*Institute of Paper Science and Technology*
*Atlanta, Georgia*

# ANNUAL PROGRAM REVIEW

# HIGH-YIELD PULPING

## Slide Material

March 25-26, 1998

## INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
## PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and
- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and
- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

## ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

## NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

# ANNUAL PROGRAM REVIEW

# HIGH-YIELD PULPING

## Slide Material

March 25-26, 1998

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia 30318
(404) 894-5700
(404) 894-4778 FAX

# Table of Contents

# High Yield Pulping - Annual Research Review
## Agenda

March 25th, 1998

| | | |
|---|---|---|
| 1:00 - 1:15 | Welcome & IPST Update | G. Baum |
| 1:15 - 2:00 | Fundamentals of Brightness Stability | A. Ragauskas |
| 2:15 - 2:45 | Chemical Modification of Lignin Rich Paper | M. Paulsson |
| 2:45 - 3:00 | Break | |
| 3:00 - 3:15 | Measurement of Fibril Angle | G. Peter |
| 3:15 - 4:00 | Southern Pine Mechanical Pulping | L. Johansson |
| 4:00 | End, afternoon session | |

# High Yield Pulping - Annual PAC Meeting
# Agenda

March 26th, 1998

| | | |
|---|---|---|
| 8:00 - 8:10 | Welcome and Antitrust | A. Rudie |
| 8:10 - 8:40 | Introductions and PAC overview | S. Eachus |
| 8:40 - 9:00 | Review of Research Lines and RAC | E. Malcolm |
| 9:00 - 9:45 | Fundamentals of Brightness Stability | A. Ragauskas |
| 9:45 - 10:00 | Break | |
| 10:00 - 10:45 | Southern Pine Mechanical Pulping | A. Rudie |
| 10:45 - 11:00 | Amine Bond Strength Project | A. Rudie |
| 11:00 - 11:30 | New Project Ideas | PAC |
| 11:30 - 11:45 | Election of Vice Chairman | S. Eachus |
| 11:45 - 12:00 | Wrap up | S. Eachus |
| 12:00 | End, morning session | |

# PROJECT F014

# FUNDAMENTALS OF BRIGHTNESS

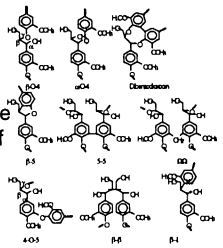
# Fundamentals of Brightness
# F014

## FY 1997-98
## 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.



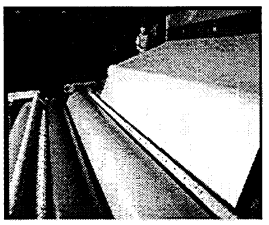
## F014: Project Goals and Staff

**Goal**

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

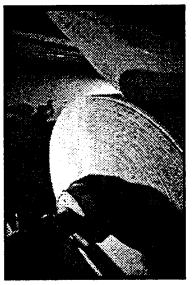
**Staff**

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



## F014: Current Research Focus

- Photostabilization Additives
- Application Technologies
- Alternative Approaches



## F014: FY 1997-98 Research Goals

- Prepare BCTMP/kraft handsheets with FWA, polymer additives and antioxidants under simulated size press conditions and study photoreversion properties$_{completed}$
- Examine role of starch, $TiO_2$ and $CaCO_3$ in brightness stabilization technology$_{completed}$
- Selective acetylation of BCTMP to retard brightness reversion$_{completed}$
- Review use of cross-linking textiles additives and examine potential use for mechanical pulps$_{completed}$

# Performance of FWA Treated High - Yield Pulp

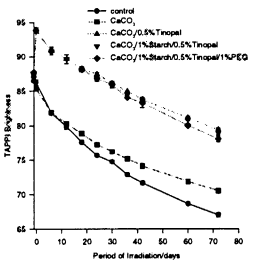
## F014: FY 1997 - 98 Research Goals

- Evaluate interactions of FWA +
  - oxidized starch
  - TiO2
  - CaCO3
  - PEG
  - antioxidants
- Applied as a simulated "size"approach

## Photoreversion of H.W. 75% kraft - 25% BCTMP

- Exp. Conditions
- Pulp slurry contained
  - 7% $CaCO_3$
  - 7% $CaCO_3$/0.5% Tinopal
  - 7% $CaCO_3$/0.5% Tinopal/ 1% starch
  - 7% $CaCO_3$/0.5% Tinopal/ 1% starch/1% PEG

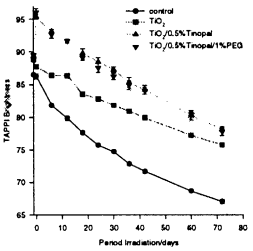
Note: benefits of $CaCO_3$



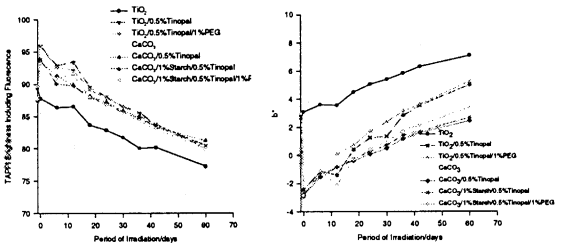

## Photoreversion of HW 75% kraft - 25% BCTMP

- Exp. Conditions
- Pulp slurry contained
  - 5% $TiO_2$
  - 5% $TiO_2$/0.5% Tinopal
  - 5% $TiO_2$/0.5% Tinopal/ 1% PEG

Note: benefits of $TiO_2$



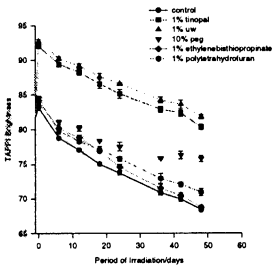
**Photoreversion Properties for CaCO3/TiO2/Tinopal**




## Photoreversion of HW 75% kraft - 25% BCTMP: Effect of drying temperature

Experimental Conditions

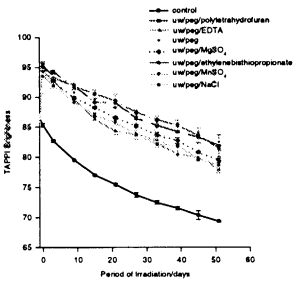
- Thermal revert sheet
- Additives applied aqueous solution
- Irradiate with office lighting
  - FWA, PEG not effected by initial drying




**Photoreversion Properties for UW Treated 75% Kraft - 25% BCTMP Testsheets**

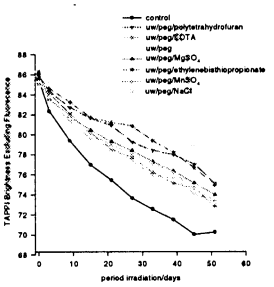
Experimental Conditions

- Handsheets prepared
- Additives applied
- Room temperature dried
- Irradiated under office lighting



**Photoreversion Properties for UW Treated 75% Kraft - 25%BCTMP Testsheets**

•FWA continue to provide initial brightness gains
•Reversion benefits more apparent longer sheets are irriated




## Conclusions from FWA Studies

- "Size" treatments do appear to impact FWA performance
- $CaCO_3$, oxidized starch, $TiO_2$ are compatible with photostabilization effects of FWA
- The use of $CaCO_3$ or $TiO_2$ provide measurable photostabilization benefits on their own

# Alternative Approaches

## Alternative Approach: Lignin Acetylation

Experimental Procedure

BCTMP sheet ⟶ Acetylated Sheet

$AcOH/Ac_2O$
100°C
5-15 minutes

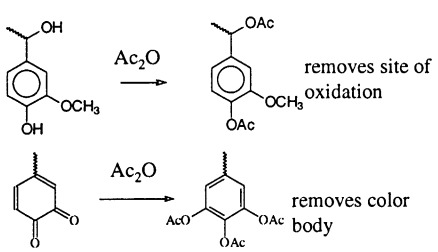
Previously employed with TMP, GSW

shown to retard brightness reversion

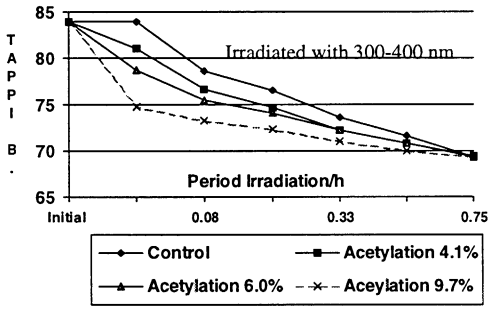
enhance wet strength

## Alternative Approach: Lignin Acetylation

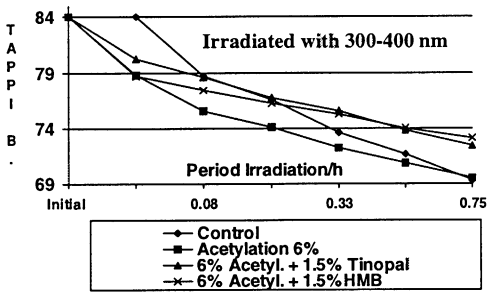
Chemistry



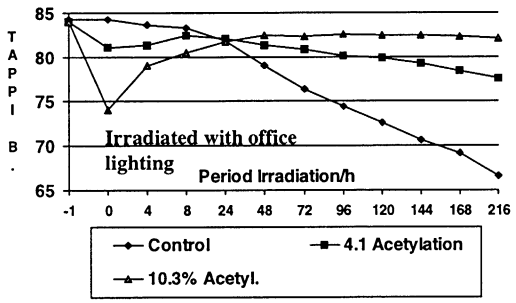

## Lignin Acetylation: BCTMP Reversion Results



## Lignin Acetylation: BCTMP Reversion Results




## Lignin Acetylation: BCTMP Reversion Results



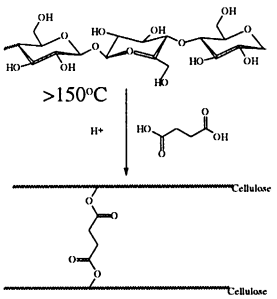

## Lignin Acetylation: Reversion Results

- Photoreversion of acetyl. BCTMP with office lighting significantly reduces reversion
- Acetyl. BCTMP appears to exhibit substantial photobleaching

- Difficulties
  - near dry conditions, $Ac_2O/AcOH$
  - level of acetyl.
- Opportunities
  - mechanism unknown
  - method of application

# Application of Textile Cross Linking Agents for Mechanical Pulp

## Background: Cross-Linking Theory

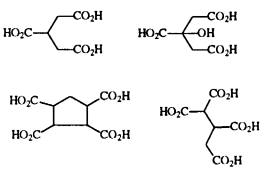



Cross-liking in Textiles:
B.A.K. Andrews et al
American Dyestuff Reported 78:6, 15 (1989)
C.M. Welch
Textile J., 58:8, 480 (1988)
C.M. Welch B.A.K. Andrews
Textile Chemist & Colorist, 21:2 13 (1989)

Cross linking in Kraft Paper
D.F. Caulfield
Tappi J., 77:3, 205 (1994)

## Cross Linking Agents: Theory

Cross Linking Agents



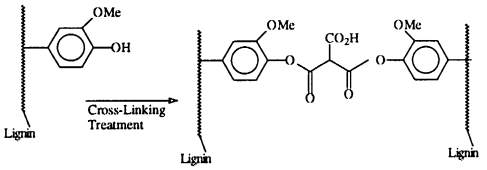
Acid Catalyst

Hypophosphite $NaH_2PO_2$

$NaH_2PO_2 +$
$N(CH_2CH_2OH)_3HCl$

$NaH_2PO_2 +$
$N(CH_2CH_2OH)_4Cl$

## Application of Cross Linking to BCTMP

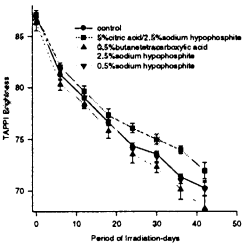



- Cross linking in principle could retard reversion and improve strength

## Photoreversion Studies with Crosslinking Agents

**Experimental Conditions**

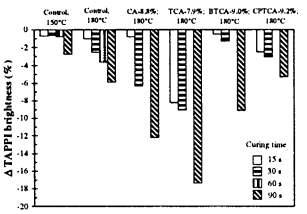
- Apply diacid + catalyst BCTMP/Kraft
- Dry handsheet 80°C
- Irradiate under office lighting



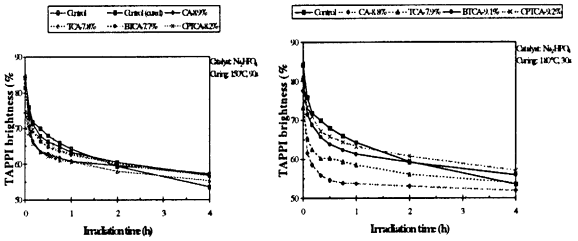

## Reversion Studies with Crosslinking Agents: Effect of higher crosslinking temperature.

**Experimental Conditions**

- Apply diacid + catalyst BCTMP
- Vary curing conditions



## Reversion Studies with Crosslinking Agents: Effect of higher crosslinking temperature on photoreversion properties




## Reversion Studies with Crosslinking Agents:

- Cross linking technology failed
- Contributing factors unknown
- Research objective still attractive

## WHAT NEXT
## Should Additional Studies Be Considered

- Examine alternative acetylation methods
  - ortho-ester
  - Metal catalyzed acetylation
  - Bio-alkylation/
  - esterification
  - AKD approach
- Fundamentals of photobleaching of acetylated BCTMP

## Related Research Issues

- Fundamentals of Lignocellulosic Photostabilization Chemistry
  - USDA
  - Dr. C. Li: photostabilization chemistry of UV absorbers
- Modification of BCTMP for improved photostabilization
  - Gunnar Nicholson Exchange Program
  - Dr. M. Paulsson: photostabilization of acetylated pulps
- Chemical Fundamentals of Bleaching - F015
- Sabbatical Leave April - September/1998
  - Gunnar Nicholson Exchange Program - STFI
  - Ragauskas - fiber surface characterization

## Related Research Issues

- High Efficiency $Cl0_2$ Delignification - DOE
  - bleachability relationship between improved Do stages & (EO)
- Improved Peroxide Bleaching - GA Consortium
  - relationship between pulping & Do(EOP)
  - use of D/Z, Z/D, $P_{HT}$, as replacements for C
- Dr. S. Moe: Extended Delignification Though O
  - delignification chemistry of double O stage

## Ph.D. Student Research

- Troy Runge
  - Bleaching chemistry of alkaline extraction
- Kaaren Haynes
  - Fiber properties of Laccase/mediator bleached pulps
- Michael Zawadzki
  - Bleaching chemistry contributing to brightness ceilings
- Fadi Chakar
  - Chemistry of Laccase/mediator delignification

## M.Sc. Student Research

- John Werner
  - NPE - black liquor complexes
- Asmeron Hagos -C.A.U.
  - Fundamental chemistry of hexenuronic acids


## *Acknowledgments*

L. Allison, T. Runge, K. Haynes,
M. Zawadzki, F. Chakar, M. Paulsson
C. Li, A. Hagos, J. Werner, P. Agrawal
Member Companies IPST


# CHEMICAL MODIFICATION OF LIGNIN-RICH PAPER

## Some Aspects on Photoyellowing and Its Inhibition

Magnus Paulsson
Arthur J. Ragauskas

Institute of Paper Science and Technology
1998

# Presentation Outline

- Introduction
  - Mechanical pulps - yellowing
  - Irradiation systems
  - Acetylation system
- Results
  - Irradiation source - aging response
  - Solid-state UV-VIS diffuse reflectance spectroscopy
- Conclusions

## Mechanical Pulps

- Cheaper than chemical pulps
- Higher yield (>90%)
- Better utilization of the worlds wood resource
- Favorable optical and printing characteristics (light scattering ability, opacity, pigment retention, etc.)
- Other features (bulk, formation, calendering)



Magnus Paulsson
March 98

## Mechanical Pulps (cont.)

- Increased production capacity with low capital investment
- Full mill closure possible
- Environmentally friendly - bleaching without chlorine containing chemicals
- Potential for wider field of application



Magnus Paulsson
March 98

## Field of Application

- Newsprint: TMP (GWP)
- Magazine paper: TMP (GWP, CTMP)
- Paper board: CTMP
- Liquid carton board: CTMP
- Soft crêpe paper: CTMP
- Fluff pulp: CTMP
- Wood-containing fine paper: GWP, CTMP



Magnus Paulsson
March 98

## Yellowing

- All types of wood pulps
  - Mechanical pulp about ten times that of fully bleached kraft pulp
- Heat-induced
  - No problem for "normal" use of paper
- Light-induced
  - Most damaging - restricts the field of application to short-life paper products



Magnus Paulsson
March 98

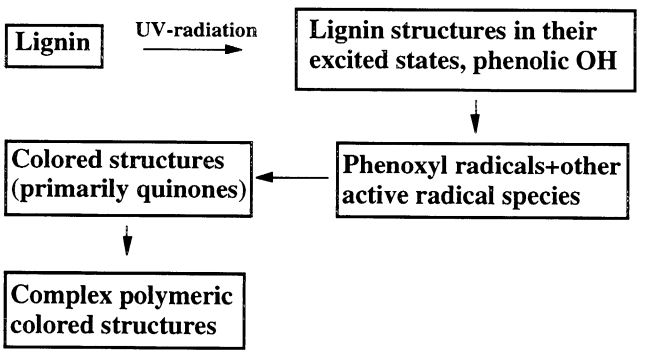
# Light-induced Yellowing

- Photochemical oxidation of lignin
- Discoloration ($\lambda$<385 nm)
- (Photo)bleaching ($\lambda$>385 nm)
- Initially a surface phenomenon (75% of discoloration at 25-30 $\mu$m)
- Radical reactions
- $O_2$ present



Magnus Paulsson
March 98

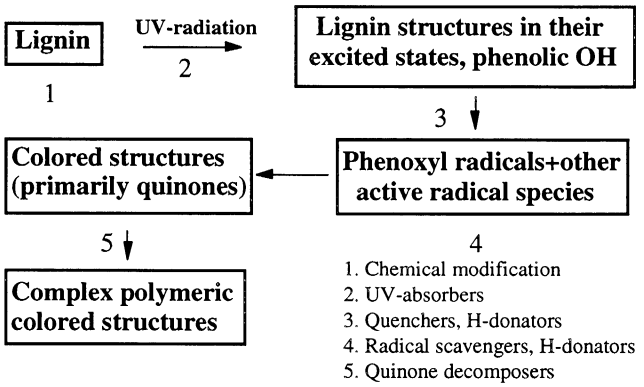
# Simplified Reaction Scheme






Magnus Paulsson
March 98

# Methods of Stabilization

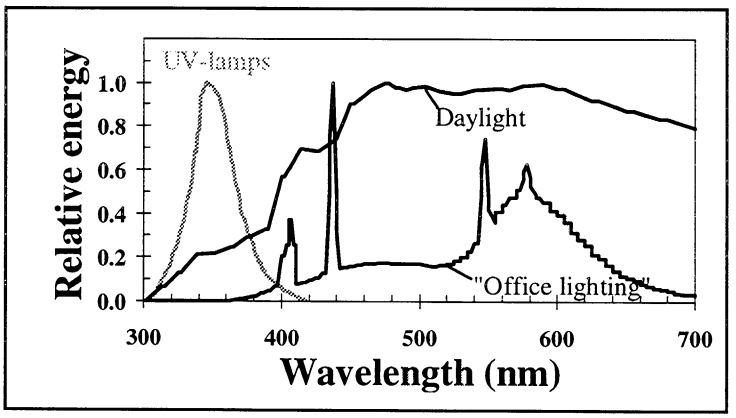



1. Chemical modification
2. UV-absorbers
3. Quenchers, H-donators
4. Radical scavengers, H-donators
5. Quinone decomposers



Magnus Paulsson
March 98

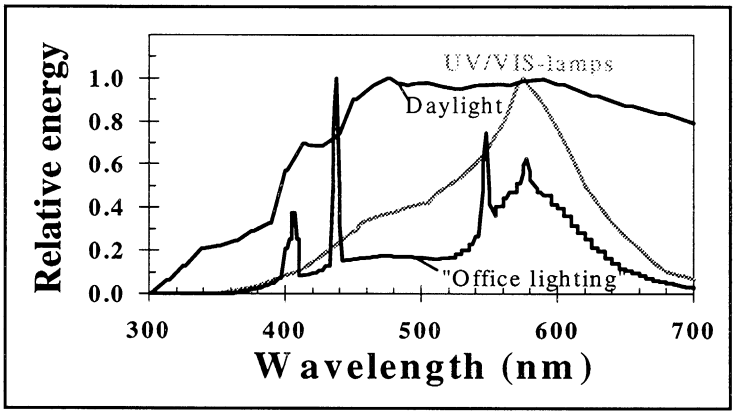
# Light Sources






Magnus Paulsson
March 98

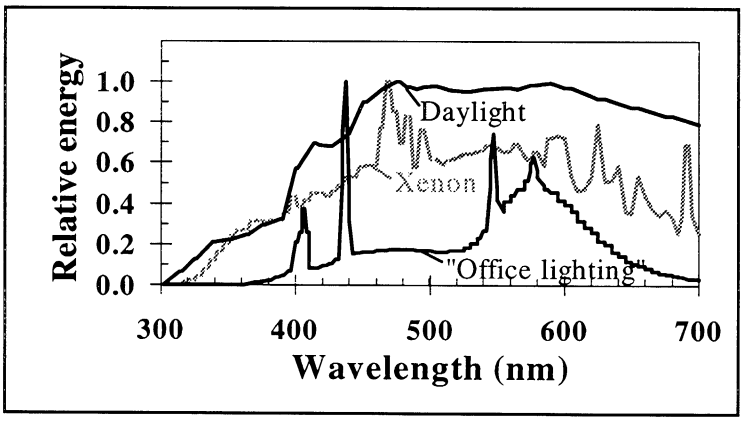
# Light Sources






Magnus Paulsson
March 98

# Light Sources






Magnus Paulsson
March 98

# Acetylation

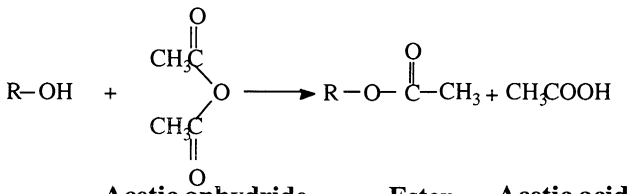
- Acetic anhydride
- No catalyst or cosolvent
- Paper product acetylated
- 100°C for 3-20 min.
- Washing with water
- Pressing for 5 min. at 400 kPA



Magnus Paulsson
March 98

# Acetylation Reactions

**Alcohol/ phenol**



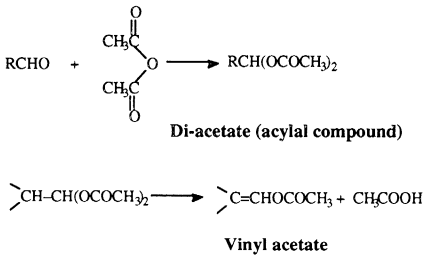

**Acetic anhydride** **Ester** **Acetic acid**



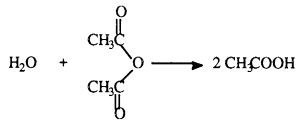
Magnus Paulsson
March 98

# Acetylation Reactions (cont.)

**Aldehyde**




**Water**



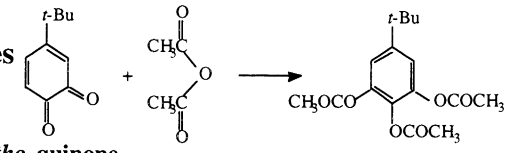



Magnus Paulsson
March 98

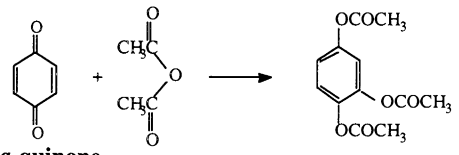
# Acetylation Reactions (cont.)

**Thiele reaction**

**Quinones**




***ortho*-quinone**




***para*-quinone**

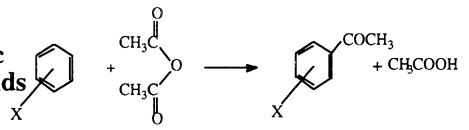


Magnus Paulsson
March 98

# Acetylation Reactions (cont.)

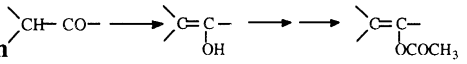
**Friedel-Craft reaction**

**Aromatic compounds**




X = Electron donating compounds

**Keto-enol tautomerism**

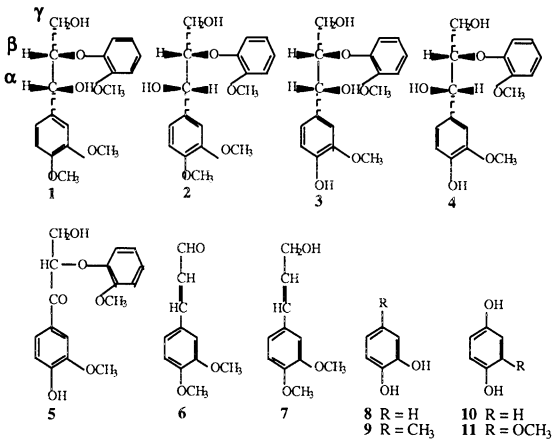



**Ether cleavage** R –O– R ⟶ ROH ⟶ ⟶ $ROCOCH_3$



Magnus Paulsson
March 98

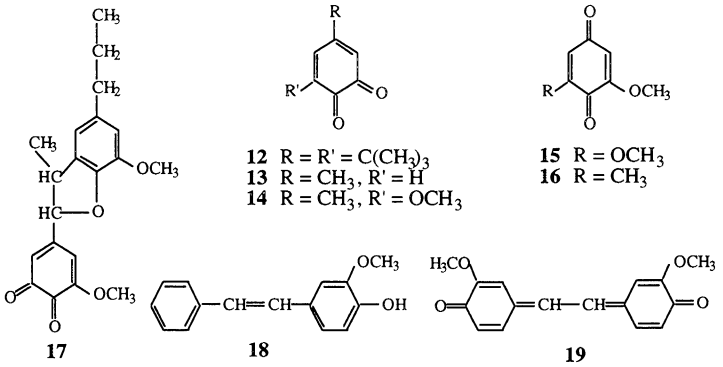
# Model Compounds






Magnus Paulsson
March 98

# Model Compounds (cont.)






Magnus Paulsson
March 98

# Acetylation

- Pulp:
  - 70% of phenolic-OH acetylated within 5 min.
- Lignin model compounds:
  - 95% of phenolic-OH in β-O-4 and stilbene models acetylated within 5 min.
  - Less than 20% of benzylic-OH acetylated within 5 min.
  - The γ-OH in β-O-4 and coniferyl alcohol structures rapidly derivatized



Magnus Paulsson
March 98

# Acetylation (cont.)

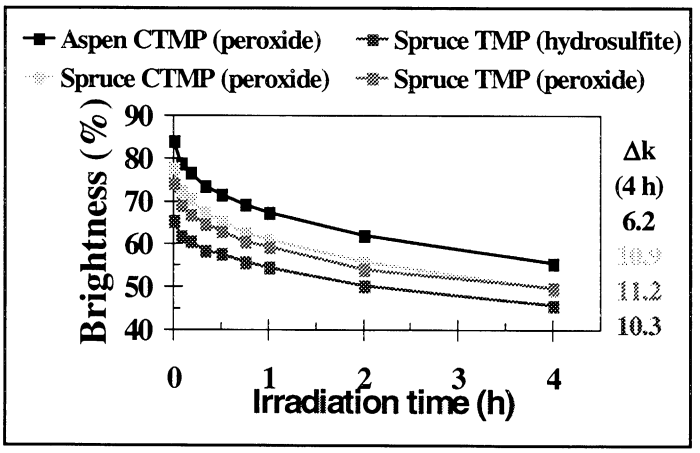
- Lignin model compounds (cont.)
  - Catechols and hydroquinones easily acetylated
  - *Ortho*-quinones rapidly decomposed and to a large extent decolored
  - *Para*-quinones essentially unaffected
  - Coniferaldehyde structures reacts slowly to yield a derivative of the acylal type



Magnus Paulsson
March 98

# Untreated Pulps

Irradiation source: UV-lamps

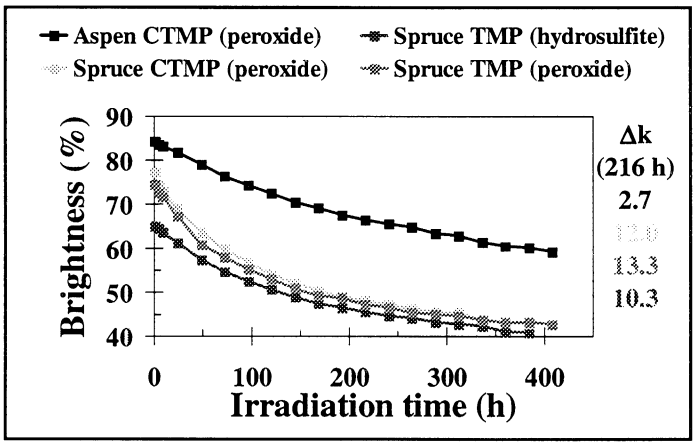





Magnus Paulsson
March 98

# Untreated Pulps

Irradiation source: UV/VIS lamps

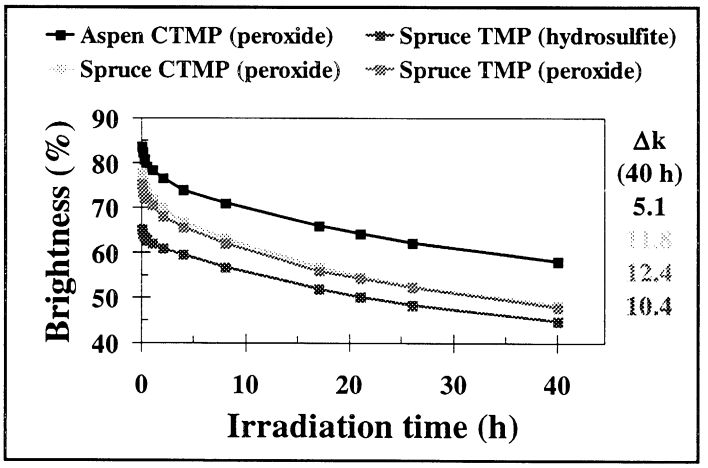





Magnus Paulsson
March 98

# Untreated Pulps

Irradiation source: Xenon lamp

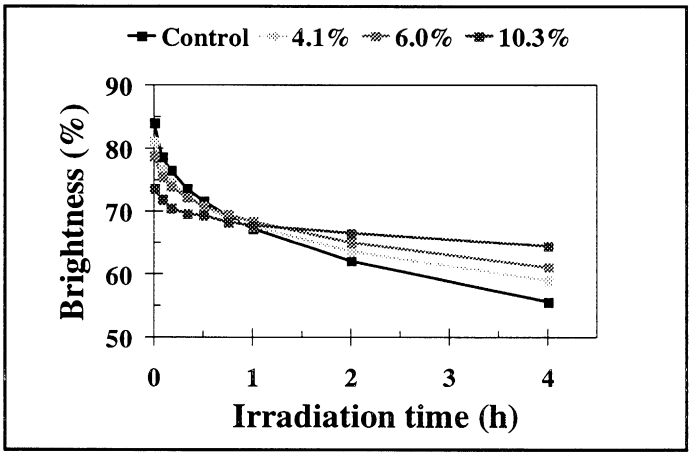





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide-Bleached Aspen CTMP

Irradiation source: UV-lamps

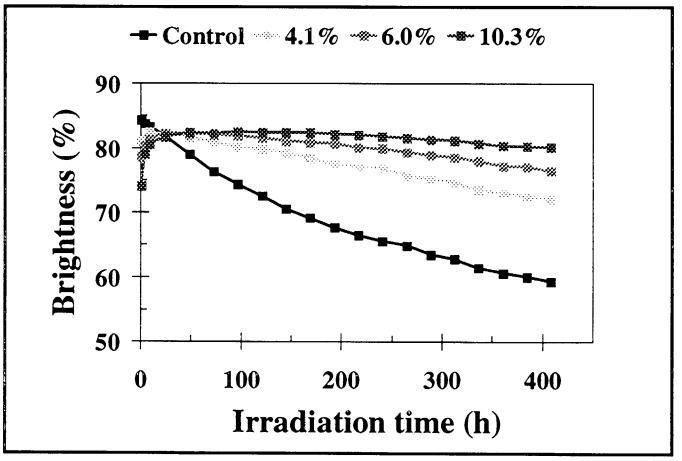





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide-Bleached Aspen CTMP

Irradiation source: UV/VIS-lamps

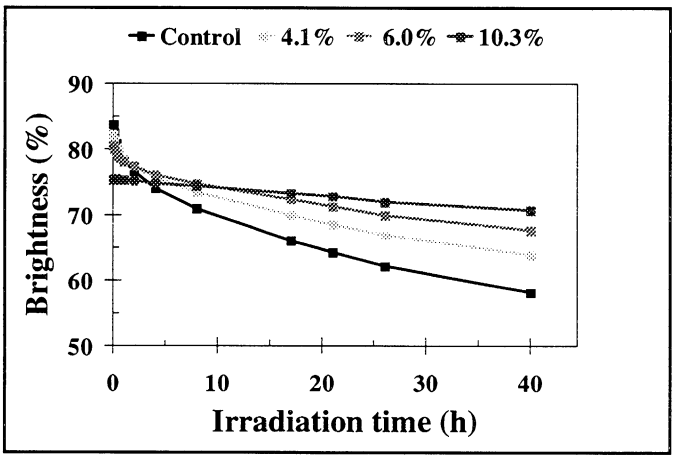





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide-Bleached Aspen CTMP

Irradiation source: Xenon lamp

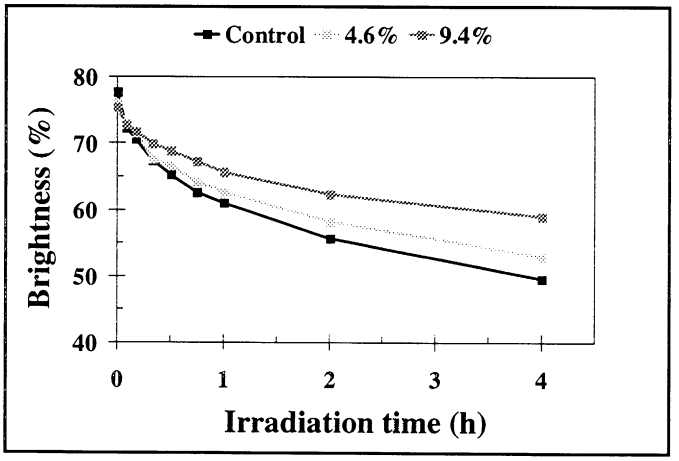





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide-Bleached Spruce CTMP

Irradiation source: UV-lamps

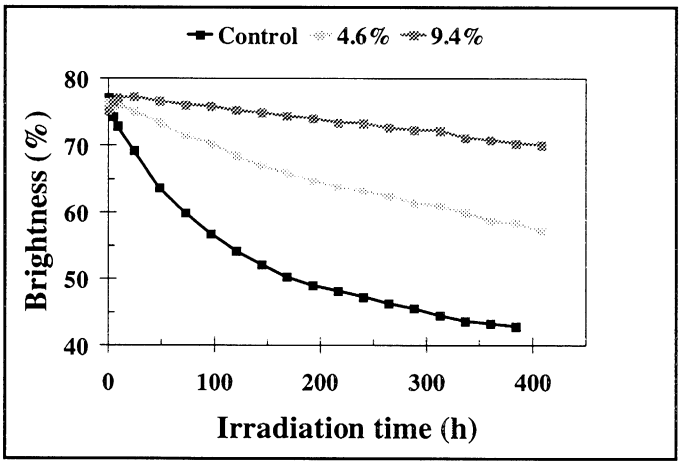





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide Bleached Spruce CTMP

Irradiation source: UV/VIS-lamps

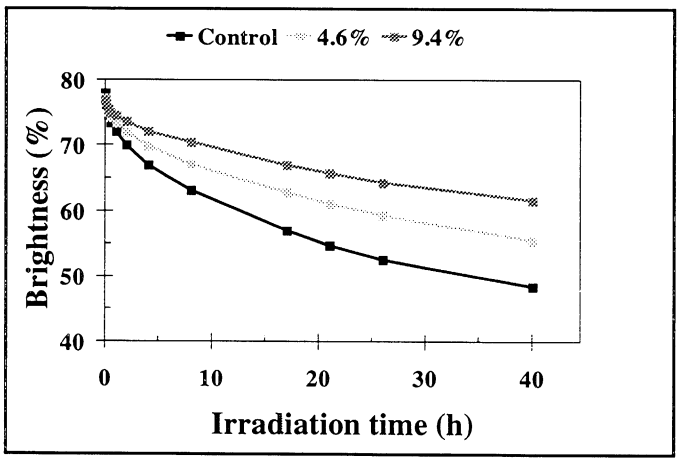





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide-Bleached Spruce CTMP

Irradiation source: Xenon lamp

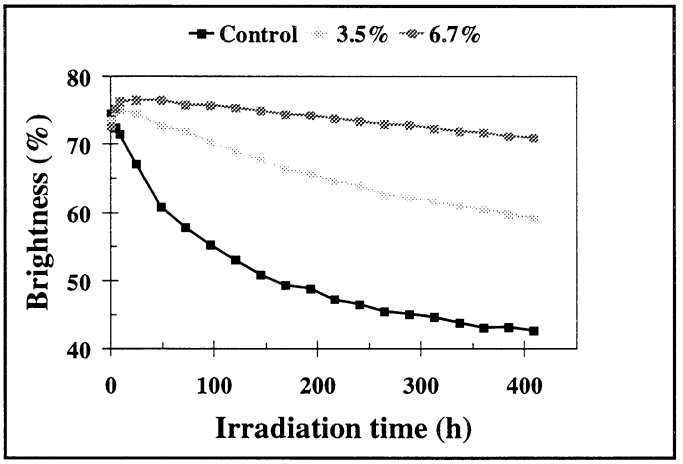





Magnus Paulsson
March 98

# Acetylated, Hydrogen-Peroxide-Bleached Spruce TMP

Irradiation source: UV/VIS-lamps

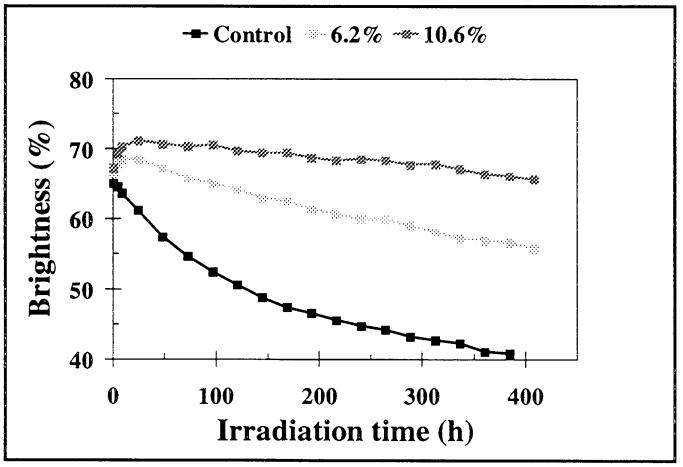





Magnus Paulsson
March 98

# Acetylated, Hydrosulfite-Bleached Spruce TMP

Irradiation source: UV/VIS-lamps

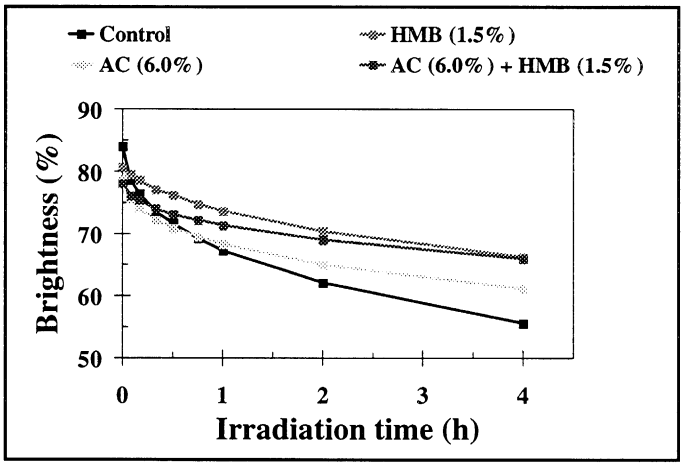





Magnus Paulsson
March 98

## Aspen CTMP, Acetylated and/or 2-Hydroxy-4-methoxybenzophenone(HMB)-Impregnated

Irradiation source: UV-lamps

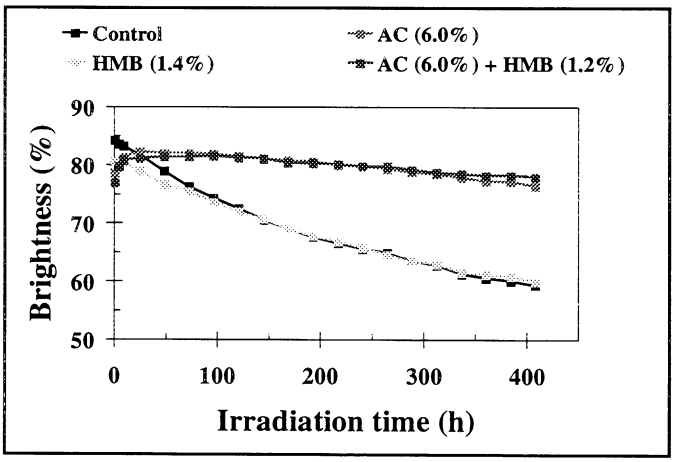





Magnus Paulsson
March 98

## Aspen CTMP, Acetylated and/or 2-Hydroxy-4-methoxybenzophenone(HMB)-Impregnated

Irradiation source: UV/VIS-lamps

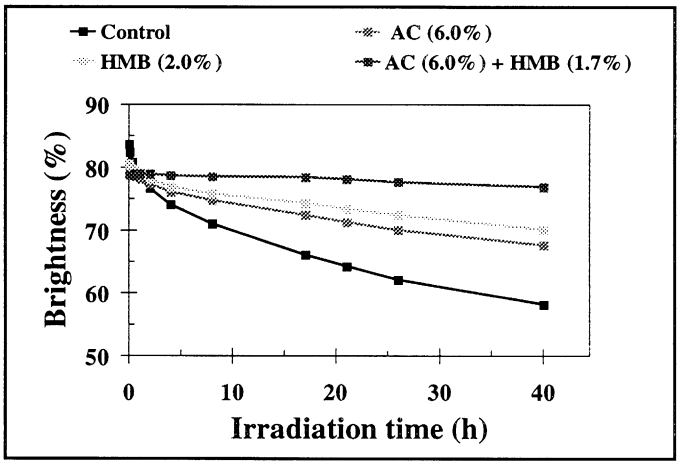





Magnus Paulsson
March 98

## Aspen CTMP, Acetylated and/or 2-Hydroxy-4-methoxybenzophenone(HMB)-Impregnated

Irradiation source: Xenon lamp






Magnus Paulsson
March 98

## Sequential Irradiation - Aspen CTMP UV - UV/VIS

| | Brightness (%) | | | | |
|---|---|---|---|---|---|
| | UV-lamps | | UV/VIS-lamps | | |
| | 0 h | 4 h | 24 h | 120 h | 408 h |
| Control | 84.3 | 55.6 | 62.6 | 61.5 | 52.4 |
| Acetylated, 4.1% | 81.1 | 59.0 | 72.5 | 72.8 | 68.4 |
| Acetylated, 10.3% | 74.0 | 64.5 | 74.7 | 76.8 | 76.1 |



Magnus Paulsson
March 98

## Sequential Irradiation - Aspen CTMP UV/VIS - UV

| | Brightness (%) | | | | |
|---|---|---|---|---|---|
| | UV/VIS-lamps | | | | UV-lamps |
| | 0 h | 24 h | 120 | 408 | 4 h |
| Control | 84.3 | 82.0 | 72.5 | 59.4 | 39.3 |
| Acetylated, 4.1% | 81.1 | 82.1 | 79.9 | 72.1 | 50.5 |
| Acetylated, 10.3% | 74.0 | 81.7 | 82.4 | 80.2 | 62.6 |



Magnus Paulsson
March 98

## Conclusions

- The light source used for reversion studies:
  - Marginally alter the aging response of unmodified softwood TMP and CTMP
  - Some effect of the aging response of unmodified hardwood CTMP
  - Strongly influence the stability of acetylated and/or UV-screen treated pulps



Magnus Paulsson
March 98

# Conclusions

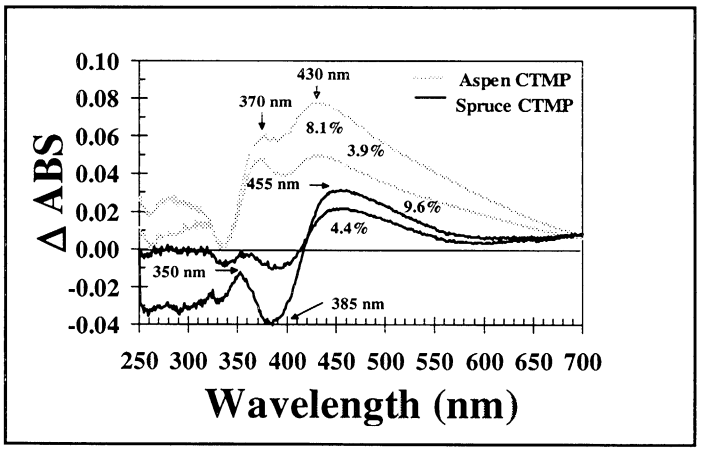
- Acetylation:
  - Retard UV-light induced chromophore forming reactions
  - Acetylation can promote photobleaching reactions



Magnus Paulsson
March 98

# Absorption Difference Spectra

$\Delta$ ABS = $ABS_{acetylated}$ - $ABS_{unacetylated}$

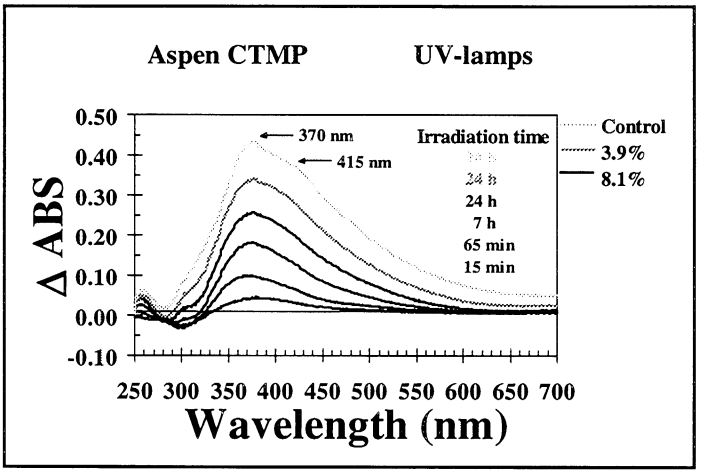





Magnus Paulsson
March 98

# Absorption Difference Spectra

$\Delta$ ABS = $ABS_{irradiated}$ - $ABS_{unirradiated}$

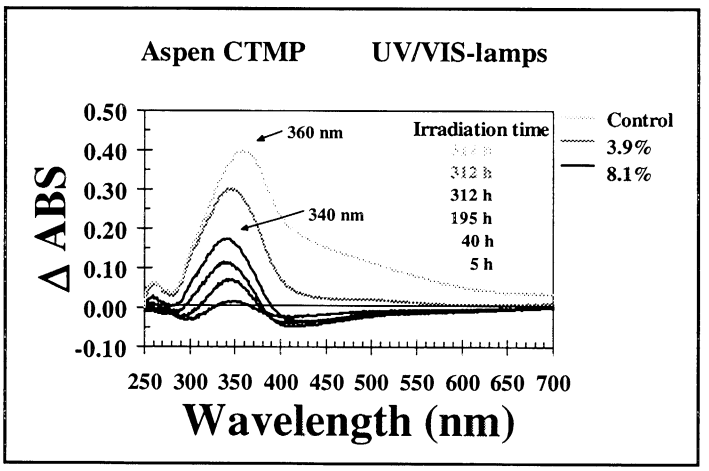





Magnus Paulsson
March 98

# Absorption Difference Spectra

$\Delta$ ABS = $ABS_{irradiated}$ - $ABS_{unirradiated}$

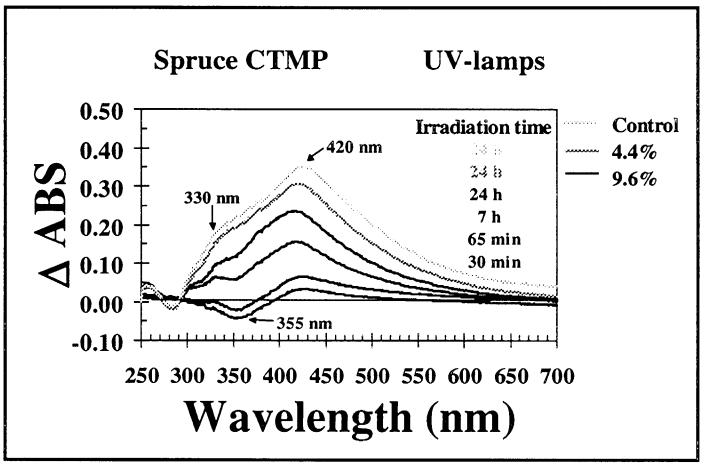





Magnus Paulsson
March 98

# Absorption Difference Spectra

$\Delta$ ABS = $ABS_{irradiated}$ - $ABS_{unirradiated}$

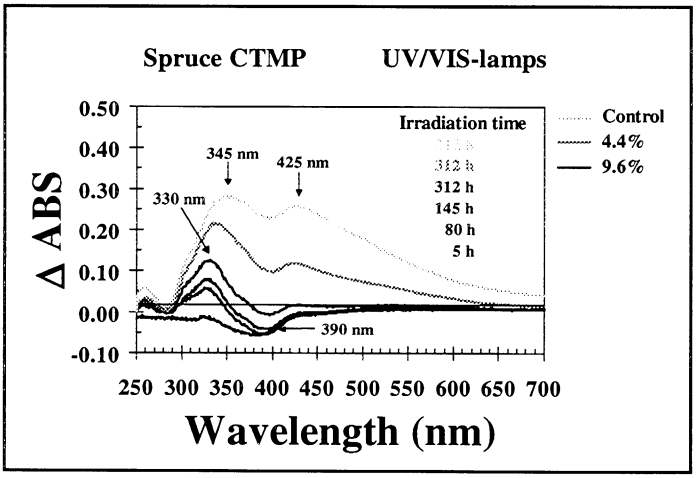





Magnus Paulsson
March 98

# Absorption Difference Spectra

$\Delta$ ABS = $ABS_{irradiated}$ - $ABS_{unirradiated}$






Magnus Paulsson
March 98

## Conclusions

- Importance of light source for:
  - Aging response - evaluation of a photostabilizing treatment
  - Photochemistry involved in untreated/modified pulps
- Photobleaching properties of acetylated lignocellulosic materials



Magnus Paulsson
March 98

## Conclusions (cont.)

- The necessity to develop a standard method for accelerated photoaging of lignin-containing materials



Magnus Paulsson
March 98

# Acknowledgments

Brita Ohlsson, Lena Fogelquist,
Chalmers University of Technology

The Gunnar and Lillian Nicholson Graduate Fellowship and Faculty Exchange Fund

Wood Chemistry Group IPST

Member Companies IPST

# MICROFIBRIL ANGLE: Importance, Measurement in Southern Pine & Fundamental Mechanisms

# Microfibril Angle: Importance, Measurement in Southern Pine & Fundamental Mechanisms

GARY PETER
DOUGLAS BENTON

Forest Biology



## Cell Wall Ultrastructure

- **Primary Wall** (0.03 - 1.0 microns)
- **Secondary Wall** (0.2 - 8 microns)
  - S1(0.1 - 0.2 μm)
  - S2(0.5 - 8 μm)
  - S3(0.07 - 0.1 μm)
- **Microfibrils** bundles of highly organized cellulose chains

- **S2 Layer** contains 90% of total cell wall mass
- **S2 Layer** contains 75% of the total cellulose
- **S2 Layer** defines the mechanical properties of the cell

(Krahmer, R.L. *Wood Technology and Utilization*. O.S.U. Bookstores, Corvallis, Oregon, 1983)

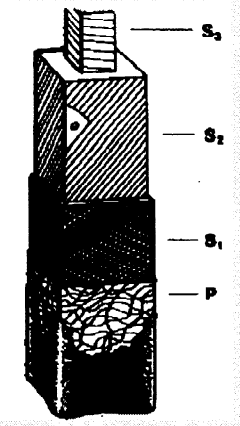
# Definition of Microfibril Angle

- MFA is defined as the angle that cellulose microfibrils are oriented relative to the long axis of the fiber cell.



# MFA in Cell Wall Layers

- S1 Layer
  - generally 90°
- S2 Layer
  - 9 - 55°
- S3 Layer
  - generally 90°



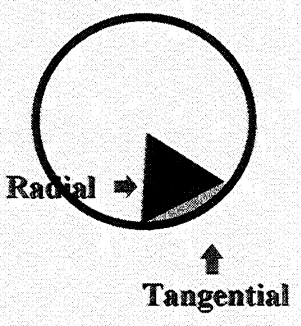
# Established Trends for MFA in Trees

| With Increasing | General Effect on MFA |
|---|---|
| • Age | Lower |
| • Growth Rate | Higher |
| • Height | Higher |
| • Fiber Length | Lower |
| • Fiber Thickness | Lower |
| • Ring Width | Higher |
| • Stand Density | Lower |



# Radial vs. Tangential Wall

| Radial | Tangential |
|---|---|
| • 45.2 | • 40 |
| • 47 | • 39.6 |
| • 56 | • 42.8 |
| • 46.4 | • 41.6 |
| • Mean 48.7 | • Mean 41.4 |



## Microfibril Angle of S2 Layer: The Critical Parameter in Defining the Mechanical Properties of Fibers

- Tensile strength
- Young's Modulus
- Longitudinal and Tangential Shrinkage
- Compressive Strength



## M.F.A. Implications to Industry

- Low M.F.A. Pulps Will Produce Stronger, High Modulus, Less Elastic Papers Which Are Less Susceptible to Distortion, Non-Uniformity, and Tensile Failure at High Stress Areas of Paper Making
- Low M.F.A. Wood Products Will Be Also Be Stronger and Less Prone to Warping

## The Problem: Fast Growing Trees Have Lower Quality Fiber

- Plantation Silviculture and Breeding Programs Have Focused on Resiliancy and Fast Growth
- Superior Growth Rates Are Critical to the Competitiveness of our Nation's Wood Products Industry.... BUT
- Southern Pine Trees are Being Harvested After 12-15 Years. Trees Do Not Typically Begin to Produce Mature Wood Until After 10-12 Years of Age
- Juvenial Wood is known to have a Significantly Higher M.F.A. Than Mature Wood.



## The Solution: Develop Faster Growing Trees with Lower M.F.A.

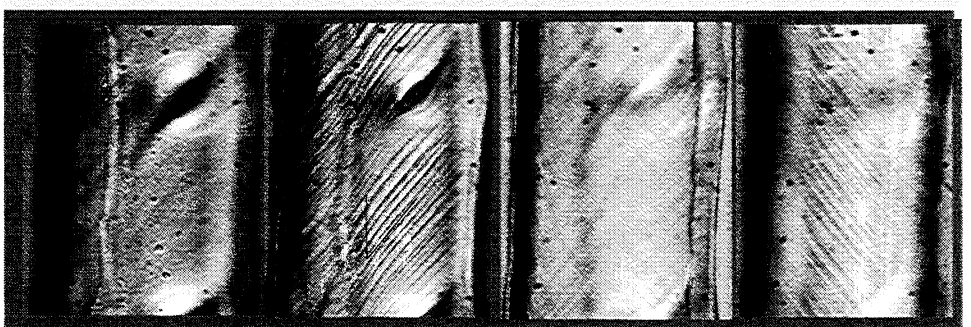
- Develop a Rapid and Simple Assay to Measure MFA that Works with Southern Pine
- Determine the Effect of Silvicultural Practices on MFA in Elite Cultivars
- Map Genes that Control MFA
- Breed for Trees with Low MFA in Juvenile Wood

# New Potential Method for MFA Measurement

- High resolution optical microscopy with differential interference optics can be used to visualize the MFA of the S2 layer in thick walled Southern Pine tracheids.



# DIC Image of Loblolly Pine Trachied



Top - S1 | Top - S2 | Mid-plane | Bottom - S2

# PROJECT F012

# SOUTHERN PINE MECHANICAL PULPING

# Southern Pine Mechanical Pulping

Lars Johansson
Alan Rudie

Project F012 March 25, 1998

## Outline

- Objectives
- Background
- Experimental
  - » Wood source
  - » Wood Classification
  - » Pulp Classification
  - » Wet Pressing
- Results
- Conclusions

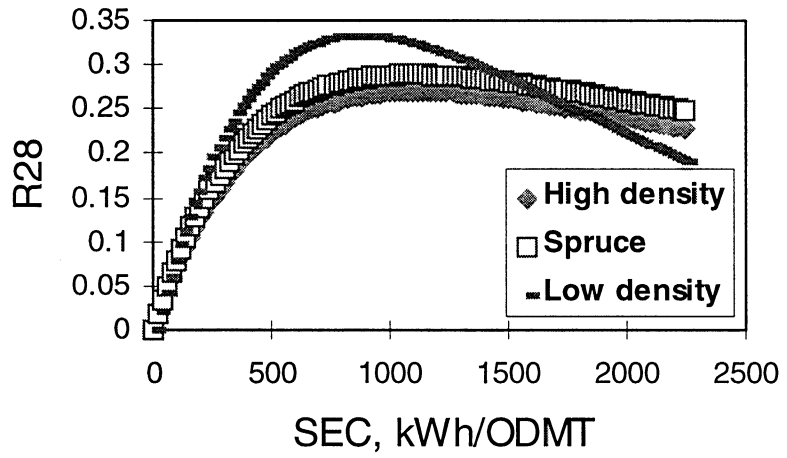
# Objectives

- Improve the understanding of the performance limitations inherent in mechanical pulping
- Evaluate juvenile and mature pine to understand how tree age influences specific bond strength, relative bonded area, and surface area

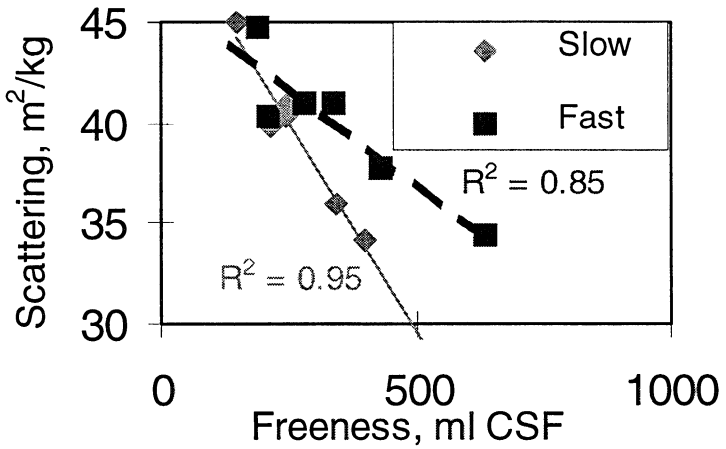
# Background

- 1995/96: demonstrated that in refining juvenile pine developed long fiber faster, but also degraded long fiber faster than mature pines
- 1996/1997: demonstrated that at a given freeness, juvenile or fast growth pine had a greater unbonded area, and at a given bond index, juvenile pine had a larger unbonded area

# Formation and Depletion of $R_{28}$




# Scattering vs Freeness



## Experimental Procedures

- Wood Source
- Wood Classification
- Pulp Classification
- Wet Pressing

## Wood Source

- Mature loblolly pine, 33 years old
- Juvenile loblolly pine, 15 years old
- Primary refiner, 12" pressurized
- Secondary and tertiary refiner, 36" atmospheric

## Wood Classification

- Wood density
- Latewood content
- Fiber length
- Microfibril angle of $S_2$ layer

## Pulp Classification

- Handsheet formation and testing
- Total ion content
- Specific hydrodynamic surface area
- Surface lignin concentration

## Specific Surface Area

- Handsheets with a basis weight of 100 g/m$^2$ were made
- Pressed once at 345 kPa for 30 s
- The transverse permeability was determined by compressing the sheets between two felts
- By knowing the flow through the sample, the pressure drop over the sample and the thickness of the sample, the specific hydrodynamic surface area could be determined

## Surface Lignin Concentration

- Sulfonation of the fibers, followed by polyelectrolyte titration of the sulfonic acid groups introduced into the lignin
- The surface charge was measured by adsorption of a large cationic molecule (p-DMDAABr), followed by titration of the equilibrium concentration of p-DMDAABr in the filtrate after adsorption

## Surface Lignin Concentration

- By extrapolating the plateau level of adsorbed p-DMDAABr to zero equilibrium concentration, the adsorbed amount of polyelectrolyte at zero concentration can be obtained
- By calculating the net increase in surface charge after sulfonation, the surface lignin concentration can be determined

## Wet Pressing

- Handsheets with a basis weight of 100 $g/m^2$ were made
- Pressed at 97 kPa for 30 s
- Pressed at 1100 - 4400 kPa for 60 s each
- Dried at 60°C and conditioned
- One set was not pressed at all, but solvent exchanged in two steps with acetone and tert-buthyl methyl ether

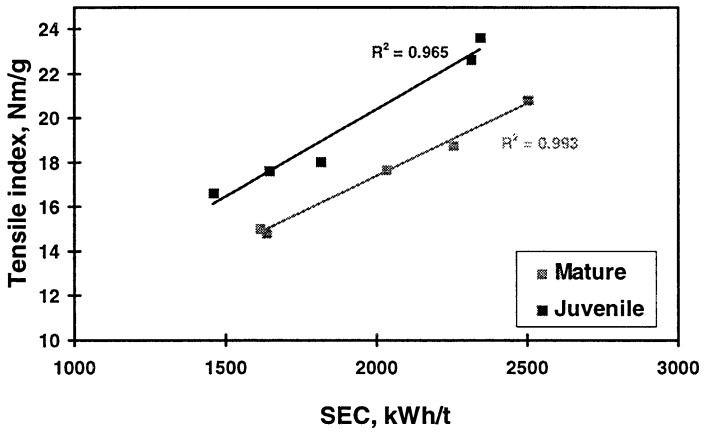
# Wood Classification

| Wood | Specific Gravity ($g/cm^3$) | Latewood (%) | Ring Width (mm) | Age (Years) |
|---|---|---|---|---|
| Mature Pine | 0.46 | 48.2 | 3.1 | 33 |
| Juvenile Pine | 0.41 | 41.5 | 7.0 | 15 |

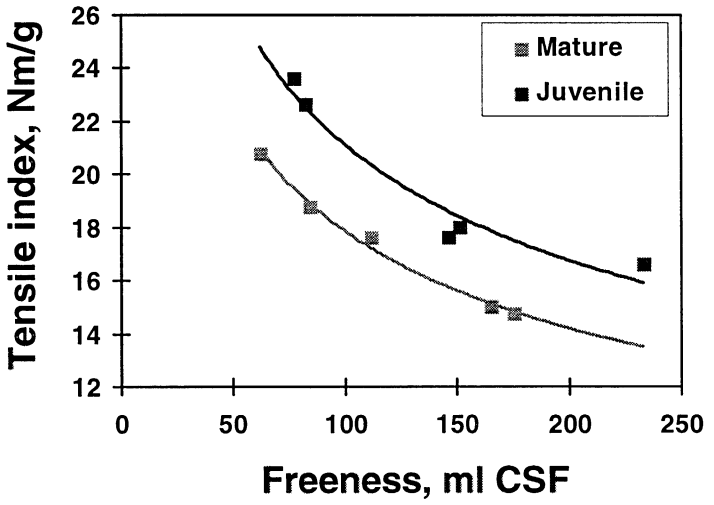
# Wood Classification

| Wood sample | Fiber length, (mm) | Microfibril angle, (°) |
|---|---|---|
| Mature, Earlywood | 2.95 | 35 |
| Mature, Latewood | 3.04 | 27 |
| Juvenile, Earlywood | 3.12 | 48 |
| Juvenile, Latewood | 3.19 | 34 |

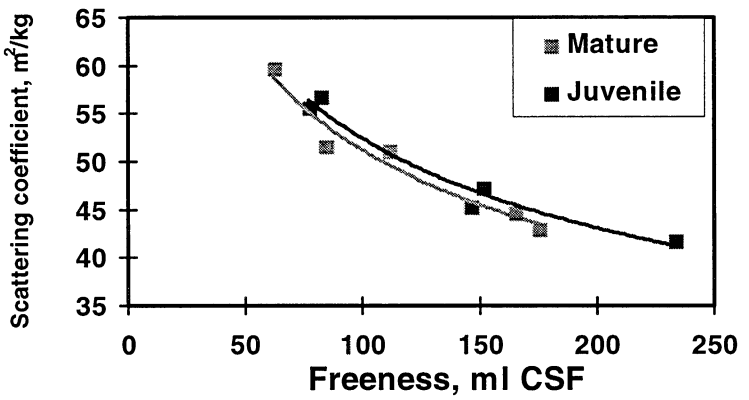
# Tensile Index vs SEC




# Tensile Index vs Freeness



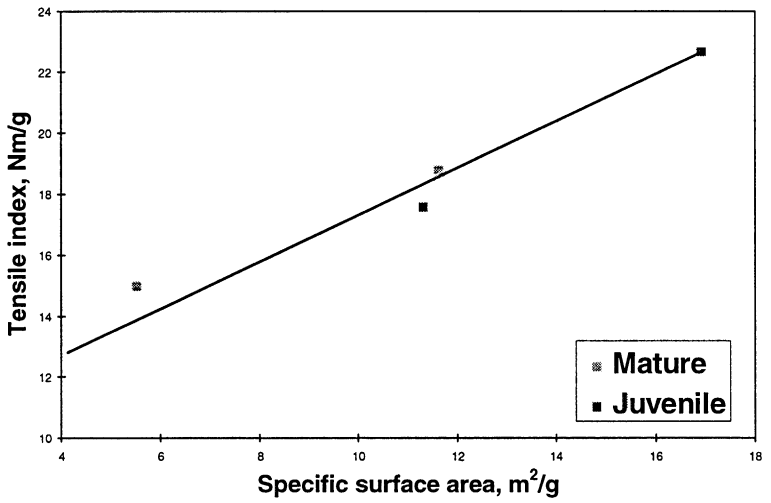
## Light Scattering Coefficient vs Freeness



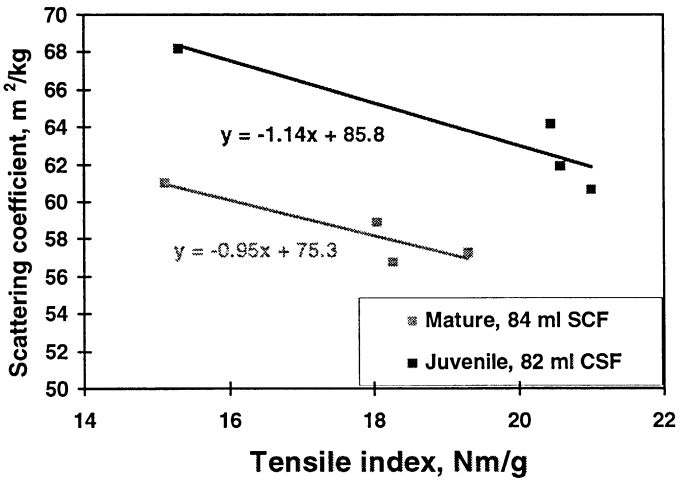

## Specific Surface Area

| Pulp sample | Specific surface area, ($m^2/g$) |
|---|---|
| Mature pulp (2), 165 ml CSF | 5.5 |
| Mature pulp (5), 84 ml CSF | 11.6 |
| Juvenile pulp (8), 146 ml CSF | 11.3 |
| Juvenile pulp (11), 82 ml CSF | 16.9 |

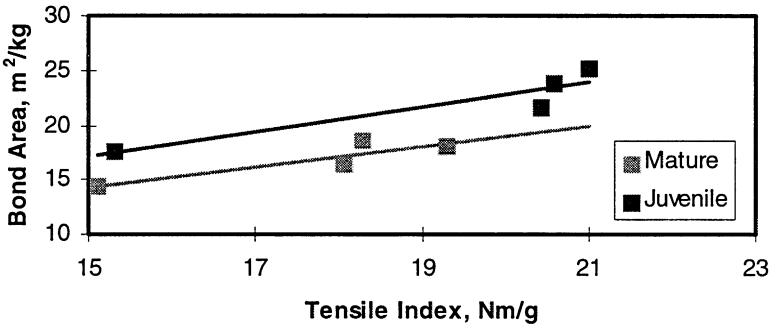
## Tensile Index vs Specific Surface Area



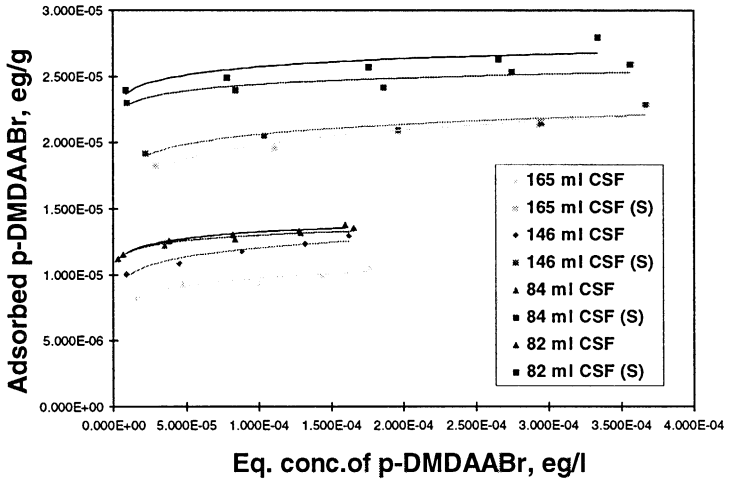

## Light Scattering Coefficient vs Tensile Index After Wet Pressing and Solvent Exchange



# Bond Area vs Tensile Index, Calculated After Extrapolation




# Adsorbed Amount of p-DMDAABr vs Equilibrium Concentration of p-DMDAABr



# Surface Lignin Concentration

| Pulp sample | Klason lignin content, (%) | Surface lignin content, (%) | Surface lignin concentration, ($g_{lignin}/m^2$) |
|---|---|---|---|
| Mature pulp (2), 165 ml CSF | 32.0 | 1.9 | $3.5 \cdot 10^{-3}$ |
| Mature pulp (5), 84 ml CSF | 32.1 | 2.3 | $2.0 \cdot 10^{-3}$ |
| Juvenile pulp (8), 146 ml CSF | 31.6 | 1.7 | $1.5 \cdot 10^{-3}$ |
| Juvenile pulp (11), 82 ml CSF | 30.8 | 2.2 | $1.3 \cdot 10^{-3}$ |

# Conclusions

- The method of analyzing the pulps has proved to be very useful
- The results found in this investigation do not seem to be typical for juvenile and mature pulps
- The juvenile wood had higher average fiber length and lower Klason lignin content
- The juvenile pulps were stronger, had higher light scattering coefficient and higher density

# Conclusions

- The juvenile pulp had much higher specific hydrodynamic surface
- The juvenile pulps also had lower surface lignin concentration

# Acknowledgments


- Champion International
- Member Companies of IPST
- Dr. Alan Rudie
- The Chemical and Biological Sciences group at IPST
- The Gunnar and Lillian Nicholson Graduate Fellowship and Faculty Exchange Fund