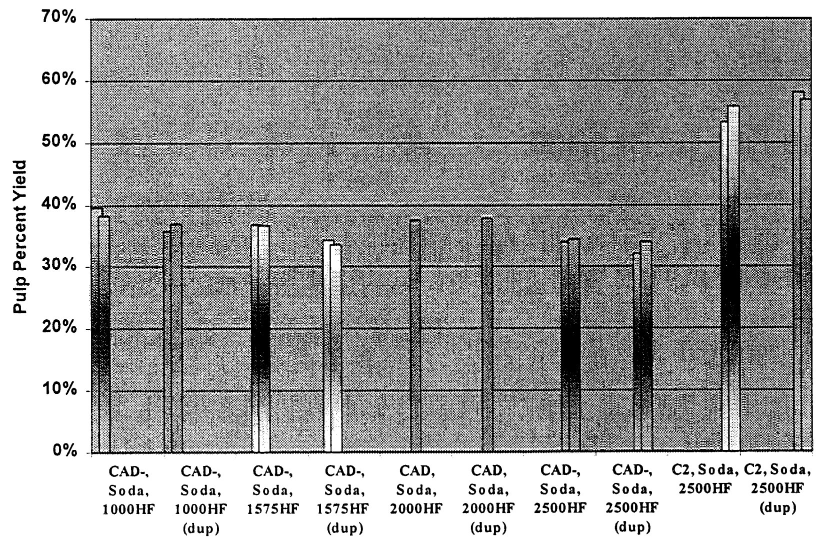
% Lignin Yield: Pulp + Liquor



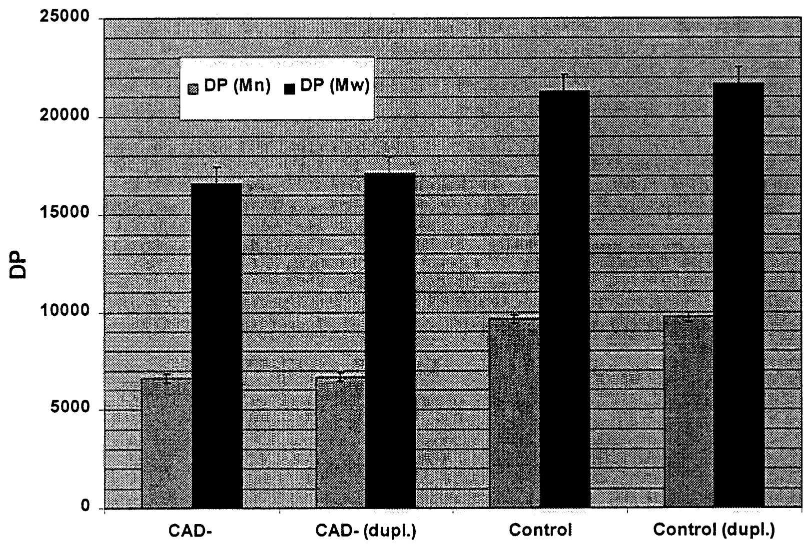
Dissolved Lignin Molecular Weight as a Function of Soda Pulping Time



Pulp Yields from Soda Cooks



Molecular Weights of Mill Wood Lignins



Additional Results

- Dissolved lignin molecular weights from CAD- and control cooks are similar.
- Addition of NaSH or AQ to the soda cooks has little effect on the CAD- cooks, but a large effect on the control cooks.

Future Studies

- ✦ Determine the accuracy of CAD- kappa #s
- ✦ Finish analysis of cooks done with different additives and NaOH levels
- ✦ Prepare CAD- and control pulps with identical kappa numbers and determine:
    - yield and dissolved lignin molecular weights
- ✦ Bleachability of CAD- pulps
- ✦ Sodium sulfite pulping of CAD- wood
- ✦ Characterize residual lignin in CAD- pulps ?

"Energy Efficient Kraft Pulping for Highly Bleachable, Low Lignin Content Pulp"

(U.S.D.O.E. Project DE-FC36-95GO10091)

T. McDonough, N. Rawat and A.J. Bacon, IPST, and G. Krishnagopalan, Auburn University

TJM981104 1

Recent and Current IPST Research

- Bleachability of Auburn profiled pulps
- Analysis of residual lignin and Hex-A
- Systematic study of effects of pulping parameters on oxygen bleachability
- Search for bleachability indicator
- Conclusion of study of methods for on-line determination of AQ in pulping liquor

TJM981104 2

Effects of Pulping Conditions on Oxygen Bleachability

- M.S. research of Aric Bacon
- 21 kraft cooks of southern pine
- Pulping conditions systematically varied, according to a factorial experimental design
- Each pulp subsequently oxygen delignified
- Alkali charge in oxygen stage limited to 1.3% to increase likelihood of detecting differences between pulps

TJM981104

3

Experimental Design

Experimental Design for Oxygen Bleachability Study Pulping Runs

Run No.	X_1	X_2	X_3	X_4	Liquor-to-Wood Ratio	Effective Alkali, % o.d.w.	Sulfidity, %	Temp., C
1	1	1	1	1	7.38	21	39	175
2	1	1	1	-1	7.38	21	39	165
3	1	1	-1	1	7.38	21	16	175
4	1	1	-1	-1	7.38	21	16	165
5	1	-1	1	1	7.38	15	39	175
6	1	-1	1	-1	7.38	15	39	165
7	1	-1	-1	1	7.38	15	16	175
8	1	-1	-1	-1	7.38	15	16	165
9	-1	1	1	1	4.63	21	39	175
10	-1	1	1	-1	4.63	21	39	165
11	-1	1	-1	1	4.63	21	16	175
12	-1	1	-1	-1	4.63	21	16	165
13	-1	-1	1	1	4.63	15	39	175
14	-1	-1	1	-1	4.63	15	39	165
15	-1	-1	-1	1	4.63	15	16	175
16	-1	-1	-1	-1	4.63	15	16	165
17	1	1	1	1.6	7.38	21	39	178
18	1	1	-1	-0.4	7.38	21	16	168
19	1	-1	-1	1.6	7.38	15	16	178
20	-1	1	1	-0.4	4.63	21	39	168
21	-1	1	-1	1.6	4.63	21	16	178

Unbleached Pulps

Oxygen Bleachability Study: Unbleached Pulp Data

Run No.	Liquor-to-Wood Ratio	Effective Alkali, % o.d.w.	Sulfidity, %	Temp., C	Kappa Number	Viscosity, mPa.s	Brightness, ISO	Total Yield, % o.d.w.	Rejects, %
1	7.38	21	39	175	29.3	45.8	31.6	43.9	0.7
2	7.38	21	39	165	44.7	63.8	27.5	46.9	1.3
3	7.38	21	16	175	36.2	40.6	28.4	45.5	0.8
4	7.38	21	16	165	28.2	37.0	30.7	43.2	0.2
5	7.38	15	39	175	44.2	71.8	23.0	49.4	3.8
6	7.38	15	39	165	33.8	71.3	25.8	46.4	0.2
7	7.38	15	16	175	34.4	42.1	25.4	47.5	1.4
8	7.38	15	16	165	50.8	63.2	22.1	47.4	3.3
9	4.63	21	39	175	31.3	46.0	32.0	44.6	2.6
10	4.63	21	39	165	28.8	45.5	33.0	44.3	0.6
11	4.63	21	16	175	27.0	28.4	32.1	45.1	0.2
12	4.63	21	16	165	42.0	42.5	27.7	45.4	0.7
13	4.63	15	39	175	25.2	41.1	28.3	44.3	0.4
14	4.63	15	39	165	38.5	57.5	26.7	48.2	7.8
15	4.63	15	16	175	35.8	44.6	25.7	47.1	1.7
16	4.63	15	16	165	25.0	38.5	28.0	44.5	0.1
17	7.38	21	39	178	34.9	45.9	29.8	47.6	3.1
18	7.38	21	16	168	29.6	26.7	31.0	43.2	0.4
19	7.38	15	16	178	40.2	37.6	26.2	43.7	4.5
20	4.63	21	39	168	37.3	52.9	32.1	45.3	3.3
21	4.63	21	16	178	40.5	27.1	29.6	47.2	1.7

Oxygen Delignified Pulps

Oxygen Bleachability Study: Bleached Pulp Data

Run No.	Liquor-to-Wood Ratio	Effective Alkali, % o.d.w.	Sulfidity, %	Temp., C	Unbl. Kappa Number	Kappa Number After Oxygen	Unbl. Viscosity, mPa.s	Viscosity After Oxygen, mPa.s
1	7.38	21	39	175	29.3	17.2	45.8	31.6
2	7.38	21	39	165	44.7	28.6	63.8	47.4
3	7.38	21	16	175	36.2	21.4	40.6	27.5
4	7.38	21	16	165	28.2	15.9	37.0	26.1
5	7.38	15	39	175	44.2	26.9	71.8	40.3
6	7.38	15	39	165	33.8	21.3	71.3	39.4
7	7.38	15	16	175	34.4	20.8	42.1	30.3
8	7.38	15	16	165	50.8	34.1	63.2	41.0
9	4.63	21	39	175	31.3	20.1	46.0	29.8
10	4.63	21	39	165	28.8	16.9	45.5	31.2
11	4.63	21	16	175	27.0	18.3	28.4	20.9
12	4.63	21	16	165	42.0	25.6	42.5	30.2
13	4.63	15	39	175	25.2	14.3	41.1	29.4
14	4.63	15	39	165	38.5	25.1	57.5	44.9
15	4.63	15	16	175	35.8	24.0	44.6	30.7
16	4.63	15	16	165	25.0	17.2	38.5	28.5
17	7.38	21	39	178	34.9	23.3	45.9	30.6
18	7.38	21	16	168	29.6	18.5	26.7	24.9
19	7.38	15	16	178	40.2	26.3	37.6	27.5
20	4.63	21	39	168	37.3	23.3	52.9	31.5
21	4.63	21	16	178	40.5	25.7	27.1	21.3

Regression Equation for Kappa No. After Oxygen

Kappa No. After Oxygen =
22.05 - 0.35(EA) - 0.30(S)
- 0.08(T) + 3.34(CK)
+ 0.48(EA)(S) + 0.54(EA)(T)

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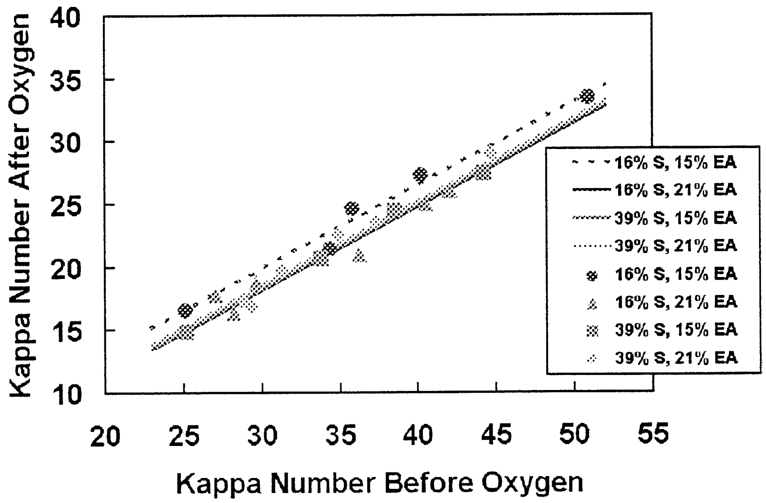
Alkali Charge and Sulfidity

Effects of Alkali Charge and Sulfidity on Kappa No. After O2 Delignification of 35 Kappa Pulp (L/W = 6; T = 170 C)

	15% EA	21% EA
16% S	23.2	21.5
39% S	21.6	21.9

- Oxygen bleachability is impaired when both alkali charge and sulfidity are low during the kraft cook

Kappa No. After Oxygen



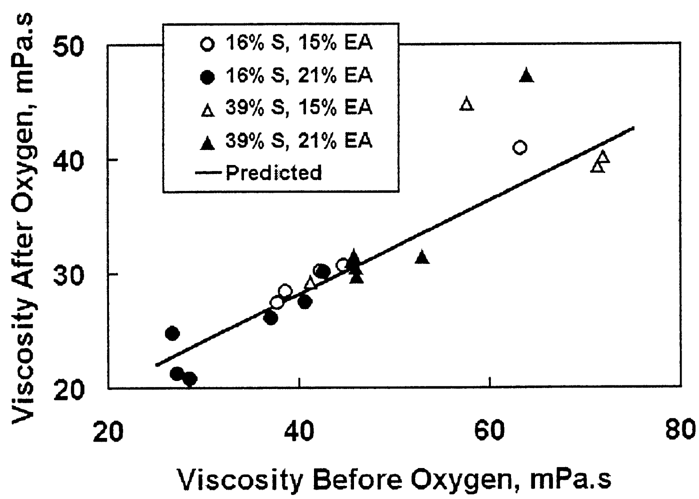
Alkali Charge and Temperature

Effects of Alkali Charge and Temperature on Kappa No. After O2 Delignification of 35 Kappa Pulp (L/W = 6, S = 28%)

	15% EA	21% EA
T = 165 C	23	21.2
T = 175 C	21.8	22.2

- Oxygen bleachability is impaired when both alkali charge and temperature are low during the kraft cook

Viscosity After Oxygen



High Efficiency ClO_2 Delignification: ClO_2 Bleaching and Kinetics

D.O.E. Cooperative Agreement

DE-FC07-961D13442

T.J. McDonough, A.J. Ragauskas, A. Shaket and H. Tang

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Effects of Carrier, Temp. on Vapor Phase Bleaching

Unbl. Kappa	Carrier Gas	Temp., °C	Δκ/ TAC	AOX, %	ClO_3^-, %
15.2	N_2	60	4.9	36	7
	N_2	35	7.6	N.A.	N.A.
	O_2	35	6.4	30	10
13.4	N_2	60	4.6	35	6
	N_2	35	5.2	25	9
	O_2	35	4.5	26	8

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HexA Removal by D_0 Filtrate

Unbl. Kappa	Acid Δκ	Filtrate Δκ	Acid Δη, cp.	Filtrate Δη, cp.
11.8	5.1	5.1	10.1	0.0
12.9	5.5	5.7	3.3	4.7
17.3	5.0	5.2	12.3	16.7
29.1	4.2	6.0	21.7	20.2

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Bleaching After Hydrolysis With Filtrate (Af Stage)

Unbl. Kappa	Af Kappa	AfD(EO) Kappa	D(EO) Kappa
16.1	9.5	2.2	5.2
11.6	7.0	2.0	4.2
24.1	15.4	3.0	5.2
14.2	8.8	2.3	5.2
7.8	5.6	1.8	3.1

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ClO_2 - Brownstock Kinetics

- HP 8453 UV-Vis system purchased by IPST
- Reactor system designed and implemented to allow continuous monitoring of UV-Vis spectrum during ClO_2 - pulp reaction
- Set of 28 runs completed to observe effects of pH, temperature and consistency
- Preliminary data analysis completed, assuming simple rate law

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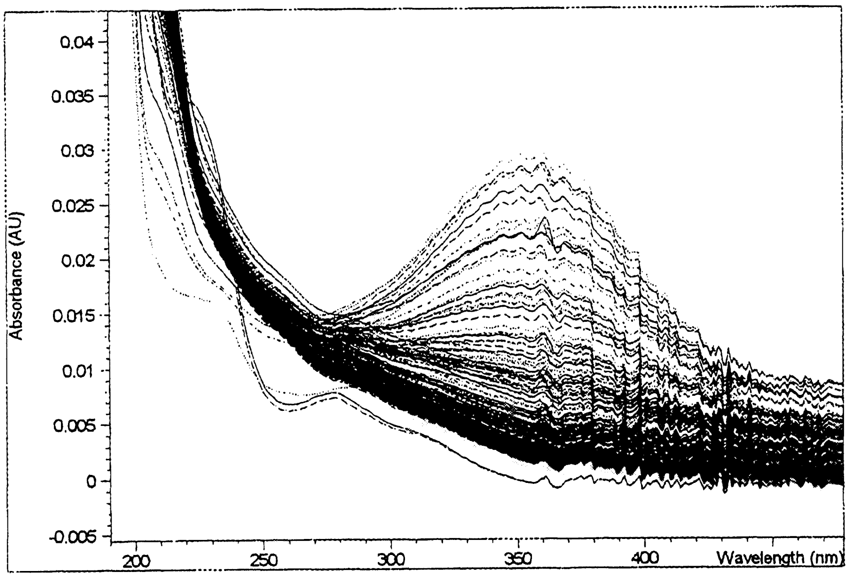
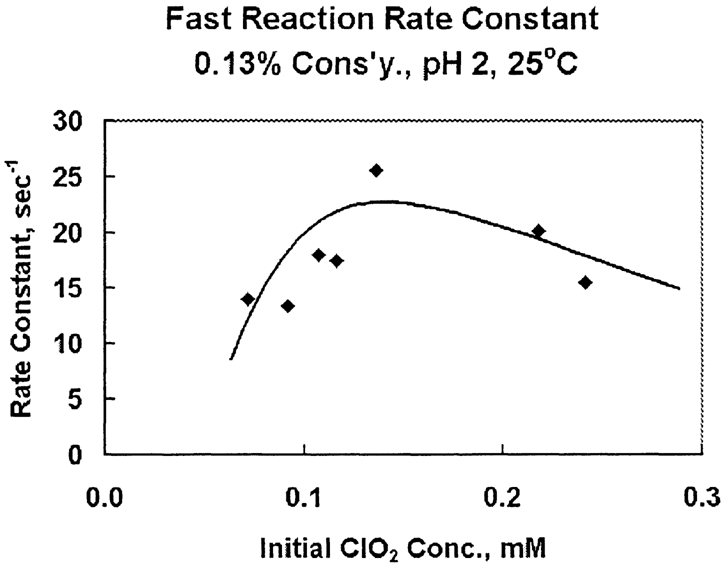
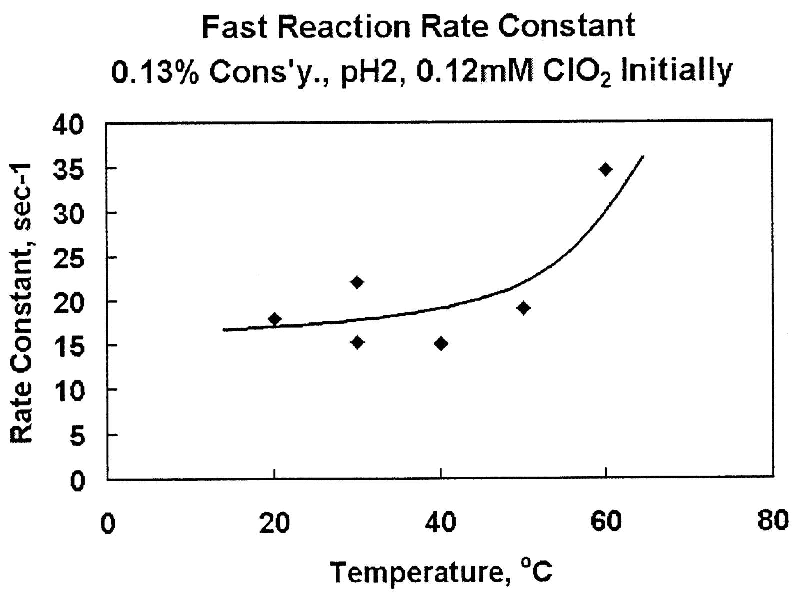


Absorbance (AU)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
-0.005
200
250
300
350
400
Wavelength (nm)



Fast Reaction Rate Constant
0.13% Cons'y., pH 2, 25°C
Rate Constant, sec-1
30
25
20
15
10
5
0
0.0
0.1
0.2
0.3
Initial ClO2 Conc., mM



Kinetics - Next Steps

- Analyze existing data in terms of rate law incorporating stoichiometry and lignin concentration
- Design and run experimental series to test and refine rate law
- Develop second-generation rate law by separating reactions of ClO_2 and HOCl after determining kinetics in presence of Cl trap

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Some Conclusions

- Vapor phase bleaching much more efficient than conventional, producing less ClO_3^-, more AOX
- Greater efficiency not simply due to decomposition to Cl_2; efficiency better and AOX lower at lower temp.
- Rapid D_0 is effective on HW pulps and produces less AOX than conventional D_0

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Some More Conclusions

- D_0 filtrate effectively removes HexA from hardwood pulps
- Bleaching after HexA removal by D_0filtrate results in markedly improved delignification
- The system developed for studying ClO_2 bleaching kinetics is likely to enable useful D_0 stage rate laws to be defined

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Bleach Plant Capital Reduction with Rapid D_0 Bleaching and Simplified (D/E/D) Stages

D.O.E. Cooperative Agreement
DE-FC07-971D13562

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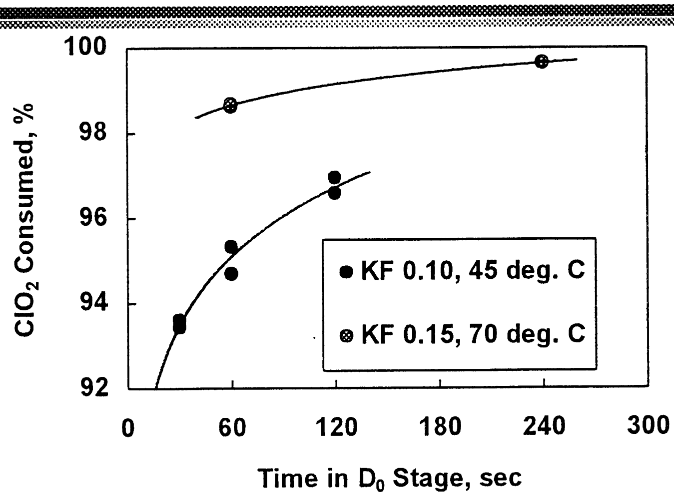
Rapid D_0 Residual vs. Time for Kappa 29 SW Pulp



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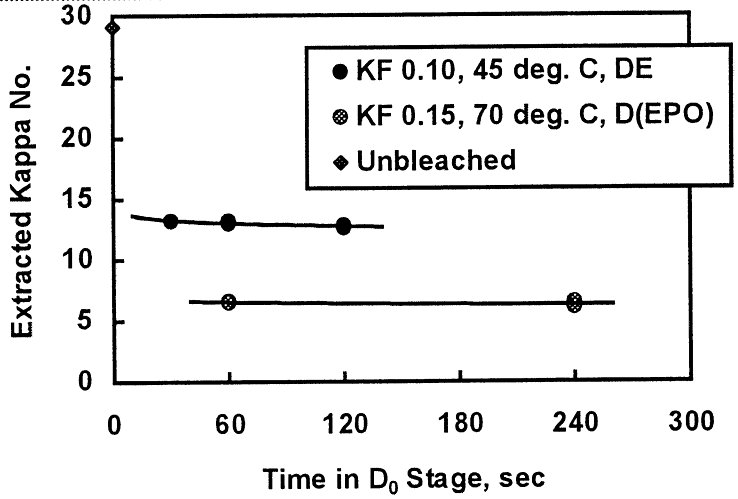
Rapid D_0 Complete in Less Than One Minute



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