PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

October 20-21, 1986

HANDOUT
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Your advice and suggestions on any of the projects will be most welcome.
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<td>DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES (Project 3477)..................Easty..............................</td>
<td>34</td>
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<td>135</td>
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<td>FUNDAMENTALS OF BRIGHTNESS STABILITY (Project 3524)..................................Malcolm....................................</td>
<td>149</td>
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RESEARCH OVERVIEW

E. W. Malcolm
CHEMICAL SCIENCES DIVISION

STAFF (JULY 1986)
8 Ph.D. (FACULTY)
21 B.S./M.S.

RESEARCH AREAS
Chemical Pulp
Kraft Chemical Recovery
High Yield Pulps

RESEARCH TYPE
IPC Funded
IPC Student
Contract
IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

**IPC FUNDED**

**Chemical Pulp**
- 3288 - Fine Structure of Wood Pulp Fibers: 75
- 3475 - Fundamentals of Selectivity in Pulping and Bleaching: 150
- 3474 - Improved Processes for Bleached Pulp: 35
- 3477* - Development and Application of Analytical Techniques: 13

**Recovery**
- 3473-1 - Fundamental Processes in Alkali Recovery Furnaces: 230
- 3456-2 - Smelt-Water Explosions: 20
- 3477* - Development and Application of Analytical Techniques: 13
- 3605 - Computer Model of Recovery Furnace: 20

**High Yield Pulp**
- 3566 - Separation of Strong, Intact Fibers: 175
- 3524 - Fundamentals of Brightness Stability: 140
- 3521-2 - Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue: 45
- 3477* - Development and Application of Analytical Techniques: 13

**Other**
- 3534 - Exploratory Research: 60
- 3477* - Analytical (Paper): 26

**TOTAL IPC FUNDED:** 929
**CONTRACT RESEARCH**

**Government Funded**

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<tr>
<th>Project Description</th>
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<td>3473-6 - Fundamental Studies of Black Liquor Combustion</td>
<td>220</td>
<td>205</td>
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<td>3521-3 - Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue</td>
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**Nongovernment Funded**

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**Total Contract Research**

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(49% Contract)
(51% Contract)
### IPC STUDENT RESEARCH

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<td>Kraft Chemical Recovery</td>
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* Does not include class entering 1986.

### IPC RESEARCH BUDGETS (1986-1987)
- **Chemical Sciences Division ($1000)**

#### CONTRACT RESEARCH

**Government Funded**

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### IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

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<td>Recovery</td>
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### IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

#### IPC FUNDED

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<td>3475 - Fundamentals of Selectivity in Pulp and Bleaching</td>
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<td>3474 - Improved Processes for Bleached Pulp</td>
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### IPC RESEARCH BUDGETS (1986-1987)
#### CHEMICAL SCIENCES DIVISION ($1000)

**IPC FUNDED**

#### RECOVERY

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<thead>
<tr>
<th>Project Code</th>
<th>Project Description</th>
<th>Budget</th>
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<tbody>
<tr>
<td>3473-1</td>
<td>Fundamental Processes in Alkali Recovery Furnaces</td>
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<td>3456-2</td>
<td>Smelt-Water Explosions</td>
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<tr>
<td>3477*</td>
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<td>3605</td>
<td>Computer Model of Recovery Furnace</td>
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#### IPC RESEARCH BUDGETS (1986-1987)
#### CHEMICAL SCIENCES DIVISION ($1000)

**IPC FUNDED**

#### HIGH YIELD PULPING

<table>
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<tr>
<th>Project Code</th>
<th>Project Description</th>
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<td>3566</td>
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<td>3524</td>
<td>Fundamentals of Brightness Stability</td>
<td>140</td>
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<tr>
<td>3521-2</td>
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<tr>
<td>3477*</td>
<td>Development and Application of Analytical Techniques</td>
<td>13</td>
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373
IPC RESEARCH BUDGETS (1986-1987)
- CHEMICAL SCIENCES DIVISION ($1000)

IPC FUNDED

Other
3534 - EXPLORATORY RESEARCH  60
3477* - ANALYTICAL (PAPER)  26  96

TOTAL IPC FUNDED  929
TOTAL CONTRACT RESEARCH  907
TOTAL FUNDED AND CONTRACT  1,836 (49% CONTRACT)
                         (51% IPC FUNDED)
Project 3475

DEVELOPMENT OF SELECTIVITY IN PULPING AND BLEACHING

D. R. Dimmel

Goal:
1. Get Dimmel into house as new leader.
2. Understand mechanisms of AQ pulping.
PROJECT 3475

FUNDAMENTALS OF SELECTIVITY
IN PULPING AND BLEACHING
DELIGNIFICATION REACTIONS
CARBOHYDRATE REACTIONS

PULPING                BLEACHING

PULPING CHEMICALS

WOOD

CARBOHYDRATES

LIGNIN

BY-PRODUCTS
(ENERGY-ORGANICS)
(RECOVERY-INORGANICS)

CHLORINE (COST)

EXTRACTIVES
(PROFITS)

BY-PRODUCTS
(PROBLEMS)

PULP (PROFITS)

PULPING MATERIAL BALANCES

REDOX CYCLE

CARBOHYDRATES

STABILIZED CARBOHYDRATES

Oxidation

Reduction

AQ

AHQ

SOLUBILIZED LIGNIN

YIELD GAIN

RATE GAIN
ALKALINE CARBOHYDRATE REACTIONS

REDUCING END

STOPPING REACTION

CHAIN CLEAVAGE

PEELING
ALKALINE CARBOHYDRATE REACTIONS

\[
\begin{align*}
\text{REDUCING END} & \quad \xrightarrow{\text{AQ (OXIDATION)}} & \quad \text{STOPPING REACTION} \\
\text{PEELING REACTION} & \\
\text{AQ-PROMOTED CHAIN CLEAVAGE} &
\end{align*}
\]
EFFECT OF AQ ON RANDOM CHAIN CLEAVAGE

<table>
<thead>
<tr>
<th>Polysaccharide</th>
<th>Effect</th>
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</thead>
<tbody>
<tr>
<td>Amylose</td>
<td>acceleration</td>
</tr>
<tr>
<td>Cellulose (Cotton Linters)</td>
<td>little, if any</td>
</tr>
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</table>

POTENTIAL REASONS FOR DIFFERENT RESPONSE TO AQ

Stereochemical

Physical

\[ \text{1,5-Anhydrocellobiitol} \]

\[ \text{1,5-Anhydromaltitol} \]
Fibrous Cellulose

DMSO/PF

Amorphous Cellulose

NaBH₄

Amorphous Cellulose
("Peeling Resistant")

NaOH/AQ

Yield and GPC Analysis

Amorphous cellulose preparation and reaction scheme.

PLANS
CARBOHYDRATE CHEMISTRY

- METHODS FOR HIGH VISCOSITY AMORPHOUS CELLULOSE
- METHODS FOR DERIVATIZING CELLULOSE SAMPLES
- STUDY RANDOM CHAIN CLEAVAGES AS A FUNCTION OF
  - PHYSICAL EFFECTS
  - CHANGES IN REACTION VARIABLES
- APPLICATIONS OF INSOLUBLE CELLULOSE MODELS
- DETAILED CHEMISTRY OF CHAIN CLEAVAGE REACTIONS
LIGNIN FRAGMENTATION

LIGNIN RECOMBINATION

DELIGNIFICATION

LIGNIN FRAGMENTATION (BENEFICIAL)

LIGNIN RECOMBINATION (DETRIMENTAL)
HYPOTHETICAL INITIAL DELIGNIFICATION CHEMISTRY

ENERGY

FRAGMENTS
(β-Ether Bond Rupture)

( OH⁻ )

( ArO⁻ )

( SH⁻ )

( AH₂O⁻ )

CONDENSATION

VINYLEETHER

REACTION COORDINATE

\[
\begin{align*}
\text{Ar} & \quad \text{O} \\
& \quad \text{Ar} \\
\alpha & \quad \beta
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{OH} \\
\text{H}_2\text{O} & \quad \text{CH}_3\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]
HYPOTHETICAL INITIAL DELIGNIFICATION CHEMISTRY

<table>
<thead>
<tr>
<th>NaOH</th>
<th>Na₂S</th>
<th>AQ</th>
<th>glucose</th>
<th>Phenol yield</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60 min.</td>
</tr>
<tr>
<td>25 eq.</td>
<td></td>
<td></td>
<td></td>
<td>8.2</td>
</tr>
<tr>
<td>20 eq.</td>
<td></td>
<td></td>
<td></td>
<td>16.1</td>
</tr>
<tr>
<td>1M</td>
<td></td>
<td>5 eq.</td>
<td></td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>5 eq.</td>
<td></td>
<td></td>
<td>24.6</td>
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<tr>
<td></td>
<td>5 eq.</td>
<td>5 eq.</td>
<td></td>
<td>19.4</td>
</tr>
<tr>
<td>0.86M</td>
<td></td>
<td></td>
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<td>11.6</td>
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<td>0.86M</td>
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<td></td>
<td></td>
<td>16.8</td>
</tr>
<tr>
<td>0.86M</td>
<td></td>
<td>5 eq.</td>
<td></td>
<td>18.9</td>
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<tr>
<td>0.86M</td>
<td></td>
<td>5 eq.</td>
<td></td>
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*NaOD / D₂O

REACTION COORDINATE
Reactions of the β-(propyl alcohol) model

\[
\begin{align*}
\text{HO}^- & \quad \text{v. slow} \quad \text{6-OH} \\
\text{HO}^- & \quad \text{slow} \quad \text{6-OH} \\
\text{slow} & \quad \text{fast} \\
\text{v. fast} & \quad \text{slow} \\
\text{AHQ}^{-3} & \quad \text{v. fast} \\
\text{SH}^- & \quad \text{moderate} \\
\end{align*}
\]
Cleavage Mechanisms of the β-(propyl alcohol) model

\[
\begin{align*}
\text{HO}^- & \leftrightarrow \\
\text{HS}^- & \leftrightarrow \\
\end{align*}
\]
SET REACTIONS OF A β-BUTENYL LIGNIN MODEL

\[
\begin{align*}
\text{HO}^- 
\rightarrow \text{QUINONEMETHIDE} \\
\Delta 
\end{align*}
\]

SYNTHESIS OF β-BUTENYL LIGNIN MODEL

\[
\begin{align*}
\text{R'} &= \text{H} \\
\text{R'} &= \text{SEM} = \text{SiMe}_3
\end{align*}
\]
RELEASE OF MODEL FROM POLYMER

UNSUCCESSFUL TRITYLATION OF A-RING MODEL

\( R = H, OAr \)
SYNTHETIC SCHEME FOR A-RING MODEL POLYMER ATTACHMENT

RESEARCH DIRECTIONS

- fundamental chemistry of pulping
- chemistry of insoluble lignin models
- importance of electron transfer reactions
- high temperature aqueous electrochemistry
Project 3474

IMPROVED PROCESSES FOR BLEACHED PULP

T. J. McDonough
PULPING AND BLEACHING GROUP

STAFF
Salman Aziz
Hugh Corbett
Harry Grady
Amy Malcolm
Tom McDonough
Tom Paulson
Kristie Rankin

STUDENTS
Dennis Boyle
Dan Bunker
Barbara Burns
Tyrone Cornbower
Tom Heazel
Stuart Lebo
Tuomo Niemi
Mike Plouff
Sebastian Pugliese
Karyn Sime
Tim Stroh

ASSOCIATE
Terry Conners
(Wood & Fiber Science Group)

PULPING AND BLEACHING GROUP
Funded Projects

Strong, Intact High Yield Fibers

Improved Process for Bleached Chemical Pulp
Low-Lignin Pulpings
Nonchlorine Bleaching

Laboratory Chlorination Procedures
Laboratory Procedures for the EQ Stage
Solvent Pulpings
Pulping Characteristics of Red Pine
PULPING AND BLEACHING GROUP
CURRENT AND RECENT CONTRACT PROJECTS

- Development of Equipment and Procedures for On-Line Determination of Pulp Lignin Content ("Nu Number")
- Development of Technology for Using Oxygen in Pulp Bleaching
- Effects of Pulping and Papermaking Conditions on Opacity
- Effects of Unbleached Lignin Content on Brightness After Bleaching
- Bleaching Secondary Fiber
- Effects of Chip Thickness in Kraft Pulping
- Evaluation of AQ Effectiveness
- Monitoring Contaminants Removal

PULPING AND BLEACHING GROUP
STUDENT RESEARCH
Ph.D. AND SPECIAL STUDENTS

Ph.D.
S. Pugliese: Kinetics of Chlorination in A CSTR
T. Heazel: Sulfur Distribution in Sulfonated Fiber Walls
B. Burns: Kinetics of Chlorination of Fluidized Medium Consistency Pulp
K. Sime: Kinetics of Sulfite-Anthraquinone Pulping
S. Lebo: Mechanism of Light-Induced Yellowing

Special
T. Niemi: Comparison of Eucalyptus and Birch Fiber and Sheet Properties
PULPING AND BLEACHING GROUP

STUDENT RESEARCH
M.S. Students

M.S.

D. Boyle: Kinetic Parameters for Burázín's Dynamic Model of Kraft and Kraft-AQ Pulping

T. Cornbower: Effects of Enzymatic Removal of Hemicellulose from Wood on Pulp Properties

T. Stroh: Catalysis of Peroxide Delignification

D. Bunker: Fiber Structure Changes During Pulping

M. Plouff: Fiber Wall Lignin Distribution

PROJECT 3474

IMPROVED PROCESS FOR BLEACHED PULP

1. Low-Lignin Pulps

2. Nonchlorine Bleaching
SULFITE-ANTHRAQUINONE
PULPING KINETICS

OBJECTIVE

DETERMINE ACTIVATION ENERGY
FOR SULFITE-AQ DELIGNIFICATION

Goal - Now to get to lower lignin
levels without unnecessary degradation.

Committee opinion: ISC Staff view: Knowledgeable blend effort.

Preferably people with indirect experience
(Perhaps from supplier companies - DuPont, Dow, etc)
EFFECT OF TEMPERATURE ON RATE OF SULFITE - ANTHRAQUINONE DELIGNIFICATION OF LOBLOLLY PINE SHAVINGS.

\[-\frac{dl}{dt} = A e^{-E/RT} L^n S^m\]

\[E = 35.2\]
\[n = 2.4\]
\[m = 0.5\]
- 30 -

**Residual Sulfite Concentration vs. Lignin Remaining in Wood.**

\[ -\frac{dL}{dt} = A_1 e^{-E_1/RT_L n_1} + A_2 e^{-E_2/RT_L n_2} \]

1 = No AQ

\[ E_1 = 29.2 \]

\[ n_1 = 2.4 \]

2 = AQ Only

\[ E_2 = 37.0 \]

\[ n_2 = 2.4 \]
RELATIONSHIP BETWEEN PULP YIELD AND LIGNIN REMAINING.

CONCLUSIONS

Sulfite-AQ pulping of Southern Pine exhibits:

- Higher activation energy than sulfite or Kraft
- Delignification an order of magnitude faster than sulfite
- A linear, temperature-invariant relationship between rates of removal of lignin, carbohydrate
- Substantially lower sulfite consumption
- A limit on the effectiveness of added AQ
- A mass transfer limitation at wood thickness > 1 mm
NONCHLORINE BLEACHING

Effect of alkali charge as zero-span tensile strength after oxygen bleaching and pretreatment with various amounts of nitrogen oxide.
Determination of Lignin in Wood Pulp by Diffuse Reflectance
Fourier Transform Infrared Spectrometry

Analysis of Pulping and Bleaching Liquors by Ion Chromatography

Pyrolysis Gas Chromatography
ADVANTAGES OF FTIR

MEASURES ALL WAVELENGTHS SIMULTANEOUSLY.
SPEED
SIGNAL AVERAGING
NO SLITS. MORE ENERGY TO SAMPLE AND DETECTOR.
GREATER ANALYTICAL SENSITIVITY.

HELIUM-NEON LASER FOR WAVELENGTH CALIBRATION.
NECESSARY FOR MANIPULATION OF MULTIPLE SCANS.

DATA SYSTEM
DATA MANIPULATION
DATA STORAGE
LIBRARY SEARCH
Concept and Instrument Attachment for Diffuse Reflection
Procedures

1. Place fiber clumps in diffuse reflectance attachment.

2. Record IR spectra for pulps and cotton linters.
   500 scans per sample in 9 minutes.

3. Subtract spectrum of cotton linters from each pulp.
   Overlay linters spectrum on pulp spectrum on CRT.
   Obtain best baseline subtraction in aliphatic C-H region (2800-3000 cm⁻¹).

4. Integrate area of lignin band at 1510 cm⁻¹.

Figure 1. Diffuse reflectance FTIR spectrum of an unbleached pulp.
Figure 2. Diffuse reflectance FTIR spectrum of cotton linters.

Figure 3. Subtraction spectrum. Unbleached pulp minus cotton linters.
Hypothesis: Intensity of lignin band should be proportional to lignin content of pulp.

IR band area may be used to measure lignin only after it is shown to correlate with results from an accepted lignin method.

Initial results: Correlation with kappa numbers of pulps from one wood.
Requests for "FTIR lignin."
Investigation

1. Obtain IR absorbance, kappa number, and Klason lignin on representative pulps.

2. Determine general utility of correlation between IR absorbance and lignin content.

Results and Discussion

Correlations with Kappa Number and Klason Lignin
Figure 4. IR band area vs. kappa number. All species.

Figure 5. IR band area vs. Klason lignin, %. All species.
Figure 6. IR band area vs. kappa number. Softwood.

Figure 7. IR band area vs. kappa number. Hardwood.
Figure 8. IR band area vs. Klason lignin, %. Softwood.

Figure 9. IR band area vs. Klason lignin, %. Larch kraft.
Comparisons with Other Work

Easier and more sensitive than differential spectra on KBr pellets in dispersive spectrometers.

Easier than multiple internal reflection IR.
Comparison with FTIR on RASH Process Products

RASH products are not conventional pulps.
Data treatment used 18 peaks.

Conclusions

Linear relationships exist between lignin IR band area and kappa number and Klason lignin.
Species differences have little effect.
Wide yield range: 1-20% lignin, 10-120 kappa.
Kraft and ASAQ pulps.

Ability to estimate: ± 4 kappa, ± 0.5% Klason lignin.
Sample size as small as 0.5 mg.
Analysis of Pulping and Bleaching Liquors by Ion Chromatography

Conclusions

Using the electrolytic conductivity detector, IC is a valuable technique for:

- sulfite
- sulfate
- thiosulfate
- chloride
- carbonate

Using the constant potential amperometric detector, IC is of limited value for sulfide.
Conclusions

IC can be used to determine:
- chlorine dioxide
- chlorine
- chlorite
- chlorate
- chloride
- hypochlorite
- oxalate

Problems in Ion Chromatographic Analysis
Studies Needed Before Preparation of T 699 Revision

1. Evaluate UV detector for sulfide determination.
2. Investigate need for dilute HCl dilution of green liquor for sulfate determination.

Conclusions -- UV Detection of Sulfide

1. Detector is less sensitive than amperometric; range 1 - 20 ppm.
   Less extensive sample dilution:
     Easier manipulation
     Reduced oxidative losses of sulfide

2. Antioxidant recommended for best results.
   Ascorbic acid more concentrated than 1 mM interferes in UV detector.

3. Valid results: Quantitative spike recovery and good agreement with potentiometric titrations.

4. Easier detector maintenance

5. Simultaneous determination of sulfide and sulfoxyl anions is impractical.
Conclusions -- Sulfate in Green Liquor

1. Dilution with HCl is unnecessary when samples are analyzed promptly after dilution.

2. Liquors diluted with 0.1% HCl and with deoxygenated water gave comparable results.

Coming soon: Revised TAPPI Test Method(s) for Ion Chromatography

Analysis of Pulping Liquors by Suppressed Ion Chromatography

Analysis of Bleaching Liquors by Suppressed Ion Chromatography
Additional Studies on the Ion Chromatographic Analysis of Pulping Liquors

Current work fine-tuning low level activity

Repeatability values for ion chromatographic analysis of pulping liquors

<table>
<thead>
<tr>
<th></th>
<th>Carbonate</th>
<th>Sulfate</th>
<th>Chloride</th>
<th>Sulfite</th>
<th>Thiosulfate</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor</td>
<td>20</td>
<td>12</td>
<td>50</td>
<td>30</td>
<td>16</td>
<td>NA</td>
</tr>
<tr>
<td>Green liquor</td>
<td>5</td>
<td>4</td>
<td>40</td>
<td>25</td>
<td>3</td>
<td>NA</td>
</tr>
</tbody>
</table>

aRepeatability expressed as percentage of mean.
bNA = not available.
Potential Sources of Error in Ion Chromatographic Analysis of Pulping Liquors

Instability of Liquor Samples

Homogeneity of Liquor and Representative Nature of Sample Taken for Analysis

Dilution Technique

Instability of Samples Diluted for Analysis

Chromatography

Carbonate Calibration lines

<table>
<thead>
<tr>
<th>Date</th>
<th>No. of Standards Run</th>
<th>Correlation Coefficient</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-01-86</td>
<td>6</td>
<td>0.9998</td>
<td>3.86</td>
</tr>
<tr>
<td>8-04-86</td>
<td>3</td>
<td>0.9998</td>
<td>4.90</td>
</tr>
<tr>
<td>8-11-86</td>
<td>4</td>
<td>0.9993</td>
<td>5.16</td>
</tr>
<tr>
<td>8-12-86</td>
<td>5</td>
<td>0.9996</td>
<td>5.30</td>
</tr>
<tr>
<td>8-18-86</td>
<td>5</td>
<td>0.9969</td>
<td>5.85</td>
</tr>
<tr>
<td>8-19-86</td>
<td>6</td>
<td>0.9967</td>
<td>5.32</td>
</tr>
</tbody>
</table>
Sodium Carbonate in Green Liquors, g/L

AM Old column: 40.6
PD New column: 92.7

Lesson: run standard frequently.

Sulfate and Thiosulfate Repeatabilities

<table>
<thead>
<tr>
<th></th>
<th>Sulfate, %</th>
<th>Thiosulfate, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable baseline</td>
<td>3.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Unstable baseline</td>
<td>42.</td>
<td>46</td>
</tr>
</tbody>
</table>
Conclusions

Actions necessary to ensure correct results in IC analysis of pulping liquors:

- Careful dilution of samples
- Prompt injection following dilution
- Running of sufficient standards
- Stop analyses when baseline becomes unstable

Eternal vigilance is the price of accuracy.

(Commonly quoted, "Eternal vigilance is the price of liberty." John Philpot Curran, 1790.)
Pyrolysis Gas Chromatography: Identification of Polymeric Additives and Contaminants in Paper

Use of PGC: To complement FTIR.

Especially for unknowns which are

- nonvolatile
- crosslinked and insoluble
- small in amount
- indistinguishable from other materials via infrared
Characteristics of pyrograms ("fingerprints"):

Affected by

- instrumentation
- pyrolysis conditions
- GC conditions

Thus each laboratory must make own library of pyrograms.

Features desired in pyrograms:

- characteristic of compound or class of compounds
- reproducible
- interpretable
Results and Discussion
Figure 2. Pyrolysis gas chromatography of polyisobutylene.
Figure 3. Pyrolysis gas chromatography of a rewinder deposit.

Future Work

To improve interpretability of pyrograms:

- pyrolysis and GC conditions
- sequential pyrolysis
- "external pyrolysis"
- identification via characteristic ions (mass spectrometer)

Expand library of pyrograms

Test with "unknowns"
Project 3288

FINE STRUCTURE OF WOOD PULP FIBERS

R. H. Atalla

Project 3521

RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE

R. H. Atalla
FINE STRUCTURE OF WOOD PULP FIBERS

RAMAN MICROPROBE STUDIES OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE

OUTLINE

- The basic premises underlying the programs
- Key topics currently incorporated into our research programs
- Overview of the key findings of prior work, and their implications
- Summary of recent results
- Looking ahead
BASIC PREMISES

Conceptual:

I. Aggregation and organization at the molecular level are primary determinants of the properties of wood fibers, and of their response to the different unit operations in pulping and paper-making. Thus, they also determine the properties of composites fabricated from wood-pulp fibers.

II. The stability of structures fabricated from wood pulp fibers, and the properties of such structures, are dependent on the capacity of the fibers to thermalize, without any irreversible changes, any energy imparted to them, whether it is mechanical, physical, or photochemical; this capacity is determined by structure and organization at the molecular level.

III. Investigation of molecular aggregation and organization requires methods of measurement that can probe structure without disrupting it.

Approach Evolving From the Above Premises:

I. Investigate the factors which determine the patterns of aggregation at the molecular level, and how these factors are influenced by the intensive variables which define process conditions.

II. Develop methods for characterizing molecular structure and organization for use in pursuit of Objective I, and for investigation of the relationships between structure and properties which are relevant to performance.
KEY TOPICS CURRENTLY INCORPORATED IN OUR FUNDED, EXPLORATORY, AND STUDENT RESEARCH PROGRAMS:

1. **The degree to which the composite nature of native celluloses influences their properties and those of cellulosic fibers from higher plants (wood, cotton, ramie). Two classes of properties are of interest:**
   
   (a) **Chemical reactivity, and the response to various solvating and swelling environments;**
   
   (b) **Physical and mechanical properties.**

2. **Development of methods, both experimental and conceptual, for characterization of the structures of native and regenerated celluloses, with particular emphasis on native structures.**

3. **The patterns of aggregation of cellulose with other cell wall polysaccharides, mainly hemicelluloses, the influence these may have on our measurement of order in cellulose, as well as their effects on properties.**

4. **The patterns of organization of lignin in wood cell walls, and their influence on fiber structure and properties.**

5. **The photophysics of electronic excitation in native lignin, and the manner in which the patterns of excitation are altered by interaction with molecular oxygen.**
OVERVIEW

3288: FINE STRUCTURE OF WOOD PULP FIBERS

1. STUDIES ON POLYMORPHY IN NATIVE CELLULOSE

2. QUANTITATIVE ANALYSIS OF THE STRUCTURE OF PULP FIBERS ON THE BASIS OF RAMAN SPECTROSCOPY

3. PROTON NMR STUDIES OF THE EFFECTS OF REFINING ON THE MOBILITY OF BOUND WATER
ABSORPTION
\[ \text{IR} \]
\[
\begin{align*}
\text{M} + h\nu_v & \rightarrow \text{M}^* \\
\text{EMISSION} & \\
\text{M}^* & \rightarrow \text{M} + h\nu_v
\end{align*}
\]
\[ 50 < \nu_v < 4000 \text{ cm}^{-1} \]
\[ 200 \mu \text{m} \quad 2.5 \mu \text{m} \]
\[ \Delta \mu \neq 0 \]

STOKES
\[ \text{RAMAN} \]
\[
\begin{align*}
\text{M} + h\nu_0 & \rightarrow \text{M}^* + h(\nu_0 - \nu_v) \\
\text{ANTI-STOKES} & \\
\text{M}^* + h\nu_0 & \rightarrow \text{M} + h(\nu_0 + \nu_v)
\end{align*}
\]
\[ \nu_0 \equiv 20,000 \text{ cm}^{-1} \]
\[ 5000 \text{ Å} \]
\[ \Delta \alpha \neq 0 \]

INFRARED AND RAMAN PROCESSES
Raman spectra of *Valonia ventricosa* cellulose, *Acetobacter xylinum* cellulose, Microcrystalline cotton cellulose, and high-crystallinity cellulose II.
Schematic representation of conformations $k_I$ and $k_{II}$. 

Legend: 
- Carbon 
- Oxygen 
- Hydrogen 
- Covalent bond 
- Hydrogen bond
$^{13}$C CP-MAS spectra of various celluloses: A - Ramie; B - cotton linters; C - regenerated cellulose I; D - Acetobacter xylinum cellulose; E - Valonia ventricosa cellulose. The "X" marks the small first spinning side band of linear polyethylene added as an internal standard; its centerband at 33.6 ppm is not included in this display.
Comparison of the $^{13}$C CP-MAS spectra of cellulose II and the spectra of the two proposed crystalline forms of cellulose I, namely, $I_\alpha$, and $I_\beta$. An "X" or a gap mark locations of the first spinning sideband of the linear polyethylene chemical shift standard.
Comparison of the Raman spectra of Valonia, ramie, and mercerized ramie. Spectra were recorded with the electric vector both at 0 and 90° to the chain axis.

(A) Low Frequency Region
Comparison of the Raman spectra of Valonia, ramie, and mercerized ramie. Spectra were recorded with the electric vector both at 0 and 90° to the chain axis.

(B) High Frequency Region
OVERVIEW

3288: FINE STRUCTURE OF WOOD PULP FIBERS

1. STUDIES ON POLYMORPHY IN NATIVE CELLULOSE

2. QUANTITATIVE ANALYSIS OF THE STRUCTURE OF PULP FIBERS ON THE BASIS OF RAMAN SPECTROSCOPY

3. PROTON NMR STUDIES OF THE EFFECTS OF REFINING ON THE MOBILITY OF BOUND WATER

STUDIES ON CELLULOSE

1. VANDERHART - SOLID STATE $^{13}$C NMR OF CELLULOSES

2. WILEY - RAMAN MICROPROBE STUDIES OF FIBRILLAR CELLULOSES

3. ISOGAI - REGENERATION AND MERCERIZATION OF DIFFERENT NATIVE CELLULOSES; AMORPHOUS CELLULOSES AND BLENDS WITH OTHER $\beta$1-4 LINKED HOMOPOLYMERS

4. WOITKOVICH - CELLULOSE DERIVATIVES DISPLAYING THE MEMORY EFFECT (HAYASHI); CELLULOSES DEGRADED BY WHITE ROT FUNGI (BLANCHETTE)

5. WHITMORE - ALGAL AND BACTERIAL CELLULOSES, CULTURE AND DUETERATION; PREPARATION OF $I_\beta$ CELLULOSES
STUDIES ON CELLULOSE

1. VanderHart - Solid State $^{13}$C NMR of Celluloses

2. Wiley - Raman Microprobe Studies of Fibrillar Celluloses

3. Isogai - Regeneration and Mercerization of Different Native Celluloses; Amorphous Celluloses and Blends with Other $\beta$1-4 Linked Homopolymers

4. Woitkovich - Cellulose Derivatives Displaying the Memory Effect (Hayashi); Celluloses Degraded by White Rot Fungi (Blanchette)

5. Whitmore - Algal and Bacterial Celluloses, Culture and Dueteration; Preparation of $\beta$ Celluloses

OVERVIEW

3521-2: Raman Microprobe Studies of Molecular Structure and Organization in the Native State of Woody Tissue

I. Current Microprobe Studies

II. Opportunities Arising from the New Raman Microprobe System

III. Studies on Highly Crystalline Algae

Current Microprobe Studies:

A. Molecular Orientation of Lignin and Cellulose in Native and Delignified Woody Tissue

B. Compositional Variation within Cell Walls and Between Adjacent Cells

C. Studies on Valonia and Ramie Celluloses
CELL WALL SECTIONS
Scattering Geometries

I - Electric vector (EV) direction parallel to the cell wall surface in a longitudinal section;
II - EV perpendicular to the cell wall surface (LS);
III - EV parallel to the cell wall surface in a cross section, and
IV - EV perpendicular to the cell wall surface (CS).
Polarized Raman spectra of a spot lying in the secondary wall - longitudinal section (LS) of spruce.
Polarized Raman spectra of a spot lying in the secondary wall - cross section (CS) of spruce.
CONCLUSIONS

(Secondary Wall)

Aromatic rings in the lignin structural units are often organized parallel to the plane of the surface of the cell wall.

Compositional variations in the distribution of cellulose and lignin are detected.

Such differences in composition are more prominent between the walls of different cells than within a particular cell wall.

LIGNIN & MICROPROBE STUDIES

1. Assessing new system

2. Agarwal - Effect of molecular oxygen; new experimental methods

3. Bond - Search for lignin precursors in tissue culture cell walls; correlations between Raman bands of lignin with IR band and Klasson lignin in groundwood and partially delignified groundwood
COMPARISON OF RAMAN MICROPROBE SYSTEMS

CURRENT SYSTEM:

Source - Continuous Argon Ion Laser

Spectrometer - Double Monochromator with coupled gratings, designed for single channel detection

Detector - Cooled photomultiplier

NEW SYSTEM:

Sources - Solid state/dye laser system capable in the sub-picosecond pulse range; present continuous laser systems

Spectrometer - Triple monochromator optimized for multichannel detection

Detectors - Diode array detectors operable continuously or in gated models
FUTURE WORK

1. QUESTIONS REGARDING NATURE OF CRYSTALLINITY IN WOOD CELLULOSE

2. AGGREGATION STUDIES AND NATURE OF AMORPHOUS CELLULOSES AND CELLULOSE/HEMICELLULOSE BLENDS

3. MICROPROBE MAPPING OF WOOD AND CHEMICALLY TREATED WOOD

4. PHOTOPHYSICS OF LIGNIN

OPPORTUNITIES ARISING FROM THE NEW RAMAN MICROPROBE SYSTEM

A. MAPPING OF BOTH ORIENTATIONAL AND COMPOSITIONAL VARIATIONS IN NATIVE WOODY TISSUE

B. MAPPING OF THE EFFECTS OF DELIGNIFICATION REACTIONS ON LIGNIN DISTRIBUTION ACROSS THE CELL WALLS

C. TIME RESOLVED STUDIES TO SEPARATE RAMAN SPECTRA FROM FLUORESCENCE, AND TO STUDY THE RISE AND DECAY OF ELECTRONIC EXCITATION

D. THE POSSIBILITY OF AN ON-LINE LIGNIN DETECTOR
Project 3473-1

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES

D. T. Clay
J. H. Cameron
T. E. Farrington
KRAFT CHEMICAL RECOVERY

PRESENTATION OUTLINE

OVERVIEW  
FUME GENERATION  
SINGLE PARTICLE BURNING  
SPRAY NOZZLE DEVELOPMENT  
FUNDAMENTALS OF COMBUSTION (DOE)  
IMPLEMENTATION  

DAVE CLAY  
JOHN CAMERON  
DAVE CLAY  
TED FARRINGTON  
DAVE CLAY  
DAVE CLAY

IPC CHEMICAL RECOVERY GROUP

FACULTY
Tom Grace  
John Cameron  
Dave Clay

STAFF
Orlie Kuehl  
Don Sachs  
Steve Lien

STUDENTS
8 Ph.D.
2 M.S.
RESPONSIBILITIES

- Two courses per faculty per year
- Direct major research efforts
  - Black liquor burning
  - Furnace modeling
  - Furnace corrosion
  - Evaporation/drying
  - Calcination
- Other efforts
  - Continuing education course
  - API/BLRBAC explosion monitoring
  - NRC explosive violence
  - Industry consulting
BLACK LIQUOR BURNING

EXPERIMENTAL PHENOMENA STUDY/MODELING

<table>
<thead>
<tr>
<th>Topic</th>
<th>Lead Researcher</th>
<th>Funding Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>Mark Robinson</td>
<td>Ph.D. Summer 1987</td>
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<tr>
<td>Sulfur Release</td>
<td>Frank Harper</td>
<td>Ph.D. Winter 1989</td>
</tr>
<tr>
<td>Particle Burning</td>
<td>Kathy Crane</td>
<td>Ph.D. Spring 1989</td>
</tr>
<tr>
<td>Pile Burning</td>
<td>Greg Aiken</td>
<td>Ph.D. Fall 1987</td>
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<tr>
<td>Particle Fuming</td>
<td>Chris Verrill</td>
<td>M.S. Spring 1987</td>
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<tr>
<td>Fume Deposition</td>
<td>Kris Goerg</td>
<td>Ph.D. Spring 1989</td>
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IPC FUNDED

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<tr>
<td>Fume Formation</td>
<td>Complete</td>
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<tr>
<td>Compositional Impacts on Burning</td>
<td>On-Going</td>
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<tr>
<td>Hydrogen Species and Smelt Reactions</td>
<td>Initiated</td>
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DOE FUNDED

<table>
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<th>Topic</th>
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<tr>
<td>In-Flight Processes</td>
<td>Winter 1987</td>
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<tr>
<td>Bed Burning</td>
<td>Fall 1987</td>
</tr>
<tr>
<td>Fume Formation/Deposition</td>
<td>Summer 1988</td>
</tr>
<tr>
<td>Furnace Simulation</td>
<td>Winter 1989</td>
</tr>
<tr>
<td>Black Liquor Spray Characterization</td>
<td>Proposed Fall 1986</td>
</tr>
</tbody>
</table>
FURNACE MODELING
Computer Steady-State Simulations

**Academic Funded**

- **Multiple Droplet Burning**
  - Allan Walsh
  - Ph.D. Winter 1989

- **Char Bed Burning**
  - Dan Sumnicht
  - Ph.D. Summer 1989

- **Overall Recovery Furnace**
  - Andrew Jones
  - Ph.D. Winter 1989

**Furnace Corrosion**

**Academic Funded**

- **Lower Furnace Corrosion**
  - Greg Kulas
  - Ph.D. Spring 1988

**Evaporation/Drying**

**Experimental Phenomena Study/Modeling**

- Ph.D. Thesis
  - 1 to begin soon

**Calcination**

**Experimental Phenomena Study/Modeling**

- **Lime Sintering**
  - John Fuller
  - M.S. Spring 1987
FINAL GOALS

COMPREHENSIVE THEORY OF BLACK LIQUOR COMBUSTION

MATHEMATICAL TOOLS TO EVALUATE

OPTIMUM BLACK LIQUOR

BURNING STRATEGIES

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES

HIGHLIGHTS

- Char burning reports issued
- Fume report issued
- Technical papers issued on swelling, sulfur release, and char gasification
- Initiated work with hydrogen species and smelt
- Successfully operating DOE flow reactors
FUNDED RESEARCH

A) FUME GENERATION DURING SULFIDE OXIDATION

B) REACTIONS INVOLVING $H_2$ IN THE KRAFT FURNACE

REACTIONS INVOLVING HYDROGEN

1) $Na_2SO_4 + 4H_2 \rightarrow Na_2S + 4H_2O$

2) $Na_2CO_3 + H_2 \rightarrow 2 NaOH + CO$

STUDENT RESEARCH

GREGG AIKEN: Ph.D. CANDIDATE, "A STUDY OF THE CO/CO_2 RATIO GENERATED FROM CHAR PILE OXIDATION"

KRISTIN GOERG: Ph.D. CANDIDATE, "FUME DEPOSITION"

CHRISTOPHER VERRILL: M.S./Ph.D. CANDIDATE, "FUME GENERATION DURING KRAFT CHAR OXIDATION"

JOHN FULLER: M.S. CANDIDATE, "EFFECT OF NONPROCESS ELEMENTS ON LIME MUD SINTERING"
Figure 1. Gas phase oxidation enhanced vaporization.

Figure 2. Experimental system.
Figure 3. Fume particles collected during sulfide oxidation.
Table 2. Effect of sulfate level on fume generation rate.

<table>
<thead>
<tr>
<th>Purge Rate = 1.0 L/min at 2.1% O₂, and Temperature = 982°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 39</td>
</tr>
<tr>
<td>Na₂CO₃ = 0.77 mole</td>
</tr>
<tr>
<td>Na₂S  = 0.03 mole</td>
</tr>
<tr>
<td>Na₂SO₄ = 0.00 mole</td>
</tr>
<tr>
<td>Run 43</td>
</tr>
<tr>
<td>Na₂CO₃ = 0.57 mole</td>
</tr>
<tr>
<td>Na₂S  = 0.03 mole</td>
</tr>
<tr>
<td>Na₂SO₄ = 0.30 mole</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Fume Generation Rate, g/min</th>
<th>Fume Generation Rate, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0157</td>
<td>0.0125</td>
</tr>
<tr>
<td>10</td>
<td>0.0159</td>
<td>0.0127</td>
</tr>
<tr>
<td>15</td>
<td>0.0161</td>
<td>0.0121</td>
</tr>
<tr>
<td>20</td>
<td>0.0145</td>
<td>0.0149</td>
</tr>
<tr>
<td>25</td>
<td>0.0158</td>
<td>0.0103</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>0.0103</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>Ave.</td>
<td>0.0158 ± 0.0006</td>
<td>0.0130 ± 0.0019</td>
</tr>
</tbody>
</table>

Table 3. Effect of sulfide level on fume generation rate.

Conditions: Temperature = 954°C

<table>
<thead>
<tr>
<th>N₂ Flow Rate = 1.0 L/Min</th>
<th>O₂ Flow Rate = 0.021 L/min</th>
<th>Fume Generation Rate g/min ± Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃ mole</td>
<td>Na₂S mole</td>
<td>Sulfidity, %</td>
</tr>
<tr>
<td>0.77</td>
<td>0.03</td>
<td>3.7</td>
</tr>
<tr>
<td>0.60</td>
<td>0.20</td>
<td>25.0</td>
</tr>
<tr>
<td>0.55</td>
<td>0.25</td>
<td>31.0</td>
</tr>
</tbody>
</table>
Table 5. Effect of purge rate on fume generation.

Initial Melt Conditions: Na₂CO₃ = 0.77 mole
Na₂S = 0.03 mole
Temperature = 927°C

<table>
<thead>
<tr>
<th>Run</th>
<th>N₂, L/min</th>
<th>Air, L/min</th>
<th>Total N₂, L/min</th>
<th>Fume Generation Rate ± Std. Dev., g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.04</td>
<td>0.1</td>
<td>0.48</td>
<td>0.00680 ± 0.00032</td>
</tr>
<tr>
<td>51</td>
<td>0.6</td>
<td>0.1</td>
<td>0.68</td>
<td>0.00850 ± 0.00076</td>
</tr>
<tr>
<td>52</td>
<td>0.8</td>
<td>0.1</td>
<td>0.88</td>
<td>0.01004 ± 0.00042</td>
</tr>
<tr>
<td>38</td>
<td>0.9</td>
<td>0.1</td>
<td>0.98</td>
<td>0.01024 ± 0.00032</td>
</tr>
<tr>
<td>53</td>
<td>1.06</td>
<td>0.1</td>
<td>1.14</td>
<td>0.01204 ± 0.00042</td>
</tr>
<tr>
<td>54</td>
<td>1.23</td>
<td>0.1</td>
<td>1.31</td>
<td>0.01474 ± 0.00198</td>
</tr>
</tbody>
</table>

Table 6. Effect of two purge tubes on fume generation rate.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp., °C</th>
<th>N₂ Flow Rate, L/min</th>
<th>O₂ Flow Rate, L/min</th>
<th>Fuming Rate, g/min ± Std. Dev.</th>
<th>Fuming Rate with Single Purge Tube, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>127</td>
<td>953</td>
<td>1.03</td>
<td>0.020</td>
<td>0.0129 ± 0.001</td>
<td>0.0126</td>
</tr>
<tr>
<td>128</td>
<td>957</td>
<td>1.03</td>
<td>0.0426</td>
<td>0.0163 ± 0.001</td>
<td>0.0156</td>
</tr>
<tr>
<td>129</td>
<td>957</td>
<td>1.01</td>
<td>0.0634</td>
<td>0.0156 ± 0.001</td>
<td>0.0172</td>
</tr>
</tbody>
</table>

Table 8. Effect of purge tube location on fume generation during sulfide oxidation.

Initial Conditions
Na₂CO₃ = 0.77 mole
Na₂S = 0.03 mole
Temperature = 955°C

<table>
<thead>
<tr>
<th>Purge Introduced Below Melt's Surface</th>
<th>Oxidation Rate, mole O₂ consumed/min x 10⁴</th>
<th>Fume Rate, g/min</th>
<th>Purge Introduced Above Melt's Surface</th>
<th>Oxidation Rate, mole O₂ consumed/min x 10⁴</th>
<th>Fume Rate, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.38</td>
<td>0.0106</td>
<td>0.84</td>
<td>12.00</td>
<td>0.00146</td>
<td>0.00100</td>
</tr>
<tr>
<td>9.46</td>
<td>0.0134</td>
<td>3.88</td>
<td>17.70</td>
<td>0.00079</td>
<td>0.00044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 8. Fume generation in a rising gas bubble.

Figure 9. Relative levels of $O_2$, Na, and $Na_2S$ at bubble interface during sulfide oxidation.
Na<sub>2</sub>CO<sub>3</sub> + \( \frac{1}{2} \)Na<sub>2</sub>S \rightleftharpoons \frac{1}{2}Na<sub>2</sub>SO<sub>4</sub> + CO<sub>2</sub> + 2Na

Figure 7. Fume generation under oxidizing conditions.

\[
\frac{d(N_2O)}{dt} = S \text{ Pt Kg} \frac{N_2O}{N_2}
\]

\[
\frac{dF}{dt} = - S K
\]

\[
\frac{dF}{d(N_2O)} = - \frac{K N_2}{\text{Kg Pt} N_2O}
\]

\[
F_M = \frac{K N_2}{\text{Kg Pt}} \left[ \ln \left( N_{02I} \right) - \ln \left( N_{02f} \right) \right]
\]
Figure 10. Effect of $O_2$ on fume generation in $N_2$, Ar, and He.
STUDENTS:
  JAMES BOND
  ERIN BYERS
  INGEGARD UHLIN
  TAN ZHENG - special student

STAFF:
  REBECCA WHITMORE
  CLARK WOITKOVICH

FACULTY:
  UMESH AGARWAL
  RAJAI ATALLA
TABLE OF CONTENTS

SUMMARY 1
PREFACE 2
OVERVIEW OF RESULTS TO DATE 4
Studies on Woody Tissue 5
Studies on Celluloses 6
The Multichannel Spectrometer System 7
Other Studies 8
LITERATURE CITED 10

APPENDIX

Raman microprobe evidence for lignin orientation in cell walls of native woody tissue

Recording Raman spectra from plant cell walls

In Situ Raman microprobe studies of plant cell walls:
macromolecular organization and compositional variability in the secondary wall of Picea mariana (Mill.) B. S. P.

Band assignments in the Raman spectra of cellulose. Carbohydrate Research, special issue on physical chemical studies on macromolecular carbohydrates


A highly crystalline cellulose from Rhizoclonium Heiroglyphicum
R. H. Atalla, R. E. Whitmore, and D. L. VanderHart.

Oxygen sensitive background in the Raman spectra of woody tissue
Proc. of 10th Int. Conf. on Raman Spectroscopy, Eugene, Oregon
U. P. Agarwal and R. H. Atalla, in press.
MICROFIBRILLAR CELLULOSE (WHATMAN CF-1)

Freeze-dried

Wet

Mercerized

Regenerated from SO₂/DEA/DMSO into water

Regenerated from SO₂/DEA/DMSO into 20% NaOH

WAVENUMBERS cm⁻¹
OTHER RECENT RESULTS:

----- DEHYDRATION EFFECTS

----- RESOLUTION OF THE OH REGION OF THE RAMAN SPECTRA INTO $I/\alpha$ AND $I/\beta$ COMPONENTS

----- OBSERVATION OF CONVERSION OF $I/\alpha$ CELLULOSE TO THE $I/\beta$ FORM UPON REVERSION FROM CELLULOSE III

----- ANALYSES OF HAYASHI RESULTS WHICH SUGGEST CONVERSION OF $I/\alpha$ CELLULOSE TO THE $I/\beta$ FORM UPON ACETYLATION AND SAPONIFICATION
H OH CH

middle lamella

H H O

primary wall

two-layered secondary wall

H H

HO

macrofibril

HO HO

micrafibril

cellulose molecule

~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~~~~~~~~

1
AGENDA

PULPING PROCESSES PAC MEETING
THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN
OCTOBER 20-21, 1986

MONDAY, OCTOBER 20, 1986
CONTINUING EDUCATION CENTER SEMINAR ROOM

7:00 BREAKFAST

8:15 CONVENE
A. Rosen

8:20 RESEARCH OVERVIEW
E. Malcolm

8:40 PROJECT PRESENTATIONS
D. Dimmel
T. McDonough

Fundamentals of Selectivity in Pulping and Bleaching
(Projects 3475)

Improved Processes for Bleached Pulp
(Projects 3474)

10:15 BREAK

D. Easty
R. Atalla

Development and Application of Analytical Techniques
(Project 3477)

Fine Structure of Wood Pulp Fibers
(Projects 3288 and 3521)

12:00 LUNCH
1:00 PROJECT PRESENTATIONS (CONTINUED)

**KRAFT CHEMICAL RECOVERY**

- **Fundamental Processes in Alkali Recovery Furnaces**
  (Project 3473-1)
  - T. Grace
  - T. J. Cameron
  - D. Clay

- **Black Liquor Combustion**
  (DOE Project 3473-6)

3:00 BREAK

**HIGH-YIELD PULPS**

- **Separation of Strong, Intact Fibers**
  (Project 3566)
  - T. McDonough
  - S. Aziz

- **Fundamentals of Brightness Stability**
  (Project 3524)
  - E. Malcolm
  - U. Agarwal
  - S. Lebo

5:30 SOCIAL HOUR

DINNER

7:00 EVENING DISCUSSIONS

- **Fiber Bonding**
  - G. Baum
  - Guest Speaker
  - Staff/Students

- **Student Research**

8:30 END OF MONDAY SESSION

**TUESDAY MORNING - OCTOBER 21, 1986**

7:00 BREAKFAST (CEC)

8:00 COMMITTEE MEETING (CEC)

12:00 LUNCH (CEC) END OF TUESDAY SESSION

**NEXT MEETING: MARCH 24-25, 1987**
ATTENDANCE LIST
PULPING PROCESSES PROJECT ADVISORY COMMITTEE MEETING
OCTOBER 20-21, 1986

COMMITTEE MEMBERS

Mr. Dean W. DeCrease
Hammermill Paper Company

Mr. Wendall B. Hammond
Willamette Industries

Mr. Gerald R. Haw
Tennessee River Pulp & Paper Company

Dr. Donald C. Johnson
Weyerhaeuser Company

Dr. Samuel McKibbins
Champion International

Dr. John K. Rogers
James River Corporation

Dr. Ivan B. Schrodt
Kimberly-Clark Corporation

Mr. Robert W. Snow
Owens-Illinois, Inc.

Dr. James Turnbull
MacMillan Bloedel Inc.

Dr. Benjamin F. Ward
Westvaco Corporation

GUESTS

Dr. Richard G. Barker
Union Camp Corporation

Mr. William Fisher
Owens-Illinois, Inc.

Mr. Phil Slagle
Consolidated Papers, Inc.

Mr. Dale Benjamin
Potlatch Corporation

Mr. Sam Lin
Owens-Illinois, Inc.

Dr. Phil Smith
Weyerhaeuser Company

Mr. Dennis Betz
P. H. Glatfelter Company

Mr. Mark Nelson
Thilmany Pulp & Paper Co.

Mr. Glen Smith
Mead Corporation

Mr. William C. Bliesner
Thilmany Pulp & Paper Co.

Mr. W. R. Nelson
Green Bay Packaging

Dr. Seika Tay
Abitibi-Price Inc.

Ms. Nancy J. Elsbury
Potlatch Corporation

Dr. Alfred Nissan
Westvaco Corporation

Mr. Krishna Vemuri
Thilmany Pulp & Paper Co.

Dr. Tim Estes
Packaging Corporation

Mr. I. Bruce Sanborn
Consolidated Papers, Inc.

Mr. Paul C. Wollwage
Weyerhaeuser Company

STAFF

Umesh Agarwal
Rajai Atalla
Salman Aziz
Sally Berben
LeRoy Borchardt
John Cameron
Dave Clay
Hugh Corbett
Don Dimmel
Dwight Easty
Tom Grace
Orlin Kuehl
Steve Lien
Earl Malcolm
Tom McDonough
Earl Malcolm
Dave Rades
Don Sachs
Lowell Sell
Art Webb
Harry Cullinan
Richard Matula
Wendall Smith
Douglas Wahren
Assignments for summarizing project activity are indicated below. Your writeup should be in Al Rosen's hands by November 27, 1986. If you have any complaints regarding your assignment, please contact Al!

<table>
<thead>
<tr>
<th>Project</th>
<th>Committee Member</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fundamentals of Selectivity in Pulping and Bleaching (Project 3475)</td>
<td>D. Johnson</td>
</tr>
<tr>
<td>Improved Processes for Bleached Pulp (Project 3474)</td>
<td>D. DeCrease</td>
</tr>
<tr>
<td>Development and Application of Analytical Techniques (Project 3477)</td>
<td>R. Snow</td>
</tr>
<tr>
<td>Fine Structure of Wood Pulp Fibers (Projects 3288 and 3521)</td>
<td>B. Ward</td>
</tr>
<tr>
<td>Fundamental Processes in Alkali Recovery Furnaces (Project 3473-1)</td>
<td>J. Rogers</td>
</tr>
<tr>
<td>Black Liquor Combustion (DOE Project 3473-6)</td>
<td>J. Rogers</td>
</tr>
<tr>
<td>Separation of Strong, Intact Fibers (Project 3566)</td>
<td>S. McKibbins</td>
</tr>
<tr>
<td>Fundamentals of Brightness Stability (Project 3524)</td>
<td>J. Turnbull</td>
</tr>
</tbody>
</table>
CONCLUSIONS

1) Fume production is a dynamic process.

2) Sodium vaporization can be significant during sulfide oxidation.

3) Fume generation during sulfide oxidation results from gas phase oxidation of sodium.
BLACK LIQUOR BURNING
(Task of Project 3473-1)

OBJECTIVE

CHARACTERIZE THE BURNING PHENOMENA OF A VARIETY OF BLACK LIQUORS USING QUANTITATIVE TEST METHODS

RATIONALE

• MINIMAL FUNDAMENTAL KNOWLEDGE OF THE BURNING PROCESS
• THERMAL EFFICIENCY INCREASES NEEDED
• INCREMENTAL CAPACITY NEEDED
• FOUNDATION FOR FUTURE RECOVERY PROCESSES
Black Liquor Droplet Burning
Air: 8.3 ft/sec, 1470°F
Droplet: 8 mg (2.2 mm ID), 76% Solids
RESEARCH APPROACH

FUNDAMENTAL STUDIES

- DRYING - M. ROBINSON
- SWELLING - P. MILLER
- BURNING - B. MORELAND
- SULFUR RELEASE - K. CRANE

SURVEY STUDIES

- ANALYTICAL TESTS
- BURNING TESTS

COLLABORATIVE STUDIES

- MIKKO HUPA
- WEVERHAEUSER PAPER COMPANY

SURVEY APPROACH

- USE MILL LIQUORS
- CONDUCT CHEMICAL AND COMBUSTION TESTS
- ANALYZE DATA FOR EMPIRICAL INTERRELATIONSHIPS
- DESIGN CONTROLLED TESTS TO CONFIRM CONTROLLING PHENOMENA
**SINGLE PARTICLE REACTOR**

- Microbalance
- Alumina Tube
- Gas In from Heater
- Flow Straightener
- Radiant Heater
- Sample
- Optical Trench to Diagram
- Lower unit (moveable)
- Insulation

Note: All gas passages are 50mm x 50mm
BLACK LIQUOR SOURCE CHARACTERIZATION

NUMBER: 52 MILL SAMPLES  
2 SYNTHETIC SAMPLES

MILL LOCATIONS: 21

COUNTRY: U.S. (14, ALL REGIONS), CANADA (3), BRAZIL (2), SWEDEN (2)

WOOD SUPPLY: SOFTWOOD, HARDWOOD, MIXTURE

TYPE OF MILL LIQUOR: KRAFT (46), SODA (1), CARBONATE-NONSULFUR (1),  
NSSC (1), GLSC (2), ALKALINE SULFITE (1)

DIGESTER KAPPA NO.: HARDWOOD 10-19.5  
(SOFTWOOD) SOFTWOOD 21-87.5

OXIDIZED: YES (11), NO (43)

BURNING ASSESSMENT: GOOD TO POOR

SURVEY ANALYTICAL RESULTS

33 N.A. KRAFT MILLS  
(BASED ON OVEN-DRY SOLIDS)

<table>
<thead>
<tr>
<th>Process Measures</th>
<th>Average ± 95% CLA</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. HIGH HEATING VALUE, BTU/LB</td>
<td>6010 ± 125</td>
<td>5190-6890</td>
</tr>
<tr>
<td>B. SULFATED ASH, % AS NaOH</td>
<td>36.7 ± 0.8</td>
<td>41.8-31.9</td>
</tr>
<tr>
<td>C. RESIDUAL ACTIVE ALKALI, % AS</td>
<td>4.6 ± 1.1</td>
<td>0-13</td>
</tr>
</tbody>
</table>

Composition Measures

<table>
<thead>
<tr>
<th>Measure</th>
<th>Average ± 95% CLA</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. NaOH</td>
<td>3.8 ± 0.9</td>
<td>0-14.5</td>
</tr>
<tr>
<td>B. Na₂S</td>
<td>2.3 ± 0.7</td>
<td>0-6.1</td>
</tr>
<tr>
<td>C. Na₂CO₃</td>
<td>8.2 ± 0.6</td>
<td>3.6-12.5</td>
</tr>
<tr>
<td>D. Na₂SO₄</td>
<td>4.0 ± 0.9</td>
<td>0.7-9.5</td>
</tr>
</tbody>
</table>
SURVEY ANALYTICAL RESULTS
33 N.A. Kraft Mills
(BASED ON OVEN-DRIED SOLIDS)

Elemental Analysis (% ODS)

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>VALUE</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Na</td>
<td>19.0 ± 0.4</td>
<td>17.1-21.0</td>
</tr>
<tr>
<td>B. K</td>
<td>2.0 ± 0.2</td>
<td>1.0-3.1</td>
</tr>
<tr>
<td>C. S</td>
<td>4.8 ± 0.4</td>
<td>3.5-6.8</td>
</tr>
<tr>
<td>D. Cl</td>
<td>0.9 ± 0.4</td>
<td>0.21-5.5</td>
</tr>
<tr>
<td>E. C</td>
<td>36.6 ± 1.1</td>
<td>34.0-40.9</td>
</tr>
<tr>
<td>F. H</td>
<td>3.4 ± 0.2</td>
<td>3.1-4.0</td>
</tr>
<tr>
<td>G. O</td>
<td>33.4 ± 1.8</td>
<td>29.7-35.6</td>
</tr>
</tbody>
</table>

Sample Balance: 100.1 ± 5.0

SURVEY BURNING RESULTS
33 N.A. Kraft Mills

Burning Tests A

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Average ± 95% CL</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis swollen volume, CC/g initial solids</td>
<td>95 ± 16</td>
<td>7-172</td>
</tr>
<tr>
<td>Combustion swollen volume, CC/g initial solids</td>
<td>26 ± 4</td>
<td>11-53</td>
</tr>
<tr>
<td>Pyrolysis normalized rate x 100, sec⁻¹</td>
<td>2.4 ± 0.3</td>
<td>1.5-4.7</td>
</tr>
<tr>
<td>Combustion normalized rate x 100, sec⁻¹</td>
<td>20 ± 7</td>
<td>8.5-52.1</td>
</tr>
</tbody>
</table>

A Combustion in air at 800°C (1470°F)
Pyrolysis in N₂ at 500°C (930°F)
SURVEY BURNING RESULTS
33 N.A. KRAFT MILLS

<table>
<thead>
<tr>
<th>Combustion Times A</th>
<th>Average ± 75% CL</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to Ignition, sec</td>
<td>1.6 ± 0.2</td>
<td>0.7-2.4</td>
</tr>
<tr>
<td>Time from Ignition to Max. Volume, sec</td>
<td>2.3 ± 0.2</td>
<td>1.4-4.0</td>
</tr>
<tr>
<td>Time from Ignition to Smelt Bead, sec</td>
<td>4.2 ± 0.2</td>
<td>3.1-6.0</td>
</tr>
<tr>
<td>Total, sec</td>
<td>5.8 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

A In air at 800°C (1470°F)
Pyr Sv (cc/gm solid) = 146

+ 3.96 (% CL)
+ 24.5 (sec\(^{-1}\), pyrolysis rate x 100)
- 24.4 (sec, time from ign. to smelt bead)
- 3.37 (% Na\(_2\)CO\(_3\) + Na\(_2\)SO\(_4\))
+ 7.00 (% Na\(_2\)S)
- 0.389 (% hardwood)
+ 0.342 (kappa number)
+ 4.17 (pulping process, arbitrary scale)

This equation's \( R^2 = 0.80 \).
PYR Sv (cc/gm solid) = 106
+ 1.17 (KAPPA NUMBER)
+ 19.8 (% CL)
+ 20.0 (sec⁻¹, pyrolysis rate x 100)
- 4.10 (% Na₂CO₃ + Na₂SO₄)
- 27.3 (sec, time from ign. to max volume)

This equation's $R^2 = 0.80$. 
Both relationships show that

Pyr SV increases as - Kappa number increases
- Liquor Cl content increases
- Pyrolysis rate increases

Pyr SV decreases as - Na$_2$CO$_3$ + Na$_2$SO$_4$ increases
- Burning time increases

SYNTHETIC BLACK LIQUOR PRODUCTION CONDITIONS

Constant Cooking Conditions

16% Effective alkali
25% Sulfidity
12.5% Na$_2$SO$_4$ based on Na$_2$S (as Na$_2$O)
25% Na$_2$CO$_3$ based on NaOH (as Na$_2$O)
4:1 Liquor:Wood ratio
90 MINUTES AT 173°C (343°F)
Maximum cooking temperature 173°C (343°F)

Ten Liquors Produced

<table>
<thead>
<tr>
<th>Wood</th>
<th>H-Factor</th>
<th>Kappa Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>690, 1600, 5500</td>
<td>72.7, 32.2, 15.0</td>
</tr>
<tr>
<td>Birch</td>
<td>160, 971, 1600</td>
<td>79.7, 39.0, 16.6</td>
</tr>
<tr>
<td>P/B 50/50</td>
<td>303, 947, 4000</td>
<td>96.5, 43.5, 17.1</td>
</tr>
<tr>
<td></td>
<td>971</td>
<td>41.2</td>
</tr>
</tbody>
</table>
COLLABORATIVE STUDIES

Dr. Mikko Hupa

- Exchange selected liquors
- Full database
- Approved reports and publications
- Meetings

Weyerhaeuser Paper Company

- Selected burning studies, summer intern
- Results reported spring PAC

DIRECTION

- Finalize data analysis
- Prepare progress report
- Evaluate synthetic liquors
- Pursue fundamentals of particle drying, burning, sulfur release, and fuming
- Incorporate understanding into mathematical models
FLASH X-RAY IMAGING OF BLACK LIQUOR SPRAYS

WET END | PRESSES | DRYERS
--- | --- | ---
66–999 kg water/kg fiber | 4 kg water/kg fiber | 1.5 kg water/kg fiber | .05 kg water/kg fiber

.1–1.5% CONSISTENCY 20.0% 40.0% 95.0%

RETENTION = 50%
Table 6. X-ray imaging systems

<table>
<thead>
<tr>
<th>Builder</th>
<th>Exposure Time (s)</th>
<th>Framing Rate (fps)</th>
<th>X-ray Spot Size (mm)</th>
<th>Energy (KEV)</th>
<th>Resolutiona (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANL (sp)</td>
<td>$10^{-4}$</td>
<td>$10^4$</td>
<td>3.0</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Realtime</td>
<td>$10^{-2}$</td>
<td>$10^2$</td>
<td>&lt;1.0</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>LLL</td>
<td>$3 \times 10^{-8}$</td>
<td>0</td>
<td>0.02</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>H-P</td>
<td>$3 \times 10^{-8}$</td>
<td>10</td>
<td>2.0</td>
<td>300</td>
<td>25</td>
</tr>
<tr>
<td>Impuls-phys</td>
<td>$10^{-7}$</td>
<td>$10^3$</td>
<td>1.0</td>
<td>150</td>
<td>50</td>
</tr>
</tbody>
</table>

aAnticipated resolution in some cases.
RESOLUTION = \( H \frac{(L-S)}{L} \)
FIGURE 4 Magnified, high-contrast copy of a typical flash radiograph. For reference, the pintle tip is 1.6 millimeters in diameter.
Figure 3.6. Flash x-ray image of water spray from small nozzle.
Figure 5.1. Black liquor spray facility.
Figure 2.1. Flash x-ray image of black liquor nozzle spray.
FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION (PROJECT 3473-6)

OBJECTIVES
- Develop Black Liquor Combustion Reactors
- Apply Advanced Spectroscopic Techniques
- Obtain Fundamental Data

UPFLOW MODE OF IPC PHASE 1 SYSTEM
ACCOMPLISHMENTS
(Since April 1986)

IPC
- Phase 1 system consistently operates
- Sustained continuous black liquor droplet injection
- Chemical/physical characteristics of char precursors studied
- Initial measurements of gas velocity profiles
- Designed and ordered bed burning furnace

NBS
- Completed temperature profile work in first units of DPFR*
- Completed high speed filming study of early in-flight processes
- Dynamic particle size/velocity measurements over a range of conditions
- The full-height DPFR is assembled and has undergone preliminary testing

* Dilute Phase Flow Reactor
OPERATING OVERVIEW
IPC Flow Reactor System
Upflow Mode

- Operates continuously with limited monitoring

- Longest sustained operating period
  - With liquor feed: 6H
  - Without liquor feed: 10H

- Black liquor feed characteristics
  - No. 41 oxidized liquor
  - Solids: 63.7 to 67.4%
  - Flow: nominal 15 G/min (1.3 LB solids/h)
  - Temperature: 200 to 240°F (93 to 115°C)

- Gas characteristics
  - Velocities: 0.7 to 4.3 ft/sec (0.2 to 1.3 m/s)
  - Temperatures: 1375 to 1675°F (746 to 913°C)

OPERATING OVERVIEW
IPC Flow Reactor System
Upflow Mode

- Gas treatment package operates unattended
- Gas analyzers and conditioner automatic
- Data acquisition automatic
- Solid sampling manual
- Video monitoring droplet formation
IPC FLOW REACTOR
TEMPERATURE PROFILES
Operating Average 1675°F (913°C)

+ = Wall temperature
• = Gas temperature

Temperature (°F)

Height above 2nd stage air heater (inches)
VELOCITY PROFILE
(MID SOS, 12 SCFM, 70°F)

- Measured velocity
- Calculated laminar velocity
- Calculated turbulent velocity

VELOCITY PROFILES
IPC Flow Reactor
(MID SOS 70°F)

- 20 SCFM
- 16 SCFM
- 12 SCFM
- 8 SCFM
- 4 SCFM
- 2 SCFM
- 0 SCFM
RESULTS

COMBUSTION CHARACTERISTICS

FEED LIQUOR 41

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV, Btu/lb</td>
<td>5540</td>
</tr>
<tr>
<td>Sulfated Ash, % NaOH</td>
<td>36.9</td>
</tr>
<tr>
<td>RAA, % Na₂O</td>
<td>1.3</td>
</tr>
<tr>
<td>Solids, %</td>
<td>67.4</td>
</tr>
<tr>
<td>Swol. Vol Pyr, (1) cc/G-solids</td>
<td>68</td>
</tr>
<tr>
<td>Swol. Vol Comb, (2) cc/G-solids</td>
<td>15</td>
</tr>
<tr>
<td>Time to Ign, sec</td>
<td>1.4</td>
</tr>
<tr>
<td>Time from Ign to Max Vol, sec</td>
<td>2.0</td>
</tr>
<tr>
<td>Time Max Vol to Smelt, sec</td>
<td>2.3</td>
</tr>
<tr>
<td>Time Total, sec</td>
<td>5.7</td>
</tr>
</tbody>
</table>

(1) In N₂ at 930°F (500°C)
(2) In air at 1470°F (800°C)

IN-FLIGHT TEST PLAN

GROUP 1

BASE CONDITIONS

Liquor Feed: 1.0 to 1.3 lb solids/hr (12 to 15 g/min) 65% solids; oxidized liquor No. 41 2 mm droplet size

Gas Feed: 1615°F (880°C) avg. gas temperature 4 SCFM (113 std LPM) gas upward flow

INDEPENDENT VARIABLES

Gas O₂ Content: 0, 10, 21%

Liquor Temperature: 200, 220, 240°F (93, 104, 116°C)

DESIGN

3 Level Complete Factorial
2 Replicates
# RESULTS

ANALYSES GROUP 1

<table>
<thead>
<tr>
<th></th>
<th>Feed Liquor 41</th>
<th>Product Char</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Carbon, % ODS</td>
<td>0</td>
<td>4.42 ± 1.41</td>
</tr>
<tr>
<td>Solids, % ODS</td>
<td>64.4 ± 0.7</td>
<td>98.47 ± 0.45</td>
</tr>
<tr>
<td>Swollen Volume CC</td>
<td>APPROX. 1.2</td>
<td>9.85 ± 2.18</td>
</tr>
<tr>
<td>Bulk Density, g/l</td>
<td>1300</td>
<td>83.0 ± 17.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.4 - 113</td>
</tr>
<tr>
<td>(All values % ODS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>35.7</td>
<td>31.1 ± 1</td>
</tr>
<tr>
<td>H</td>
<td>3.25</td>
<td>2.59 ± 0.22</td>
</tr>
<tr>
<td>O</td>
<td>34.29</td>
<td>35.5 ± 0.4</td>
</tr>
<tr>
<td>S</td>
<td>4.56</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td>Na</td>
<td>19.8</td>
<td>22.3 ± 0.8</td>
</tr>
<tr>
<td>K</td>
<td>1.4</td>
<td>2.93 ± 0.12</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>7.97</td>
<td>27.8 ± 3.3</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>5.87</td>
<td>8.08 ± 1.11</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.96</td>
<td>1.66 ± 0.38</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>8.19</td>
<td>4.64 ± 0.54</td>
</tr>
<tr>
<td>Na₂S</td>
<td>0</td>
<td>0.85 ± 0.41</td>
</tr>
</tbody>
</table>

Sample Material Balance, % 99 98.5 ± 0.8 96.8 - 100
RESULTS

Compositional Changes Group 1

<table>
<thead>
<tr>
<th></th>
<th>Average ± 95% CL</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon loss, %</td>
<td>22.2 ± 4.9</td>
<td>9.3 - 33.8</td>
</tr>
<tr>
<td>Hydrogen loss, %</td>
<td>33.2 ± 7.6</td>
<td>12.6 - 46.5</td>
</tr>
<tr>
<td>Oxygen loss, %</td>
<td>11.2 ± 3.3</td>
<td>2.0 - 20.5</td>
</tr>
<tr>
<td>Sulfur loss, %</td>
<td>11.9 ± 6.3</td>
<td>0.1 - 32.8</td>
</tr>
<tr>
<td>Na₂S₂O₃ loss, %</td>
<td>49.2 ± 7.2</td>
<td>34.6 - 67.9</td>
</tr>
<tr>
<td>Na₂CO₃ gain, %</td>
<td>208 ± 27</td>
<td>170 - 288</td>
</tr>
<tr>
<td>Na₂SO₄ gain, %</td>
<td>23.2 ± 14.7</td>
<td>-1.7 - 71.9</td>
</tr>
<tr>
<td>Na₂SO₃ gain, %</td>
<td>52.7 ± 32</td>
<td>3.1 - 151</td>
</tr>
<tr>
<td>S⁺/S, %</td>
<td>7.7 ± 3.7</td>
<td>1.5 - 20.0</td>
</tr>
<tr>
<td>0.78FC/C, %</td>
<td>12.7 ± 4.4</td>
<td>7.2 - 31.7</td>
</tr>
</tbody>
</table>

EARLY IN-FLIGHT

Inorganic Sulfur Reactions

4Na₂S₂O₃ —> 3Na₂SO₄ + Na₂S₅
   • Decomposition above 435°F (225°C)
   • Completed at 878°F (470°C)

Na₂S₅ —> Na₂S + 4S
   • Decomposition above 527°F (275°C)

4Na₂SO₃ —> 3Na₂SO₄ + Na₂S
   • Decomposition above 300°F (150°C)

[Kubelka, V., Votupal, J., Sbornik Vyzkum, Prací, Oboru Celulozy a Papiřu 2:49-73 (1957)]
STATISTICAL RELATIONSHIPS

TEST GROUP 1

DEPENDENT VARIABLES DEPENDENT ON $O_2$ AND $T_L$

**Bulk Density** = $160.5 + 1.12O_2 - 1.855S_{203NAPL}$

$r^2 = 0.88$, $0.72$, $0.16$

**$S_{2NAR}$** = $0.0564 - 0.00157SV + 0.000746O_2 - 0.01825H_2O$

$r^2 = 0.82$, $0.16$, $0.56$

**$SNAR$** = $0.658 - 0.00625FC - 0.00271T_L - 0.00128S_{203NAPL}$

$r^2 = 0.84$, $0.48$, $0.24$, $0.11$

RESULTS

SUMMARY

- TESTED CONDITIONS HAVE PRODUCED CHARS WHICH WERE QUENCHCED DURING THE VOLATILES BURNING STAGE.
- SIGNIFICANT COMPOSITIONAL CHANGES OCCURRED IN ALL MAJOR CONSTITUENTS.
- LARGE AMOUNT OF $Na_2CO_3$ FORMED.
- INORGANIC SULFUR SPECIES SHIFTS OCCURRED.
- THE GAS-PHASE $O_2$ CONTENT AND LIQUOR TEMPERATURE HAD ONLY MINOR EFFECTS.
- MEASURABLE $Na_2S$ CAN FORM IN THE EARLY IN-FLIGHT PHASES.
IN-FLIGHT TEST PLAN

GROUP 2

BASE CONDITIONS

LIQUOR FEED: 1.4 LB SOLIDS/HR (16 G/MIN)
63.8% SOLIDS, OXIDIZED LIQUOR NO. 41
2 MM DROPLET SIZE
104°C (220°F)

O2 Content: 0

INDEPENDENT VARIABLES

GAS FLOW: 1, 2, 6 SCFM (28, 57, 170 STD LPM)

GAS TEMPERATURE: 1290, 1470, 1670°F (700, 800, 910°C)

DESIGN

3 LEVELS COMPLETE FACTORIAL
(ONLY 7 CONDITIONS POSSIBLE)

RESULTS (PRELIMINARY)

GROUP 2

- INTERMEDIATE SAMPLE OKAY FOR SOLIDS.

- SOLIDS PROFILES STRONG FUNCTION OF GAS TEMPERATURE.

- COMPOSITIONAL CHANGES NOT YET EVALUATED.
NEXT TESTING WORK

GROUP 3

- PARTICLE SIZE
- SOLIDS
- FLOW RATE

MODELING

- DRYING MODEL DEVELOPMENT/VALIDATION

IPC BED BURNING FURNACE DESIGN BASIS

- Continuous and semicontinuous operation
- 1 ft\(^2\) cross section
- Flexible bed and air port geometries
- Maximum temperature + 2000°F (+1100°C)
- Gas tight inner metal retort
- Modular electrical panel heaters
- Two-zone temperature control
- Continuous yet contained smelt runoff
- Optical and instrument access
- Manual sampling of bed and smelt
- Removable base
NEAR TERM PLANS
(THROUGH JUNE 1987)

IPC
- Design black liquor flows reached
- Complete Phase 1 work
- Bed burning furnace operable

NBS
- Complete in-flight photographic studies in full-height DPFR
- Complete Phase 1 work
- Initiate gas-phase diagnostic work
NEAR TERM PLANS
(THROUGH JUNE 1987)

IPC
- Design black liquor flows reached
- Complete Phase 1 work
- Bed burning furnace operable

NBS
- Complete in-flight photographic studies in full-height DPFR
- Complete Phase 1 work
- Initiate gas-phase diagnostic work
SUMMARY
IMPLEMENTATION OF BLACK LIQUOR COMBUSTION KNOWLEDGE

IMPROVED PERFORMANCE

TARGET SELECTION

IMPLEMENTATION STRATEGY

IMPROVED PERFORMANCE

- Reduce capital cost
- Reduce operating/maintenance costs
- Improve energy effectiveness
- Reduce insurability risk
- Reduce environmental impacts
- Improve operability

TARGET SELECTION

- Upper furnace plugging
- Combustion and chemical processes
- Heat transfer in furnace
- Bed conditions
IMPLEMENTATION STRATEGY

PRIORITY: Develop firing technique for
- higher firing rates
- minimal carryover

REQUIREMENTS: Mathematical furnace model spray
nozzle characterization and development

NEAR TERM TECHNOLOGY TRANSFER:

API 3 Volume Series by
Dr. T.N. Adams and W.J. Frederick
Project 3566

SEPARATION OF STRONG, INTACT FIBERS

T. J. McDonough
PROJECT 3566

SEPARATION OF STRONG, INTACT FIBERS

OBJECTIVE

MINIMIZE THE CHANGES IN FIBER STRENGTH AND GEOMETRY WHICH ACCOMPANY FIBER SEPARATION

MEDIUM RANGE GOALS

• IDENTIFY FACTORS GOVERNING RETENTION OF FIBER STRENGTH AND INTEGRITY

• DEVELOP CONTROL METHODS
Fiber attributes needed to make strong paper:
- Length
- Strength
- Conformability
- Active bonding surface

To give sheet strength equal to Kraft, high yield fiber strength retention must be increased if:
- The load carrying capacity of Kraft fibers has been substantially decreased by pulping
- Existing high yield processes also cause appreciable fiber strength losses
EARLY EFFORT SHOULD BE CONCENTRATED ON MAXIMIZING FIBER STRENGTH WITH RELATIVELY LITTLE REGARD FOR BONDING ABILITY.

RELEVANT QUESTIONS

○ HOW LONG AND STRONG ARE THE FIBERS IN WOOD?
○ HOW LONG AND STRONG ARE THE FIBERS IN KRAFT PULP?
○ HOW LONG AND STRONG ARE THE FIBERS IN HIGH YIELD PULP MADE UNDER STANDARD CONDITIONS?
○ HOW CAN HIGH YIELD PULPING CONDITIONS BE CHANGED TO MINIMIZE EFFECTS ON FIBER LENGTH AND STRENGTH?

RELEVANT QUESTIONS

○ CAN STRONG HIGH YIELD FIBERS BE BONDED TOGETHER TO FORM A SHEET IN WHICH A FIBER NUMBER DISADVANTAGE RELATIVE TO KRAFT IS LARGELY OR COMPLETELY COMPENSATED FOR BY A FIBER STRENGTH ADVANTAGE?
○ TO WHAT EXTENT ARE THE ANSWERS TO THE ABOVE QUESTIONS DEPENDENT ON SPECIES?
○ CAN THE STRENGTH OF A WOOD FIBER BE INCREASED BEYOND ITS NATIVE VALUE?
DIRECT MEASUREMENT OF FIBRIL ANGLE
Category A. No fibrils observable - No picture.

Safranin stained spruce TMP fiber - Category B
(Few fibrils visible)

Safranin stained spruce TMP fiber - Category C
(Fibrils locally visible)
SAFRANIN STAINED SPRUCE TMP FIBER - CATEGORY D
(MANY FIBRILS VISIBLE)

SAFRANIN STAINED SPRUCE TMP FIBER - CATEGORY E
(FIBRILS SEPARATED)
DIRECT FIBRIL ANGLE MEASUREMENT

<table>
<thead>
<tr>
<th>FIBRIL VISIBILITY</th>
<th>CONTROL</th>
<th>AFTER HIGH INTENSITY STIRRING</th>
<th>AFTER LOW INTENSITY STIRRING</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIL</td>
<td>46</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
<td>FEW</td>
<td>41</td>
<td>30</td>
<td>39</td>
</tr>
<tr>
<td>LOCAL</td>
<td>8</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>MANY</td>
<td>5</td>
<td>19</td>
<td>27</td>
</tr>
<tr>
<td>SEPARATED</td>
<td>1</td>
<td>25</td>
<td>5</td>
</tr>
</tbody>
</table>

EFFECTS OF PULPING CONDITIONS ON FIBER PROPERTIES

- Asplund Mill
- Pilot TMP Refiner

Effect of fiberization temperature on yield of fibers from untreated chips at various retention times.
Effect of fiberization temperature on yield of fiber fragments (including fines) from untreated chips at various retention times.

Effect of fiberization temperature on yield of fibers from 74% yield sulfonated chips at various retention times.
Effect of fiberization temperature on yield of fiber fragments (including fines) from 74% yield sulfonated chips at various retention times.

Zero-span tensile strength of handsheets made from fibers separated under various conditions.
Density of handsheets made from fibers separated under various conditions.

Tensile strength density-relationships for handsheets made from fibers separated under various conditions.
Scattering coefficient-density relationships for handsheets made from fibers separated under various conditions.

Tear factor-density relationships for handsheets made from fibers separated under various conditions.
MAKING STRONG, HIGH YIELD FIBERS
BOND TO ONE ANOTHER

Tensile strength-density relationships for untreated (squares) and 2% ozone treated (circles) spruce fibers from sulfonated chips.

Tear factor-density relationships for untreated (squares) and 2% ozone treated (circles) spruce fibers from sulfonated chips.
<table>
<thead>
<tr>
<th>Pulp Type</th>
<th>Yield</th>
<th>Pressing</th>
<th>Density (g/cm³)</th>
<th>Burst (kPa·m²/g)</th>
<th>Tensile (Nm/g)</th>
<th>Zero-Span (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRAFT</td>
<td>48</td>
<td>Conv.</td>
<td>0.61</td>
<td>6.8</td>
<td>101</td>
<td>22</td>
</tr>
<tr>
<td>SCMP</td>
<td>74</td>
<td>Conv.</td>
<td>0.18</td>
<td>0.6</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hot</td>
<td>0.60</td>
<td>5.0</td>
<td>64</td>
<td>11</td>
</tr>
<tr>
<td>SCMP</td>
<td>87</td>
<td>Conv.</td>
<td>0.15</td>
<td>0.4</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hot</td>
<td>0.61</td>
<td>4.2</td>
<td>68</td>
<td>12</td>
</tr>
</tbody>
</table>
Project 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

E. Malcolm
S. Lebo
U. Agarwal
OBJECTIVE

Define mechanism for brightness loss in high-yield pulps
Figure 10. The mechanism of the light-induced yellowing reaction of high-yield pulps.

ROLE OF SINGLET OXYGEN

?
No Singlet $O_2$ Change on U.V. Exposure

No Brightness Loss on Exposure to Singlet Oxygen

Radical Involvement

ESR Use
Irradiation with light of wavelength > 300 nm

CuSO₄ Filter

No Light

---

5.53 ± 0.06 μV

5.35 ± 0.06 μV

5.17 ± 0.06 μV

5.00 ± 0.06 μV

4.83 ± 0.06 μV

4.67 ± 0.06 μV

4.50 ± 0.06 μV

4.33 ± 0.06 μV

4.17 ± 0.06 μV

4.00 ± 0.06 μV

3.83 ± 0.06 μV

3.67 ± 0.06 μV

3.50 ± 0.06 μV

3.33 ± 0.06 μV

3.17 ± 0.06 μV

3.00 ± 0.06 μV

2.83 ± 0.06 μV

2.67 ± 0.06 μV

2.50 ± 0.06 μV

2.33 ± 0.06 μV

2.17 ± 0.06 μV

2.00 ± 0.06 μV

1.83 ± 0.06 μV

1.67 ± 0.06 μV

1.50 ± 0.06 μV

1.33 ± 0.06 μV

1.17 ± 0.06 μV

1.00 ± 0.06 μV

0.83 ± 0.06 μV

0.67 ± 0.06 μV

0.50 ± 0.06 μV

0.33 ± 0.06 μV

0.17 ± 0.06 μV

0.00 ± 0.06 μV

-0.17 ± 0.06 μV

-0.33 ± 0.06 μV

-0.50 ± 0.06 μV

-0.67 ± 0.06 μV

-0.83 ± 0.06 μV

-1.00 ± 0.06 μV

-1.17 ± 0.06 μV

-1.33 ± 0.06 μV

-1.50 ± 0.06 μV

-1.67 ± 0.06 μV

-1.83 ± 0.06 μV

-2.00 ± 0.06 μV

-2.17 ± 0.06 μV

-2.33 ± 0.06 μV

-2.50 ± 0.06 μV

-2.67 ± 0.06 μV

-2.83 ± 0.06 μV

-3.00 ± 0.06 μV

-3.17 ± 0.06 μV

-3.33 ± 0.06 μV

-3.50 ± 0.06 μV

-3.67 ± 0.06 μV

-3.83 ± 0.06 μV

-4.00 ± 0.06 μV

-4.17 ± 0.06 μV

-4.33 ± 0.06 μV

-4.50 ± 0.06 μV

-4.67 ± 0.06 μV

-4.83 ± 0.06 μV

-5.00 ± 0.06 μV

-5.17 ± 0.06 μV

-5.35 ± 0.06 μV

-5.53 ± 0.06 μV
FUTURE WORK

COMPLETE EXPERIMENTS TO CONFIRM GENERAL MECHANISM

USE ANALYTICAL TECHNIQUES TO MONITOR RESULTS OF STANDARD BLEACHING METHODS

INITIATE WORK ON FUNDAMENTALS OF INITIAL PHOTOCHEMISTRY
Figure 10. The mechanism of the light-induced yellowing reaction of high-yield pulps.

Figure 4. The photochemical induction cycle.
Figure 6. The various products formed in the "dark reactions."

Structure A

Structure B

Figure 7. Softwoods and hardwoods generate the very same chromophore.
Figure 9. Dependence of relative rates of yellowing on the irradiating wavelength.
310nm, RELATIVE HUMIDITY = 15% at 75°F

IRRADIATION TIME (minutes)

IRRADIATION WAVELENGTH: 310nm

INCIDENT FLUX (PHOTONS/CM² SEC × 10¹³)
Figure 5. Humidity assisted rearrangement.

Figure 2. An "ortho-quinone specific" reagent.

(Stuart Lebo, PhD thesis)
Model Compounds:

A. 3,5-di-t-butyl-1,2-benzoquinone

\[
\begin{align*}
\text{Phosphorus distribution after irradiation with simulated} & \\
\text{sunlight and reaction with trimethoxy phosphine within a} & \\
\text{cross sectioned sheet. (Each layer consists of about 20 fibers).} & 
\end{align*}
\]
FREMY'S SALT OXIDATION: Adler and Lundquist*; Singh**

\[
\begin{align*}
\text{ON}(\text{SO}_3\text{K})_2 \\
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{3HCO} \\
\text{R'} \\
\end{array} \quad \rightarrow \\
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{3HCO} \\
\end{array} \\
\begin{array}{c}
\text{O} \\
\text{R} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
R = R' &= \text{H} \\
R &= \text{H}; \quad R' = \text{C} \\
R &= \text{C}; \quad R' = \text{H} \\
R &= \text{C}; \quad R' = \text{C}
\end{align*}
\]


**Tappi 49(7): 281 (1966)
PROBING EXCITED STATES
BY
LASER RAMAN TECHNIQUES

LIGNIN
OR
MODIFIED LIGNIN

\[ \text{MOD. LIGNIN}^* \]

WHAT ARE THE PRIMARY EVENTS??

TIME RESOLVED RAMAN STUDIES
(TR\textsuperscript{2}S)

(a) CHARACTERIZE
(b) FOLLOW ENERGY DEGRADATION PATHWAYS

TIME RESOLVED LUMINESCEENCE STUDIES
KINETIC AND STRUCTURAL INFORMATION
WHAT IS AVAILABLE?

(1) Nd:YAG (1064 nm):
   MODE LOCKED
   REP. RATE 76 MHz
   PULSE WIDTH <100 PS
   AVE. POWER 9 WATTS

(2) Frequency Doubler (532 nm)
   KTP CRYSTAL
   REP. RATE 76 MHz
   PULSE WIDTH <70 PS
   AVE. POWER 1 WATT
(3) Ultrafast Dye Laser System:
   R6G dye
   AVE. POWER        90 mW
   PULSE WIDTH       <0.8 ps
   TUNABILITY        585-610 nm
   OTHER DYES CAN ALSO BE USED.

(4) SPEX Triplemate Spectrometer

(5) Detector
   GATED
   INTENSIFIED
   MULTICHANNEL (1024)

MIGHT NEED:
UV TUNABLE DYE LASER
THIRD HARMONIC GENERATOR