THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

October 21-22, 1985

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<td>FUNDAMENTALS OF BRIGHTNESS STABILITY (Project 3524)</td>
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<td>SEPARATION OF STRONG, INTACT FIBERS (Project 3566)</td>
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</table>
RESEARCH OVERVIEW

E. W. Malcolm
CHEMICAL SCIENCES

OVERVIEW

CHEMICAL SCIENCES DIVISION

Staff - 40 total (12 Ph.D.)

'86 Research Budget

Member Funded - $1.1M
Contract - $1.0M

Dues Funded Research
Contract Research
Student Research

Kraft Recovery
Bleached Chemical Pulp
High Yield Pulp

'86 CONTRACT PROJECTS

Fiber Structure (DOE) - $243K ($194K equip.)
Black Liquor Combustion (DOE) - $670K ($265K NBS)
Smelt - H$_2$O Explosions (NRC) - $100K
Explosion Monitoring (API) - $23K
STUDENT RESEARCH (JUNE 1985)

<table>
<thead>
<tr>
<th></th>
<th>M.S.*</th>
<th>Ph.D.</th>
</tr>
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<tr>
<td>Recovery</td>
<td>8</td>
<td>3</td>
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<tr>
<td>Chemical Pulp</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>High Yield Pulp</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 (~50%)</td>
<td>17 (40%)</td>
<td></td>
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</table>

*Second year class only, total number will approximately double when first year class enters program.

Kraft Recovery
- Fundamental Processes in Alkali Recovery Furnace
- Incremental Capacity in Recovery Boilers
- Smelt-Water Explosions

Bleached Chemical Pulp
- Fundamentals of Selectivity
- Improved Process for Bleached Pulp
- Analytical Techniques

High Yield Pulp
- Separation of Strong, Intact Fibers
- Fine Structure of Wood Fibers
- Fundamentals of Brightness Stability

EXPLORATORY
Project 3474

IMPROVED PROCESS FOR BLEACHED PULP

Low Lignin Pulps - T. J. McDonough
Nonchlorine Bleaching - N. S. Thompson
IMPROVED PROCESS FOR BLEACHED PULP

* Low - Lignin Pulping
* Nonchlorine Bleaching

SUMMARY OF EARLIER WORK

* Low - Lignin Kraft and Kraft - AQ Pulping
* Bleaching of Low - Lignin Pulps
* Sulfite - AQ Pulping Fundamentals
RECENT ACTIVITY

* Simulation and Economic Evaluation of Kraft and Kraft - AQ Low - Lignin Operations

* Sulfite - AQ Pulping Fundamentals

KRAFT MILL SIMULATION

* Constant bleached pulp production
* Fixed digester capacity
* Temperature varied
* Liquor/wood constant
* Variables studied: Kamma No. (H-Factor), EA Charge Sulfidity, AQ Charge
General flowsheet of the mill simulated, showing interconnections between departments.
Flowsheet of the pulping department.

- Digester Relief
- Pressure Relief (145 psig HP Steam)
- Condensate
- LP Steam
- Weak Black Liquor
- DED Effluent
- BLD Effluent
- Bleached Pulp
- NaOH
- ClO₂ / Cl₂
- Blow Steam
- Wash Water
- Wood
Effects on steam generated (lb). Basis: 20 tons bleached pulp.
Effects on revenue. Basis: 20 tons bleached pulp.
Effects on pulp viscosity (mPa \cdot s).
Assumed unit costs.

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>BLEACHED SLUSH PULP</td>
<td>375 $/T</td>
</tr>
<tr>
<td>SOFTWOOD</td>
<td>72</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>55</td>
</tr>
<tr>
<td>NaOH</td>
<td>171</td>
</tr>
<tr>
<td>LIME</td>
<td>7</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>157</td>
</tr>
<tr>
<td>ClO$_2$</td>
<td>802</td>
</tr>
<tr>
<td>FUEL OIL</td>
<td>171</td>
</tr>
<tr>
<td>STEAM (70 psi)</td>
<td>6</td>
</tr>
<tr>
<td>ANTHRAQUINONE</td>
<td>3600</td>
</tr>
<tr>
<td>ELECTRICAL ENERGY</td>
<td>1.70/kwh</td>
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</tbody>
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Case comparison.

<table>
<thead>
<tr>
<th>CASE</th>
<th>BASE CASE</th>
<th>1</th>
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<tbody>
<tr>
<td>EA. %</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>AQ. %</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
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<tr>
<td>SULFDITY, %</td>
<td>25</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>DIG. TEMP., °F</td>
<td>343.6</td>
<td>350.1</td>
<td>343.3</td>
</tr>
<tr>
<td>KAPPA NO.</td>
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<td>20</td>
<td>20</td>
</tr>
<tr>
<td>YIELD, %</td>
<td>46.2</td>
<td>44.2</td>
<td>45.3</td>
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<tr>
<td>VISCOSITY, mPa·s</td>
<td>30.0</td>
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<td>ORGANICS TO RECOVERY, T/HR</td>
<td>23.9</td>
<td>25.4</td>
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<td>STEAM GENERATED, T/HR</td>
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<td>STEAM TO EVAPS, T/HR (EV + CON)</td>
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<td>27.5</td>
<td>27.6</td>
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<tr>
<td>PULP PRODUCED, T/HR</td>
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</table>
### Pulping costs.

<table>
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<tbody>
<tr>
<td>EA/AQ/S</td>
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<td>16/0/35</td>
<td>16/0.1/35</td>
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<tr>
<td>KAPPA NO.</td>
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<tr>
<td>WOOD</td>
<td>3322</td>
<td>3380</td>
<td>3290</td>
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<tr>
<td>MAKEUP</td>
<td>44</td>
<td>31</td>
<td>31</td>
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<tr>
<td>AQ</td>
<td>0</td>
<td>0</td>
<td>165</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>3366</td>
<td>3411</td>
<td>3486</td>
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</table>

### Energy and recovery costs.

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<tbody>
<tr>
<td>EA/AQ/S</td>
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<td>16/0/35</td>
<td>16/0.1/35</td>
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<tr>
<td>KAPPA NO.</td>
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<td>20</td>
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<tr>
<td>KILN FUEL</td>
<td>212</td>
<td>209</td>
<td>202</td>
</tr>
<tr>
<td>LIME</td>
<td>7</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>219</td>
<td>216</td>
<td>208</td>
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</tbody>
</table>
Bleaching costs, $/hr.

<table>
<thead>
<tr>
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<th>BASE</th>
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<tr>
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<td>Cl₂</td>
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<td>ClO₂</td>
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<tr>
<td></td>
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Credits, $/hr.

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<tr>
<td>KAPPA NO.</td>
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<tr>
<td>PULP</td>
<td>7500</td>
<td>7500</td>
<td>7500</td>
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<tr>
<td>POWER</td>
<td>275</td>
<td>288</td>
<td>277</td>
</tr>
<tr>
<td>STEAM</td>
<td>239</td>
<td>236</td>
<td>218</td>
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<tr>
<td>EFFLUENT SAVINGS</td>
<td>0</td>
<td>43</td>
<td>43</td>
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<tr>
<td></td>
<td>8014</td>
<td>8067</td>
<td>8038</td>
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</table>
Summary, $/hr.

<table>
<thead>
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<th>CASE</th>
<th>BASE</th>
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<td>EA/AQ/S</td>
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<td>16/0.1/35</td>
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<td>PULPING</td>
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<td>3486</td>
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<td>BLEACHING</td>
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<tr>
<td>RECOVERY</td>
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<tr>
<td>TOTAL COSTS</td>
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<td>4132</td>
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<tr>
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<td>POWER</td>
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<td>288</td>
<td>277</td>
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<td>STEAM</td>
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<td>236</td>
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<tr>
<td>EFFLUENT SAVINGS</td>
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<tr>
<td>TOTAL CREDITS</td>
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<td>NET REVENUE, $/T</td>
<td>190.25</td>
<td>196.75</td>
<td>191.95</td>
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Equipment capacities relative to the BASE CASE.

<table>
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<th>CAPACITY RELATIVE TO BASE CASE</th>
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<td>WOOD HANDLING</td>
<td>46</td>
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<td>BROWNSTOCK WASHERS</td>
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<td>1.01</td>
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<tr>
<td>BLACK LIQUOR OPERATIONS</td>
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<td>1.02</td>
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<td>RECOVERY BOILER</td>
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<td>1.05</td>
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<td>WHITE LIQUOR CLARIFIER</td>
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<tr>
<td>LIME KILN</td>
<td>9</td>
<td>0.98</td>
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</table>
Yield selectivity of SAQ and kraft pulping as a function of degree of delignification. SAQ conditions: 24% Na₂O on wood, 80% as Na₂SO₃, 20% as Na₂CO₃, 0.1% AQ, L/W 4 mL/g, 1 1/2 to 4 1/2 h at 180°C; kraft conditions: 18% eff. alk. 25% sulfidity, L/W 4 mL/g, max. temp. 173°C, H-factor 1074-3724.
Viscosity selectivity of SAQ and kraft pulping as a function of degree of delignification. For conditions, see Figure 1.
FACTORS AFFECTING RATE AND SELECTIVITY

* Mass Transfer

* Chemical Kinetics
  - Delignification
  - Carbohydrate loss
  - Chain cleavage

PRELIMINARY MODEL:

\[- \frac{dL}{dt} = 0.416 \cdot C_{OH^-}^{0.038} \cdot C_{AQ}^{0.059} \cdot C_S^{0.127}\]

for \( t < 30 \text{ min at } 180^\circ C \), and

\[- \frac{dL}{dt} = 2.15 \cdot 10^{-3} \cdot C_{OH^-}^{0.18} \cdot C_{AQ}^{0.121} \cdot C_S^{1.00} \cdot (L - 1)\]

for \( t > 30 \text{ min at } 180^\circ C \), where

\( L \) = lignin yield, g lignin/100 g wood

\( C_{OH^-} \) = Concentration of hydroxide ion inferred from cold liquor pH

\( C_{AQ} \) = Initial AQ concentration g/L liquor

\( C_S \) = Total concentration of \( Na_2SO_3 \) and \( NaHSO_3 \), g \( Na_2O \)/L liquor

\( t \) = time in minutes
Yield (% o.d. wood) as a function of total cooking time (min) in a sulfite-anthraquinone cook of southern pine, 19.2% Na$_2$SO$_3$ and 48% Na$_2$CO$_3$, both as Na$_2$O, o.d. wood basis; 0.1% AQ; 4 mL liquor/g wood; 1°C/min from 90 to 180°C.
Lignin yield (% o.d. wood) vs. total cooking time (min) in a sulfite-anthraquinone cook of southern pine. Conditions as in Fig. 12.
Arabinoxylan yield (% o.d. wood) vs. total cooking time (min) in a sulfite-anthraquinone cook of southern pine. Conditions as in Fig. 12.
Galactoglucomannan yield (% o.d. wood) vs. total cooking time (min) in a sulfite-anthraquinone cook of southern pine. Conditions as in Fig. 12.
Cellulose yield (% o.d. wood) vs. total cooking time (min) in a sulfite-anthraquinone cook of southern pine. Conditions as in Fig. 12.
Pulp viscosities (mPa * s) vs. total cooking time (min) in a sulfite-anthraquinone cook of southern pine. Conditions as in Fig. 12.
$\text{Na}_2\text{SO}_3$ concentration (g/L) in spent liquor vs. total cooking time (min) in a sulfite-anthraquinone cook of southern pine. Conditions as in Fig. 12.
Effect of Na$_2$SO$_3$ concentration on rate of pulping in a sulfite-anthraquinone cook of 1 mm thick southern pine wafers (yield as % o.d. wood, time in min). 12 g/L (Na$_2$CO$_3$ + NaHCO$_3$), 48 g/L (Na$_2$SO$_3$ + Na$_2$SO$_4$), all expressed as Na$_2$O, pH 9.5-9.3, 0.25 g AQ/L; 40 mL liquor/g wood, 1°C min rise from 90°C.
Effect of Na$_2$SO$_3$ concentration on delignification rate in a sulfite-anthraquinone cook of 1 mm thick southern pine wafers. (Lignin yield 25% o.d. wood, time in min.) Conditions as in Fig. 19.
Effect of AQ concentration on delignification rate in a sulfite-anthraquinone cook of 1 mm thick southern pine wafers (lignin yield as % o.d. wood, time in min). Conditions as in Fig. 19, except initial Na₂SO₃ concentration constant at 48 g/L and AQ concentration varied.
PLANS: DATA ANALYSIS

- Literature review
- Postulate mechanisms
- Fit parameters
- Model discrimination
- Parameter estimation
- Repeat for bulk phase
- Repeat for resid. phase
The Formation of Radicals During Oxygen Bleaching

Lignin Phenolates + Oxygen + Alkali

\[ \text{Lignin Radicals + Superoxide Radical + Hydroxyl Radical} \]

Publications Based on Project 3474-2

The Cleavage of Fibers by Potassium Superoxide
Thompson, Corbett, Tappi 64(5):126(1981)

The Effect of Superoxide on Cellulose Structure
Thompson, Corbett, in press

The Reaction of Model Lignins with Oxygen Radicals
Barkaw, Bastian, Thompson, in press

Effect Liquor Composition on Reaction of Lignin Models with Oxygen
## EFFECT OF ANTIOXIDANTS ON PULP QUALITY

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<thead>
<tr>
<th>ANTIOXIDANT</th>
<th>PULP QUALITY</th>
</tr>
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<tbody>
<tr>
<td>O (control)</td>
<td>0</td>
</tr>
<tr>
<td>Fluorene</td>
<td>-</td>
</tr>
<tr>
<td>Cyanox</td>
<td>-</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>0</td>
</tr>
<tr>
<td>Butylated Phenol</td>
<td>+</td>
</tr>
<tr>
<td>Styrenated Phenol</td>
<td>+</td>
</tr>
<tr>
<td>BHT</td>
<td>+</td>
</tr>
<tr>
<td>BHA</td>
<td>+</td>
</tr>
<tr>
<td>Phenolsulfonic Acid</td>
<td>+</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>+</td>
</tr>
<tr>
<td>Magnesium (control)</td>
<td>+++</td>
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MODIFICATION OF KRAFT LIGNIN

Change Aromatic Component

Change Aliphatic Component
Some functional groups of kraft and native lignins.\textsuperscript{a}

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<thead>
<tr>
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<th>Spruce Wood</th>
<th>Softwood Kraft</th>
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<tr>
<td>Aromatic nuclei</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>Phenolic hydroxyl</td>
<td>7</td>
<td>18</td>
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<tr>
<td>Aliphatic hydroxyl</td>
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<td>10</td>
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<tr>
<td>Carboxyl groups</td>
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<td>Carbonyl groups</td>
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<td>Quinone groups</td>
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<tr>
<td>Unsaturation</td>
<td>5</td>
<td>8</td>
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</table>

\textsuperscript{a}The number of functional groups for 23 aromatic nuclei.
Oxidation Pathways for Peroxyacetic Acid Reaction with 4-Methylpyrocatechol Derivatives

from D.C. Johnson, Oxygen Symposium, Raleigh, N.C., May 1975
Possible Reagents for Pulp Pretreatments

NaClO₂
ClO₂
Peroxyacetic Acid
  low pH
  medium pH
  alkaline pH
  Mn catalysis
  Other Peroxides

The effect of O₂ bleaching on chlorited pulps.a

<table>
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<tr>
<th></th>
<th>Controls</th>
<th>Chlorited Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity, % of pulp</td>
<td>6.4</td>
<td>1.7</td>
</tr>
<tr>
<td>O₂ consumed, g/100 g pulp</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Yield, %</td>
<td>93.4</td>
<td>99</td>
</tr>
<tr>
<td>Viscosity, cp</td>
<td>13.5</td>
<td>22.2</td>
</tr>
<tr>
<td>K-number</td>
<td>6.1</td>
<td>13.8</td>
</tr>
<tr>
<td>Brightness</td>
<td>45.5</td>
<td>28.6</td>
</tr>
<tr>
<td>Zero-span, km</td>
<td>13.6</td>
<td>14.7</td>
</tr>
</tbody>
</table>

a100°C, 130 psig, 60 minutes, 100 g pulp.
Experimental Difficulties

Measurement of Lignin.

Chemical Characteristics of Lignin.

Proposed Research

Destroy the Aromatic Character of Lignin
Retain as Much as Possible
Choose Techniques of Analysis
React with Oxygen
Test Pulp
Examine Oxidative Mechanisms
Project 3288

FINE STRUCTURE OF WOOD PULP FIBERS

Project 3521

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

I. 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.

II. 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

III. STUDIES ON HIGHLY CRYSTALLINE ALGAE
**Infrared and Raman Processes**

**Infrared (IR) Processes**

**Absorption**

\[
M + h\nu \rightarrow M^* 
\]

\[50 < \nu < 4000 \text{ cm}^{-1}\]

\[200\mu \quad 2.5\mu\]

\[\Delta \mu \neq 0\]

**Emission**

\[
M^* \rightarrow M + h\nu 
\]

**Raman Processes**

**Stokes**

\[
M + h\nu_0 \rightarrow M^* + h(\nu_0 - \nu) 
\]

\[\nu_0 \approx 20,000 \text{ cm}^{-1}\]

\[5000 \AA\]

\[\Delta \alpha \neq 0\]

**Anti-Stokes**

\[
M^* + h\nu_0 \rightarrow M + h(\nu_0 + \nu) 
\]
Raman spectra of Valonia ventricosa cellulose, Acetobacter xylinum cellulose, Microcrystalline cotton cellulose, and high-crystallinity cellulose I.
Schematic representation of conformations $k_I$ and $k_{II}$.

Legend:
- $\bullet$ = Carbon
- $\bigcirc$ = Oxygen
- $*$ = Hydrogen
- $\ldots$ = Covalent bond
- $\ldots\ldots$ = 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.
A set of Raman spectra used as standards for the basic molecular conformations of cellulose.
Conformational distributions obtained for a partially mercerized wood pulp using three different sets of standards.

<table>
<thead>
<tr>
<th>Standards</th>
<th>k₁</th>
<th>k₁ΙΙ</th>
<th>k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-31</td>
<td>25 (+1)</td>
<td>49 (+5)</td>
<td>27 (+4)</td>
</tr>
<tr>
<td>CC-31, mercerized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF-1, ball-milled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF-1</td>
<td>26 (+1)</td>
<td>58 (+3)</td>
<td>17 (+3)</td>
</tr>
<tr>
<td>CF-1, mercerized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF-1, ball-milled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avicel</td>
<td>32 (+1)</td>
<td>61 (+2)</td>
<td>8 (+2)</td>
</tr>
<tr>
<td>Avicel, mercerized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF-1, ball-milled</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Error spectra generated from the linear fit of three different sets of conformational standards to the Raman spectrum of a partially mercerized wood pulp.

CC-31, mercerized
CF-1, ball-milled

CF-1, mercerized
CF-1, ball-milled

Avicel, mercerized
CF-1, ball-milled

WAVENUMBERS, cm⁻¹
Raman spectra of two different kT standards, CC-31 and Avicel
A representative plot of \( \ln(M_o - M_T) \) vs. \( \tau \) for an unrefined Southern Pine kraft pulp at a single moisture content.
Plot of $T_1$ vs. moisture content for both an unrefined and refined spruce kraft pulp.
The effect of refining on the $T_1$ vs. moisture content curve for a spruce kraft pulp.
Plot of $T_1$ vs. moisture content for both unrefined and refined Southern Pine kraft pulp.
Conformational distributions in two species of unrefined and refined kraft pulps after caustic treatment. Values in parentheses indicate 95% confidence limits.

<table>
<thead>
<tr>
<th>Species</th>
<th>Revs PFI Mill</th>
<th>CSF (ml)</th>
<th>Caustic Treatment 7.5%</th>
<th>Caustic Treatment 8%</th>
<th>Caustic Treatment 10%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>k_i  k_ii  k_0</td>
<td>k_i  k_ii  k_0</td>
<td>k_i  k_ii  k_0</td>
</tr>
<tr>
<td>Loblolly Pine</td>
<td>0</td>
<td>755</td>
<td>65  8  27</td>
<td>29  51  20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7000</td>
<td>300</td>
<td>(+1) (+3) (+3)</td>
<td>(+1) (+4) (+4)</td>
<td></td>
</tr>
<tr>
<td>Spruce</td>
<td>0</td>
<td>700</td>
<td>65  16  19</td>
<td>63  25  13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1) (+2) (+2)</td>
<td></td>
<td>(+1) (+3) (+3)</td>
<td>(+1) (+3) (+3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>163</td>
<td>73  17  10</td>
<td>67  28  7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(+1) (+2) (+2)</td>
<td>(+1) (+3) (+3)</td>
<td></td>
</tr>
</tbody>
</table>
CELL WALL SECTIONS

S1: Middle lamella + primary walls

S2

S3
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.
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.

EXPLORATORY STUDIES

EFFECTS OF HIGHER LASER POWER

CELLULOSE ORIENTATION IN DELIGNIFIED TISSUE

BOUND WATER IN THE CELL WALLS
OBJECTIVES:
- Band Assignments
- Polymorphy
- Orientation

Diagram of the Raman microprobe experiments in which the polarization of exciting light was varied relative to the geometry of the samples.
Raman spectra from an oriented aggregate of Valonia cellulose. The angle between the electric vector and the chain axis was varied from 0 to 90°.
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
Raman spectra from a ramie cross section in which the angle between the electric vector and the cell wall surface was varied from 0 to 90°.
Band Assignments:

Bands can be divided into two groups:
1. maximum = 0 or 90°
2. maximum is between 0 and 90°

Cellulose Polymorphy:

Valonia & ramie \(\rightarrow\) same conformation
Native celluloses & mercerized ramie \(\rightarrow\) different conformations
Valonia, ramie, & mercerized ramie \(\rightarrow\) different hydrogen bonding patterns

Orientation:

Cellulose orientation is anisotropic in the plane perpendicular to the fiber axis
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 modes.
Project 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

Delignification Reactions - D. R. Dimmel
Carbohydrate Reactions - L. R. Schroeder
PROJECT 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

DELIGNIFICATION REACTIONS

CARBOHYDRATE REACTIONS

PULPING CHEMICALS

BY-PRODUCTS

(ENERGY-ORGANICS)

(RECOVERY-INORGANICS)

WOOD

CARBOHYDRATES

LIGNIN

PULP (PROFITS)

EXTRACTIVES (PROFITS)

BY-PRODUCTS (PROBLEMS)

CHLORINE (COST)

PULPING MATERIAL BALANCES
SELECTIVITIES OF ALKALINE PULPING PROCESS

SODA | KRAFT | SODA/AQ | KRAFT/AQ
---|---|---|---
18%NaOH | 18%NaOH | 18%NaOH | 18%NaOH
6%NaSH | 0.1%AQ | 2-6%NaSH | .01-.05 AQ

CLEAVAGE OF C₆-H₂-O₄ ETHER BONDS

where X = O or S
REDOX CYCLE

CARBOHYDRATES

OXYDATION

AQ

REDUCTION

AHQ

SOLUBILIZED LIGNIN

STABILIZED CARBOHYDRATES

YIELD GAIN

RATE GAIN

Delignification via AHQ Adduct Reactions

\[
\text{AHQ}^2^- + \text{QM} \xrightarrow{4} \text{adduct} \xrightarrow{5} \text{AHQ}^- + \text{phenol fragments}
\]

Delignification via AHQ-induced SET Reactions

\[
\text{AHQ}^- + \text{QM} \xrightarrow{1} \text{AHQ}^- + \text{AQ}
\]

\[
\text{AHQ}^- + \text{AHQ}^- + \text{AQ} \xrightarrow{2} \text{AHQ}^- + \text{AHQ}^- + \text{AQ}
\]

\[
\text{AHQ}^- + \text{AHQ}^- + \text{AHQ}^- + \text{AQ} \xrightarrow{3} \text{AHQ}^- + \text{AHQ}^- + \text{AHQ}^- + \text{AQ}
\]
STERIC EFFECTS IN PULPING MECHANISMS

STERIC EFFECTS ON LIGNIN MODEL FRAGMENTATION REACTIONS
ELECTROCHEMICAL STUDIES

\[ 2\text{AQ} + 2e^- \rightarrow 2\text{AHQ}^- \quad (1) \]

\[ \text{AHQ}^- + \text{QM} \rightarrow \text{AQ} + \text{QM}^- \quad (2) \]

\[ \text{QM}^- \rightarrow \text{13}^- + \text{14}^- \quad (3) \]

\[ \text{AHQ}^- + 14^- \rightarrow \text{AQ} + 14^- \quad (4) \]

\[ \text{CH}_3\text{CH-O-}[\text{CH} = \text{CHCH}_3] + 2e^- \rightarrow \text{[\( \text{O}_-\text{OCH}_3 \) + \( \text{O}_-\text{OCH}_3 \)}] \quad (5) \]
ELECTRONIC EFFECTS IN PULPING MECHANISMS

Possible fragmentation routes in SET reaction of the indicated model

Phenol yields as a function of time in the simultaneous degradation of the indicated models at 170° in the presence of 150 equivalents of NaOH (Upper four curves) and the single degradation of the m-methyl model at 170° with 12.5 equiv. of NaOH (lower curve).
Correlation of $\sigma_M$ values with the log of the phenol liberation yields obtained from the previous figure: □, 10 min yields; ○, 60 min yields.

Modes of Soda Induced Decomposition of Models

$\text{HO}^- \text{CH}_2\text{OAr} \xrightleftharpoons{b_1} \text{CH} \text{OAr}$

$\text{HO}^- \text{CH}_2\text{OAr} \xrightarrow{b_2} \text{CH} \text{OAr}$

$\text{CH} \text{OAr} \xrightarrow{c} \text{FRAGMENTS, including ArO}^-$
PHENOL YIELDS AS A FUNCTION OF TIME (5, 10, 15, 20, 30, 40, 60, 80, AND 160 MIN) FOR THE DEGRADATION OF THE INDICATED MODELS (DONE AS 1 EQUIV. PAIRS IN THE SAME REACTOR) AT 150°C IN THE PRESENCE OF 75 EQUIV. OF NaOH AND 6 EQUIV. OF AHQ DIACETATE (---) AND IN THE PRESENCE OF 50 EQUIV. OF NaOH (—). DATA POINTS HAVE BEEN OMITTED FOR CLARITY REASONS.

AHQ, NaOH, 150°C

PHENOL YIELDS AS A FUNCTION OF TIME FOR DEGRADATIONS OF THE INDICATED MODEL IN THE PRESENCE OF DIFFERENT ADDITIVES AT THE 5 EQUIV. LEVEL AT 135°C.

PHENOL YIELDS AS A FUNCTION OF TIME FOR DEGRADATIONS OF MODELS DIFFERING IN THEIR RING A SUBSTITUENTS IN THE PRESENCE OF EXCESS LEVELS OF AHQ (—) AND SH− (—−−) AT 135°C IN AQUEOUS ALKALI.
REACTION COORDINATE

Hypothetical energy diagram for the reactions of phenolic lignin end units.

HYPOTHETICAL PARTIAL ENERGY DIAGRAM FOR FRAGMENTATION OF \( \beta \)-ARYL ETHER BONDS VIA SET REACTIONS OF QUINONEMETHIDES.
Phenol yields as a function of time for the 120°C degradation of 1 equiv. each of the two indicated models in the same reactor in the presence of (A) 25 equiv. of NaOH (lower arrows) and (B) 25 equiv. of NaOH, 1 equiv. of glucose and 1 equiv. of AQ (upper curves).

Possible SET modes of degradation of the indicated model.
SUMMARY OF MODEL STUDIES

- SODA SYSTEM
  - Slow Fragmentation Step
  - NaOH Levels Effect Reaction Course

- ADDITIVE SYSTEMS
  - Slow QM Formation Step
  - AHQ\(^-\)^2 > SH^- > Glucose > OH^-
  - Mechanism?

SYRINGYL ALCOHOL CONDENSATION REACTIONS

A SEARCH FOR RADICAL REACTIONS

Dean A. Smith and Donald R. Dimmel

SET Reactions at 135°C in IM NaOH Between Quinonemethides and AHQ^-2, Glucose, etc.

HIGH TEMPERATURE AQUEOUS REACTIONS OF SYRINGYL ALCOHOL
(D. SMITH THESIS)
Reactions of a pentenyl substituted quinonemethide (upper right) which show electron transfer processes.

**Future Directions**

- Relative Importance of SET chemistry
- Extended Electrochemical Studies
- Student Thesis Follow-up
CONSTRUCTION, MODIFICATION, AND TESTING OF ANALYTICAL AND PREPARATIVE CELLS

< 130°  |  130-150°  |  150-170°

WORKING AND REFERENCE ELECTRODE
TESTING AND SELECTION

HIGH TEMP. ELECTROCHEMICAL MODEL COMPOUND TESTING

ELECTROCHEMICAL MONITORING OF PULPING
Soda  |  Soda/AQ  |  Kraft  |  Scale-up

DIRECT ELECT. OF WOOD UNDER SODA
CONDITIONS TO PROMOTE DELIGNIFICATION

PREP./TEST FUNCTIONALIZED LIGNINS AS PULPING AIDS
LOW TEMP. GENERATION  |  HIGH TEMP. GENERATION

DEVELOP FUEL CELL FOR
OXIDIZING LIGNIN

INDIRECT ELECTROLYSIS OF PULPING LIQUORS FOR CATALYST REGENERATION
SMALL SCALE  |  LARGE SCALE

BLEACHING CONTROL AND MONITORING
SMALL SCALE  |  LARGE SCALE

PROJECTED WORK SCHEDULE OUTLINED IN THE MARCH 1985 PROPOSAL TO DOE FOR STUDIES IN HIGH TEMPERATURE ELECTROCHEMISTRY.
<table>
<thead>
<tr>
<th>Item</th>
<th>1977</th>
<th>1978</th>
<th>1979</th>
</tr>
</thead>
<tbody>
<tr>
<td>Personnel-Salaries and Wages(^a)</td>
<td>8.9</td>
<td>9.4</td>
<td>10.0</td>
</tr>
<tr>
<td>Personnel-Overhead (165% of S&amp;W)</td>
<td>14.7</td>
<td>15.5</td>
<td>16.5</td>
</tr>
<tr>
<td>Personnel-Total</td>
<td>23.6</td>
<td>24.9</td>
<td>26.5</td>
</tr>
<tr>
<td>Supporting Equipment</td>
<td>55.0(^d)</td>
<td>--</td>
<td>25.0(^e)</td>
</tr>
<tr>
<td>Electrochemical Equipment</td>
<td>10.0</td>
<td>15.0</td>
<td>--</td>
</tr>
<tr>
<td>Operating Expenses(^b)</td>
<td>20.0</td>
<td>16.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Travel(^c)</td>
<td>7.4</td>
<td>7.1</td>
<td>6.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>116</td>
<td>63</td>
<td>69</td>
</tr>
<tr>
<td><strong>Grand Total</strong></td>
<td>266</td>
<td>243</td>
<td>279</td>
</tr>
</tbody>
</table>

\(^a\) Based on data given in Table A.

\(^b\) Electrodes, cells, chemicals, supplies, cell construction costs.

\(^c\) Between organizations, DOE, national and international meetings.

\(^d\) High pressure liquid chromatography-data acquisition system.

\(^e\) Modifications to existing pulping and bleaching reactors.

**Requested monies as outlined in the March 1985 proposal to DOE for studies in high temperature electrochemistry.**
EFFECT OF AQ ON RANDOM CHAIN CLEAVAGE

<table>
<thead>
<tr>
<th>Polysaccharide</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amylose</td>
<td>acceleration</td>
</tr>
<tr>
<td>Cellulose (Cotton Linters)</td>
<td>little, if any</td>
</tr>
</tbody>
</table>
Table 1. The effect of anthraquinone (AQ) and yield in kraft and soda cooking of cotton linters.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time, h</th>
<th>Kraft</th>
<th>Kraft-AQ</th>
<th>Soda</th>
<th>Soda-AQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>--</td>
<td>96.4</td>
<td>99.5</td>
<td>96.6</td>
<td>99.2</td>
</tr>
<tr>
<td>170</td>
<td>0.0</td>
<td>95.3</td>
<td>98.1</td>
<td>95.3</td>
<td>98.7</td>
</tr>
<tr>
<td>170</td>
<td>0.5</td>
<td>94.9</td>
<td>95.1</td>
<td>94.4</td>
<td>96.2</td>
</tr>
<tr>
<td>170</td>
<td>1.0</td>
<td>92.4</td>
<td>93.0</td>
<td>92.0</td>
<td>94.1</td>
</tr>
<tr>
<td>170</td>
<td>2.0</td>
<td>89.5</td>
<td>90.2</td>
<td>90.4</td>
<td>87.5</td>
</tr>
<tr>
<td>170</td>
<td>4.0</td>
<td>83.5</td>
<td>83.9</td>
<td>84.4</td>
<td>84.5</td>
</tr>
<tr>
<td>170</td>
<td>8.0</td>
<td>73.7</td>
<td>73.6</td>
<td>75.0</td>
<td>75.0</td>
</tr>
</tbody>
</table>

---

*1.0M NaOH, 0.15M Na₂S, 25:1 liquor-to-cellulose ratio.  
1.15M NaOH, 25:1 liquor-to-cellulose ratio.  
0.0048M AQ, comparable to 0.5% addition at 5:1 liquor-to-wood ratio.
Treatment of cotton cellulose at 170°C with 1M NaOH, without AQ (X) and with 5% AQ addition (O).

WALLIS and WEARNE

Figure 2. Effect of anthraquinone (0.0048M) on cuene viscosity in soda (1.15M NaOH) cooking of cotton linters.
Figure 1. Effect of anthraquinone (0.0048M) on DPw in soda (1.15M NaOH) cooking of cotton linters.

POTENTIAL REASONS FOR DIFFERENT RESPONSE TO AQ

Stereochemical
Physical
1,5-Anhydrocelllobitol

1,5-Anhydromaltitol

AQ

AHQ
Degradation of 1,5-Anhydrocellobiitol (0.01 M) in 0.985 M NaOH at 169.8° C.

<table>
<thead>
<tr>
<th>Additive</th>
<th>$10^6 k_r$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>6.25 (0.08)</td>
</tr>
<tr>
<td>AQ (0.00480 M)*</td>
<td>6.72 (0.08)</td>
</tr>
<tr>
<td>AHQ (0.00480 M)*</td>
<td>6.27 (0.06)</td>
</tr>
</tbody>
</table>

* ∼ 0.5% at 5:1 Liquor-to-wood

Degradation of 1,5-Anhydromaltitol (0.01 M) in 0.984 M NaOH at 169.9° C.

<table>
<thead>
<tr>
<th>Additive</th>
<th>$10^6 k_r$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1.12 (0.02)</td>
</tr>
<tr>
<td>AQ (0.00480 M)</td>
<td>1.65 (0.06)</td>
</tr>
<tr>
<td>AHQ (0.00480 M)</td>
<td>1.20 (0.06)</td>
</tr>
</tbody>
</table>

* ∼ 0.5% at 5:1 Liquor-to-wood

Incremental Effect of Anthraquinone

<table>
<thead>
<tr>
<th></th>
<th>$10^6 \Delta k_r$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5-Anhydrocellobiitol</td>
<td>0.47</td>
</tr>
<tr>
<td>1,5-Anhydromaltitol</td>
<td>0.53</td>
</tr>
</tbody>
</table>
Fibrous Cellulose

\[ \stackrel{\text{DMSO/PF}}{\longrightarrow} \]

Amorphous Cellulose

\[ \stackrel{\text{NaBH}_4}{\longrightarrow} \]

Amorphous Cellulose ("Peeling Resistant")

\[ \stackrel{\text{NaOH}}{\longrightarrow} \quad \stackrel{\text{NaOH/AQ}}{\longrightarrow} \]

Yield and GPC Analysis

**FUTURE WORK**

- Continue Anthraquinone Study
  - Effect of Cellulose Structure
  - Mechanism Study
- Effect of Dead Load on Polysaccharide DP in Pulping
Project 3477

DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES

D. B. Easty
J. E. Johnson
Determination of Elemental and Polysulfide Sulfur

Analysis of Pulping and Bleaching Liquors by Ion Chromatography

Determination of Lignin in Wood Pulp by Diffuse Reflectance Fourier Transform Infrared Spectrometry

Ion chromatogram of chlorine-containing anions sensed by the electrolytic conductivity detector.
TAPPI Test Method T 699 pm-83
Analysis of Bleaching and Pulping Liquors
by Ion Chromatography

Intents of IPC investigation:
- supplement
- evaluate
- validate

ANALYSIS OF BLACK LIQUOR
CONCLUSIONS

Ion chromatography is a valuable technique for

- sulfite
- sulfate
- thiosulfate
- carbonate

Limited value for sulfide determinations

- narrow linear range
- antioxidant needed

Ion Chromatographic Analysis of Black Liquor

Proposed Contributions to T699

Use HPIC-AS3 column for black liquor.

Dilute samples with deoxygenated water.

Use equal amounts of HCHO in sulfite standards and samples.

Add SAOB to dilute sulfide standards and samples.

Extensive dilution of samples for electrochemical detector.

Incompatibility of SAOB with conductivity detector.

- Can't run sulfide and sulfoxy anions simultaneously.

Standardization of stock sulfide solution.

Determination of carbonate.

Column equilibration times.
ANALYSIS OF BLEACH LIQUORS

CHLORINE DIOXIDE
Analysis of dilute chlorine dioxide liquor. Anions determined by ion chromatography; chlorine dioxide by ACVK method.

\[ 6 \text{ClO}_2 + 3 \text{H}_2\text{O} \rightarrow 5 \text{HClO}_3 + \text{HCl} \]
Most valuable finding of ClO₂ studies:

Injection of ClO₂ liquor into IC produced chlorite response.

Chlorite response from injected chlorine dioxide solutions.
Comparison of Methods for Determination of ClO₂

<table>
<thead>
<tr>
<th>Method</th>
<th>Result, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>3.87 ± 0.04</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>3.85 ± 0.03</td>
</tr>
<tr>
<td>Iodometric</td>
<td>3.78</td>
</tr>
</tbody>
</table>

Ion Chromatographic Analysis of ClO₂ - Chlorite Mixtures

<table>
<thead>
<tr>
<th>Prepared mixture, ppm</th>
<th>Measured concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₂</td>
<td>Chlorite</td>
</tr>
<tr>
<td>1.93</td>
<td>1.00</td>
</tr>
<tr>
<td>1.93</td>
<td>1.00</td>
</tr>
<tr>
<td>1.93</td>
<td>2.00</td>
</tr>
<tr>
<td>1.93</td>
<td>2.00</td>
</tr>
<tr>
<td>0.96</td>
<td>3.00</td>
</tr>
<tr>
<td>0.96</td>
<td>3.00</td>
</tr>
</tbody>
</table>
Analysis of Chlorine - ClO$_2$ Mixture

<table>
<thead>
<tr>
<th>Time, min$^a$</th>
<th>Method</th>
<th>ClO$_2$, g/L</th>
<th>Cl$_2$, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>Prepared conc.</td>
<td>0.10</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>IC (conductivity)</td>
<td>0.10</td>
<td>---</td>
</tr>
<tr>
<td>30</td>
<td>Tyrosine</td>
<td>0.102</td>
<td>---</td>
</tr>
<tr>
<td>90</td>
<td>Iodometric</td>
<td>0.099</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>IC (conductivity)</td>
<td>0.10</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$Time of analysis, minutes after preparing sample. Sample pH 1.98

Reduction of Cl$_2$ in the Ion Chromatograph

<table>
<thead>
<tr>
<th>Cl$_2$, g/L</th>
<th>Cl$^-$, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration</td>
<td>3.23$^a$</td>
</tr>
<tr>
<td>IC (conductivity)</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$Iodometric titration of chlorine water at pH 7. 
$^b$Potentiometric titration after sparging. IC after sparging gave same value.
Hypochlorite and Chlorine

\[ \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{HCl} \]

\[ \text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \]
### Determination of Chlorine

#### Chlorine Water Samples

<table>
<thead>
<tr>
<th>Method</th>
<th>A, g/L</th>
<th>B, g/L</th>
<th>Tap Water, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC (electrochem.)</td>
<td>0.75</td>
<td>0.81</td>
<td>1.26</td>
</tr>
<tr>
<td>Iodometric</td>
<td>0.77</td>
<td>0.80</td>
<td>1.24</td>
</tr>
</tbody>
</table>

#### Analysis of Chlorine - ClO₂ Mixtures

<table>
<thead>
<tr>
<th>Method</th>
<th>ClO₂, g/L</th>
<th>Cl₂, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared conc.</td>
<td>0.05</td>
<td>0.50</td>
</tr>
<tr>
<td>IC (electrochem.)</td>
<td>---</td>
<td>0.50</td>
</tr>
<tr>
<td>Iodometric</td>
<td>0.049</td>
<td>0.50</td>
</tr>
<tr>
<td>Approx. conc.</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>IC (electrochem.)</td>
<td>---</td>
<td>0.44</td>
</tr>
<tr>
<td>Iodometric</td>
<td>0.50</td>
<td>0.44</td>
</tr>
</tbody>
</table>
### Chlorate and Chlorite

#### Chlorate, mg/L

<table>
<thead>
<tr>
<th></th>
<th>Iodometry</th>
<th>IC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0 Influent</td>
<td>N.D.</td>
<td>16</td>
</tr>
<tr>
<td>C0 Effluent</td>
<td>49</td>
<td>66</td>
</tr>
<tr>
<td>D1 Influent</td>
<td>331</td>
<td>260</td>
</tr>
<tr>
<td>D1 Effluent</td>
<td>307</td>
<td>294</td>
</tr>
<tr>
<td>D2 Influent</td>
<td>50</td>
<td>52</td>
</tr>
<tr>
<td>D2 Effluent</td>
<td>78</td>
<td>93</td>
</tr>
</tbody>
</table>
Recovery of Chlorite and Chlorate Added to a Chlorine Dioxide Liquor

<table>
<thead>
<tr>
<th></th>
<th>Original, ppm</th>
<th>Added, ppm</th>
<th>Expected, ppm</th>
<th>Found, ppm</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorite</td>
<td>N.D.(^c)</td>
<td>1.00</td>
<td>0.50</td>
<td>0.495</td>
<td>99</td>
</tr>
<tr>
<td>Chlorate</td>
<td>1.18</td>
<td>1.00</td>
<td>1.09</td>
<td>1.06</td>
<td>97</td>
</tr>
</tbody>
</table>

\(^a\)Spiked sample prepared by mixing 1 part spiking standard plus 1 part diluted Cl\(_2\)O\(_2\) liquor.
\(^b\)Mean of six replicate determinations.
\(^c\)None detected.
Recovery of Oxalate Added to Bleaching Effluents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original, ppm</th>
<th>Added, ppm</th>
<th>Total Found, ppm</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C Stage</td>
<td>0.20</td>
<td>1.0</td>
<td>1.20</td>
<td>100</td>
</tr>
<tr>
<td>Diluted 1:10</td>
<td>0.20</td>
<td>1.0</td>
<td>1.20</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>2.0</td>
<td>2.15</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>2.0</td>
<td>2.15</td>
<td>98</td>
</tr>
<tr>
<td>D Stage</td>
<td>0.20</td>
<td>2.0</td>
<td>2.19</td>
<td>99.5</td>
</tr>
<tr>
<td>Diluted 1:100</td>
<td>0.20</td>
<td>2.0</td>
<td>2.10</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>3.0</td>
<td>3.20</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>3.0</td>
<td>3.30</td>
<td>103</td>
</tr>
</tbody>
</table>

Conclusions

IC can be used to determine:

- chlorine dioxide
- chlorine
- chlorite
- chlorate
- chloride
- hypochlorite
- oxalate
Sources of Error in the Amalgam Method for Determining Polysulfide in Kraft White Liquor

Sodium Amalgam Method

Reaction with sodium sulfite:

\[ \text{Na}_2\text{SS}_x + x \text{Na}_2\text{SO}_3 \rightarrow \text{Na}_2\text{S} + x \text{Na}_2\text{S}_2\text{O}_3 \]

Reaction with sodium amalgam:

\[ \text{Na}_2\text{SS}_x + 2x \text{NaHg} \rightarrow (x + 1) \text{Na}_2\text{S} + 2x \text{Hg} \]
Influences on Results from Amalgam Method

Sample dilution and quantity on amalgam

Contact with air during amalgam treatment

Effect on Measured Polysulfide of Sample Volume and Concentration in Contact with Amalgam

<table>
<thead>
<tr>
<th>Liquor Dilution</th>
<th>Volume of Diluted Liquor Placed on Amalgam, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mL → 100 mL</td>
<td>5: 16.7 16.0 16.7 16.0 16.7 16.1 16.7 15.9</td>
</tr>
<tr>
<td>10 mL → 100 mL</td>
<td>5: 16.7 16.0 16.7 16.1 16.7 15.9 16.0 15.1</td>
</tr>
</tbody>
</table>

Polysulfide values are in g/L. Fifteen mL of amalgam was used for each sample.
Polysulfide Determinations Run With and Without Nitrogen Protection During Reduction on Amalgam

<table>
<thead>
<tr>
<th>Liquor</th>
<th>N\textsubscript{2} Protected, g/L</th>
<th>Not Protected, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.9 16.0</td>
<td>14.9 14.6</td>
</tr>
<tr>
<td>2</td>
<td>6.2 6.1</td>
<td>5.6 5.3</td>
</tr>
<tr>
<td>3</td>
<td>7.7 7.6</td>
<td>6.8 6.8</td>
</tr>
<tr>
<td>4</td>
<td>14.5 14.6</td>
<td>14.0 14.1</td>
</tr>
<tr>
<td>5</td>
<td>13.7 13.8</td>
<td>12.2 12.3</td>
</tr>
</tbody>
</table>

Conclusions

Liquor dilution, volume placed on amalgam, and contact with air during amalgam treatment are sources of error.
Future Work

Incorporate ion chromatography results in revised T699.
Perform limited studies on chlorine dioxide decomposition.
Resume investigation of FTIR lignin method.
Recovery Overview

T. M. Grace
CURRENT DUES-FUNDED RESEARCH PLAN

7-1-85 ——> 6-30-86

3473-1: Fundamental processes in alkali recovery furnaces
$220k
a. fume formation fundamentals
b. phenomenological burning study
c. fundamentals of S release and recapture
d. physical properties of smelt and char

3456-2: Smelt-water explosions
$20k
a. supplement API explosion monitoring
b. interpret NRC project results
c. collaborate with Corradini at UW

3558: Incremental capacity in recovery boilers
$50k
a. detailed checklist of capacity limits
b. define research needs
PRESENT STUDENT RESEARCH

Ph.D.:  Paul Miller  Pyrolysis/swelling of black liquor
       Mark Robinson  Convective drying of black liquor
       Greg Aiken  Pile burning of char

M.S.:  Kris Goerg  Char gasification with CO$_2$
       Kathy Crane  Single-particle combustion model
       Dan Sumnicht  Bed burning model
       Terry Coenen  Sulfate reduction with CO
       Ed Buehler  Cocurrent burning
       Tim Cartwright  Fluid bed drying of black liquor
       Nancy Sell  Fluid bed modeling with MAPPS
       James Cantrell  Sulfur release during combustion
*Goran Nyman  Sulfur release during pyrolysis

* Summer Student
### ANTICIPATED FALL 1985 STUDENT RESEARCH

<table>
<thead>
<tr>
<th>Ph.D.</th>
<th>Project</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mark Robinson</td>
<td>Convective drying of black liquor</td>
</tr>
<tr>
<td>Greg Aiken</td>
<td>Pile burning of char</td>
</tr>
<tr>
<td>Greg Kulas</td>
<td>Smelt electrochemistry</td>
</tr>
<tr>
<td>Jim Truax</td>
<td>Gas-phase fume intermediates</td>
</tr>
<tr>
<td>James Cantrell</td>
<td>Fume morphology or condensation/solidification</td>
</tr>
<tr>
<td>Andy Jones</td>
<td>Recovery boiler overall model</td>
</tr>
<tr>
<td>James Burns</td>
<td>Modeling - air and gas flows</td>
</tr>
<tr>
<td>Allan Walsh</td>
<td>Modeling - liquor delivery</td>
</tr>
<tr>
<td>Dan Sumnicht</td>
<td>Modeling - char bed</td>
</tr>
<tr>
<td>Kris Goerg</td>
<td></td>
</tr>
<tr>
<td>Ed Buehler</td>
<td></td>
</tr>
</tbody>
</table>
CONTRACT RESEARCH

1. DOE Project - Black Liquor Combustion Fundamentals
2. NRC Project - Energetics of Smelt-Water Explosions
3. API - Recovery Boiler Explosion Monitoring
COMPLETED RESEARCH
(Formal Reports)

1. Char Burning - Operational Implications
2. Char Burning - Summary Technical Report
3. Carbon Oxidation in Carbonate Melts
4. Sulfate Reduction with Carbon - Report Two
5. Sulfate Reduction with Carbon - Report One
Small Scale - Knowledge Needs

Drying
1. Black liquor drying with convective heating
2. Radiation dominated B.L. drying behavior

Pyrolysis
1. Swelling behavior in nonoxidizing environments
2. Swelling behavior during volatiles burning
3. Fuel split during pyrolysis-reductive and oxidative environments

Sulfur Release
1. Sulfur release during pyrolysis-reductive environment
2. Sulfur release during pyrolysis-oxidative environment
3. Sulfur release during char burning
4. Sulfur release from melt-scanning experiments
5. Verification of equilibrium predictions on sulfur retention

Char Gasification
1. Fundamental kinetic data on CO2-C in molten salt
2. Data on relation between C concentration in smelt and CO/CO2 ratio-high C loadings
3. Fundamental kinetic data on H2O-C in molten salt
4. Can char be directly gasified to CO by reaction with oxygen gas
5. Can CO2 oxidize sulfide

Char Reactivity
1. Method of measuring char reactivity (C-SO4)
2. Relationship between swelling and reactivity
3. Gasification reactivity - O2, CO2, H2O
4. Intrinsic reactivity vs. char particle burning rate

Reactions Involving Hydrogen
1. H2 reduction of sulfate
2. H2O-smelt reactions
3. H2O gasification of char
Fume Formation

1. Use SOLGASMIX to determine thermodynamic boundaries for liquid Na presence and formation in smelt
2. Kinetic limitations to Na formation
3. What actually causes oxidative fuming
4. Are exotic volatiles present
5. Condensation/deposition phenomena

Funded 86
Funded 86
Funded 86
(Truax)
DOE P3 + Cantrell
+ Reeve/Tran

Smelt Chemistry

1. What sulfur species are actually present in smelt
2. How does NaOH behave in smelt
3. What H containing compounds might we have

Properties

1. Physical properties of smelt that affect drainage or slagging behavior

Funded 86-87

Char Physical Behavior

1. Quantification of when char liquifies
2. Development of a physical model of char structure
3. Strength (mechanical) of char

Burning Phenomena

1. Characterization of burning times
2. Definition of burning phenomena
3. Modeling of single-particle burning

Hupa/Funded 86
Funded 86
Crane
MACROSCALE PHENOMENA
(Modeling Effort)

Overall Model - integrating 5 elements
1. Liquor delivery
2. Gas flow patterns
3. In-flight burning
4. Bed burning
5. Cooling processes
Project 3473-1

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES

Fume Generation - J. H. Cameron
Black Liquor Burning - R. J. Kapheim
THEORIES OF FUME GENERATION

A) FUME RESULTS FROM A VOLATILE SODIUM OXIDE FORMED DURING SULFIDE OXIDATION

B) FUME RESULTS FROM GAS PHASE OXIDATION ENHANCED SODIUM VAPORIZATION
Typical experimental fume generation results with purge introduced below the melt surface.

Run 38
Initial Melt Composition
Na$_2$CO$_3$ = 0.77 mol
Na$_2$S = 0.03 mol

<table>
<thead>
<tr>
<th>Time, s</th>
<th>Na$_2$SO$_4$, mol/L</th>
<th>Na$_2$S, mol/L</th>
<th>Fume Generation Rate, g/min</th>
<th>Fume Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>755</td>
<td>0.136</td>
<td>0.549</td>
<td>0.0099</td>
<td>0.00214</td>
</tr>
<tr>
<td>1280</td>
<td>0.231</td>
<td>0.455</td>
<td>0.0104</td>
<td>0.00224</td>
</tr>
<tr>
<td>1760</td>
<td>0.318</td>
<td>0.368</td>
<td>0.0106</td>
<td>0.00288</td>
</tr>
<tr>
<td>2240</td>
<td>0.405</td>
<td>0.281</td>
<td>0.0104</td>
<td>0.00224</td>
</tr>
<tr>
<td>2721</td>
<td>0.492</td>
<td>0.195</td>
<td>0.0099</td>
<td>0.00214</td>
</tr>
<tr>
<td>3114</td>
<td>0.563</td>
<td>0.124</td>
<td>0.0088</td>
<td>0.00190</td>
</tr>
<tr>
<td>3639</td>
<td>0.656</td>
<td>0.029</td>
<td>0.0005</td>
<td>0.00011</td>
</tr>
</tbody>
</table>

Effect of oxygen in purge on rate of fume generation.

Temperature = 1200°K (1700°F)

<table>
<thead>
<tr>
<th>Run</th>
<th>N$_2$, L/min</th>
<th>O$_2$, L/min</th>
<th>Fume Generation Rate, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1.02</td>
<td>0.0105</td>
<td>0.00892</td>
</tr>
<tr>
<td>46</td>
<td>1.02</td>
<td>0.021</td>
<td>0.0105</td>
</tr>
<tr>
<td>47</td>
<td>1.02</td>
<td>0.042</td>
<td>0.0121</td>
</tr>
<tr>
<td>48</td>
<td>1.01</td>
<td>0.063</td>
<td>0.0145</td>
</tr>
<tr>
<td>49</td>
<td>1.02</td>
<td>0.084</td>
<td>0.0146</td>
</tr>
</tbody>
</table>
Effect of Temperature on Fume Generation

Initial Conditions
\( \text{Na}_2\text{CO}_3 = 0.77 \text{ mole} \)
\( \text{Na}_2\text{S} = 0.03 \text{ mole} \)

Purge rate = 1.0L/min
\( \text{O}_2 \text{in Purge} = 2.1\% \)
Effect of purge rate on fume generation.

Initial Melt Conditions: \( \text{Na}_2\text{CO}_3 = 0.77 \text{ mole} \)
\( \text{Na}_2\text{S} = 0.03 \text{ mole} \)
Temperature = 1200°K
(1700°F)

<table>
<thead>
<tr>
<th>Run</th>
<th>( \text{N}_2 ), L/min</th>
<th>Air, L/min</th>
<th>Total ( \text{N}_2 ), L/min</th>
<th>Fume Generation Rate ± Std. Dev., g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.4</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>53</td>
<td>0.9</td>
<td>0.1</td>
<td>0.98</td>
<td>0.01024 ± 0.00032</td>
</tr>
<tr>
<td>54</td>
<td>1.06</td>
<td>0.1</td>
<td>1.14</td>
<td>0.01204 ± 0.00042</td>
</tr>
<tr>
<td>55</td>
<td>1.23</td>
<td>0.1</td>
<td>1.31</td>
<td>0.01474 ± 0.00198</td>
</tr>
</tbody>
</table>

Rate expression describing fume generation from a carbonate melt.

Rate Fume Generation, g/min = \( K(\text{N}_2, \text{L/min})^M(\text{O}_2, \text{L/min})^N e^{-\Delta E/RT} \)

Parameter, Value

- \( K = 161 \)
- \( M = 0.907 \)
- \( N = 0.274 \)
- \( \Delta E = 20,540 \text{ cal/mol} \)

Linear Estimate of Std. Dev.

- 26
- 0.096
- 0.024
- 1,360 cal/mol
Effect of NaOH on fume generation.

Temperature = 1228°K (1750°F)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Na₂CO₃ mole</th>
<th>Na₂S mole</th>
<th>NaOH mole</th>
<th>Purge O₂, L/min</th>
<th>Purge N₂, L/min</th>
<th>Fume Generation, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.77</td>
<td>0</td>
<td>0.012</td>
<td>0</td>
<td>1.0</td>
<td>No fume measured</td>
</tr>
<tr>
<td>191</td>
<td>0.77</td>
<td>0</td>
<td>0.031</td>
<td>0</td>
<td>1.0</td>
<td>0.00006</td>
</tr>
<tr>
<td>192</td>
<td>0.77</td>
<td>0.03</td>
<td>0.010</td>
<td>0</td>
<td>1.0</td>
<td>0.0007</td>
</tr>
<tr>
<td>193</td>
<td>0.77</td>
<td>0.03</td>
<td>0.10</td>
<td>0</td>
<td>1.0</td>
<td>0.0007</td>
</tr>
<tr>
<td>194ᵃ</td>
<td>0.77</td>
<td>0.03</td>
<td>0.02</td>
<td>0.021</td>
<td>1.0</td>
<td>0.013</td>
</tr>
<tr>
<td>195</td>
<td>0.77</td>
<td>0.03</td>
<td>0.03</td>
<td>0.021</td>
<td>1.0</td>
<td>0.0048</td>
</tr>
<tr>
<td>196</td>
<td>0.77</td>
<td>0.03</td>
<td>0.06</td>
<td>0.021</td>
<td>1.0</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

ᵃStandard, no NaOH.

BEHAVIOR OF NONPROCESS ELEMENTS
DURING OXIDATIVE FUMING
Behavior of Potassium during Oxidative Fuming

Conditions: Temp = 1228°C (1750°F)
O₂ Flow Rate = 0.021 L/min
N₂ Flow Rate = 1.0 L/min

<table>
<thead>
<tr>
<th>Melt K/Na Molar ratio</th>
<th>Fume K/Na Molar ratio</th>
<th>Enrichment Factor K/Na fume/K/Na fume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0256</td>
<td>0.0225</td>
<td>0.88</td>
</tr>
<tr>
<td>0.0811</td>
<td>0.0888</td>
<td>1.09</td>
</tr>
<tr>
<td>0.143</td>
<td>0.141</td>
<td>0.99</td>
</tr>
<tr>
<td>1.00</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>5.46</td>
<td>6.01</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Behavior of Chloride during Oxidative Fuming

Conditions: Temp = 1228°C (1750°F)
O₂ Flow Rate = 0.021 L/min
N₂ Flow Rate = 1.0 L/min

<table>
<thead>
<tr>
<th>Melt Cl/Na Molar ratio</th>
<th>Fume Cl/Na Molar ratio</th>
<th>Enrichment Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>.049</td>
<td>.082</td>
<td>1.7</td>
</tr>
<tr>
<td>.122</td>
<td>.222</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Effect of Chloride on Potassium Behavior During Oxidative Fuming

Conditions: Temp = 1228°K (1750°F)

\[ \text{O}_2 \text{ Flow Rate } = 0.021 \text{ L/min} \]
\[ \text{N}_2 \text{ Flow Rate } = 1.0 \text{ L/min} \]

<table>
<thead>
<tr>
<th>Melt Cl/Na Molar ratio</th>
<th>Fume Cl/Na Molar ratio</th>
<th>Enrichment Factor Cl/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>.119</td>
<td>.181</td>
<td>1.5</td>
</tr>
<tr>
<td>.019</td>
<td>.0492</td>
<td>2.62</td>
</tr>
<tr>
<td>.127</td>
<td>.169</td>
<td>1.3</td>
</tr>
<tr>
<td>.028</td>
<td>.0564</td>
<td>2.02</td>
</tr>
<tr>
<td>.116</td>
<td>.196</td>
<td>1.7</td>
</tr>
<tr>
<td>.013</td>
<td>.0272</td>
<td>2.11</td>
</tr>
<tr>
<td>.123</td>
<td>.183</td>
<td>1.5</td>
</tr>
<tr>
<td>.061</td>
<td>.115</td>
<td>1.89</td>
</tr>
</tbody>
</table>

Purging above melt with low oxygen partial pressures
(Oxidation Rate, Moles O_2/min) (1% O_2 in Off Gas)

Initial Conditions:
- 0.77 mole Na_2CO_3
- 0.03 mole Na_2S
- Temperature = 1550°F (843°C)

<table>
<thead>
<tr>
<th>RUN</th>
<th>Air Flow Rate L/min</th>
<th>N_2 Flow Rate L/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>0.20</td>
<td>0.86</td>
</tr>
<tr>
<td>80</td>
<td>0.40</td>
<td>0.60</td>
</tr>
<tr>
<td>81</td>
<td>0.60</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Purging above melt with high oxygen partial pressure

Effect of oxidation on fume generation.

Initial Conditions:
- Na_2CO_3 = 0.77 mole
- Na_2S = 0.03 mole
- Temperature = 1228°F (1700°C)

<table>
<thead>
<tr>
<th>Purge Introduced Below Melt</th>
<th>Oxidation Rate, moles O_2 consumed/min x 10^6</th>
<th>Fume Rate, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.38</td>
<td>0.0106</td>
<td>3.88</td>
</tr>
<tr>
<td>9.46</td>
<td>0.0134</td>
<td>7.80</td>
</tr>
<tr>
<td>12.00</td>
<td>0.0079</td>
<td>17.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Purge Introduced Above Melt</th>
<th>Oxidation Rate, moles O_2 consumed/min x 10^6</th>
<th>Fume Rate, g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.84</td>
<td>0.00146</td>
<td>0.00100</td>
</tr>
<tr>
<td>3.88</td>
<td>0.00100</td>
<td>0.00115</td>
</tr>
<tr>
<td>7.80</td>
<td>0.00079</td>
<td>0.00044</td>
</tr>
</tbody>
</table>
**Oxidation Enhanced Metal Vaporization**

![Diagram of Oxidation Enhanced Metal Vaporization]

**Molten Metal**

Gas phase oxidation enhanced vaporization

Effect of oxygen partial pressure on metal vaporization
Fume Generation Rates Using Ar and He

<table>
<thead>
<tr>
<th>Gas System</th>
<th>Fume Generation Rate at $O_2 = 0.02$ L/min</th>
<th>$O_2 = 0.10$ L/min</th>
<th>Relative to $N_2$ at $O_2 = 0.02$ L/min</th>
<th>$O_2 = 0.10$ L/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2-O_2$</td>
<td>0.0121</td>
<td>0.0189</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$Ar-O_2$</td>
<td>0.00899</td>
<td>0.0155</td>
<td>0.74</td>
<td>0.82</td>
</tr>
<tr>
<td>$He-O_2$</td>
<td>0.00496</td>
<td>0.0118</td>
<td>0.41</td>
<td>0.62</td>
</tr>
</tbody>
</table>

CONCLUSIONS:

1) Sulfide Oxidation is a Major Source of Fume

2) Vaporization of NaOH is a Minor Source of Fume

3) A Significant Feature of Fume Generation During Sulfide Oxidation is a Gas Phase Oxidation Reaction
PROJECT 3473-1

BLACK LIQUOR BURNING
(SINGLE PARTICLE REACTOR)

OBJECTIVES

- CHARACTERIZE BLACK LIQUOR BURNING
- DEVELOP & USE ANALYTICAL TESTS
- WIDE RANGE OF SAMPLES (SURVEY)

BACKGROUND

- FALL 1984: 3 CONDITIONS, 4 MEASUREMENTS
  PARTIAL CONFIRMATION OF OUTSIDE RESEARCH
  ON PARTICLE BEHAVIOR (HUPA)

- SPRING 1985: 14 LIQUORS, 10 MEASUREMENTS
  DEPENDENCY OF SWOLLEN VOLUME ON RESIDUAL ACTIVE ALKALI
  HEAT VALUE
  SULFATED ASH
  % VOLATILE

- FALL 1985: 26 LIQUORS, 5 PARTICLE MEASUREMENTS
  COMBUSTION RATES
  SWELLING BEHAVIOR

- FALL 1985: 15 LIQUOR TESTS
SINGLE PARTICLE REACTOR

Microbalance

Alumina Tube

Gas In from Heater

Flow Straightener

Gas Bypass

Sample

Optical Trench to Diagram

lower unit (moveable)

Gas Out to Analyzers

Insulation

Note: All gas passages are 50mm x 50mm
Simplified Burning Picture
(Medium size droplets)

SPR—TYPICAL PARTICLE BEHAVIOR
NITROGEN PYROLYSIS 932° F

VOLUME

MASS

SPECIFIC VOLUME
$\frac{cm^3}{gm\ SOLID}$

MAX SWELLING

MASS
$mg$
slope
$\frac{mg}{sec}$

PYROLYSIS TIME

TIME
SPECIFIC SWOLLEN VOLUME

PHOTOGRAPHIC AREA \( \rightarrow \) PARTICLE VOLUME

\[ Y \frac{A}{X} V = f(Dp) \]

SSV = Volume of sphere whose diameter, \( Dp \), equals the diameter of a circle of measured area \( A \).

BLACK LIQUOR PROPERTIES

- PROCESS MEASURES
  - HIGH HEATING VALUE
  - SULFATED ASH
  - RESIDUAL ACTIVE ALKALI

- COMPOSITION
  - \( \text{NaOH} \)
  - \( \text{Na}_2\text{S} \)
  - \( \text{Na}_2\text{CO}_3 \)
  - \( \text{Na}_2\text{SO}_4 \)

- ELEMENTAL
  - Na.
  - K.
  - S.
  - Cl.
  - C.
  - H.
  - O.

p. 30
p. 35
COMBUSTION TESTS

TOTAL BURN TIME ............... sec
TIME TO MAX. SPECIFIC VOLUME .... ""
CHAR BURN TIME ............... ""

PYROLYSIS SPECIFIC SWOLLEN VOLUME .. cc/gm SOLID
PYROLYSIS WEIGHT LOSS RATE ......... mg/sec/mg SOLID
PYROLYSIS SPECIFIC TIME ............. sec/mg SOLID

COMBUSTION WEIGHT LOSS RATE ....... PENDING
TIME TO MAX GAS CONCENTRATION ....... PENDING
**BL SURVEY**

**LEGEND**
- + = Softwood
- # = Hardwood
- ○ = <50% Softwood
- × = <50% Hardwood
- * = Eucalyptus

Diagram showing a scatter plot with axes for **SWOL VOL CC/GM S** and **NA₂SO₄ %**. The plot includes various markers for different categories of material and a legend explaining their significance.
BL SURVEY

LEGEND
+ = Softwood
# = Hardwood
○ = <50% Softwood
× = <50% Hardwood
* = Eucalyptus
BL SURVEY

LEGEND
+ = Softwood
# = Hardwood
○ = <50% Softwood
× = <50% Hardwood
* = Eucalyptus

TIME-3 MV-SB SEC

NA₂SO₄ %
BL SURVEY

LEGEND
+ = Softwood
# = Hardwood
○ = <50% Softwood
× = <50% Hardwood
* = Eucalyptus
BL SURVEY

LEGEND

+ = Softwood

# = Hardwood

○ = <50% Softwood

× = <50% Hardwood

* = Eucalyptus

SOLIDS % BURNED

PYR RATE x 10 SEC-1
CONCLUSIONS

- SINGLE VALUED, ONE CAUSE – ONE EFFECT RELATIONSHIPS DO NOT DESCRIBE ACTUAL BURNING BEHAVIOR ADEQUATELY

- LIQUOR BURNING PROGRESSES IN FOUR STAGES
  SEQUENTIAL IN SMALL PARTICLES
  SEQUENTIAL & PARALLEL IN LARGE PARTICLES

- SODIUM SALTS STRONGLY INFLUENCE SWELLING/BURNING BEHAVIOR

- OTHER VARIABLES MAY BE OPERATING

FUTURE: 4 QTR '85 – 1 QTR '86

- FINISH ANALYSIS OF COMBUSTION TESTING
  (EXPERIMENTATION IS COMPLETE)
  COMBUSTION SWOLLEN VOLUME
  COMBUSTION WEIGHT LOSS RATE

- MEASURE MAX. LEVELS OF RELEASED GAS
  \( \text{CO}_2, \text{CO}, \text{SO}_2 \)

- ROUTINE ANALYSIS OF 6 NEW SAMPLES
  (TOTAL 30)

- DESIGN/RUN CONTROL EXPERIMENTS TO CONFIRM SUGGESTED CONCLUSIONS
Project 3473-6

FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

D. T. Clay
FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

OBJECTIVES

- DEVELOP A BLACK LIQUOR COMBUSTION REACTOR
- APPLY ADVANCED SPECTROSCOPIC TECHNIQUES
- OBTAIN FUNDAMENTAL DATA
FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

PROJECT SCHEDULE
YEARS FROM PROJECT START

<table>
<thead>
<tr>
<th>Start</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase I.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In Flight Processes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase II.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char Bed Processes</td>
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<td></td>
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<tr>
<td>Phase III.</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Inorganic Fume Formation</td>
<td></td>
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</tr>
<tr>
<td>Phase IV.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recovery Simulation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Five-year project schedule. Project began September, 1983.

FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

PROJECT MILESTONES

PHASE 1

**MILESTONE** | **TARGET COMPLETION BY END OF YEAR.QUARTER**
---|---
In-Flight Chemical Processes | 
1. REACTOR PREENGINEERING | 84.1
2. PRELIMINARY COMBUSTION EXPERIMENTS | 84.3
3. PHASE I REACTOR DETAILED ENGINEERING | 84.4
4. IPC REACTOR CENTRAL UNITS AND NBS REACTOR FIRST MODULES INSTALLED | 85.2
5. REACTOR TEMPERATURE/FLOW/DROPLET CHARACTERIZATION | 85.3
6. PHASE I REACTORS COMPLETELY INSTALLED | 85.4
7. PHASE I REACTORS FULLY OPERATIONAL | 86.1
8. PROCESS AND DIAGNOSTIC TESTS, LIQUID FEED | 86.2
9. PROCESS AND DIAGNOSTIC TESTS, SOLID FEED | 86.3
10. PHASE I REPORT | 86.4

Phase I Milestones
IPC flow reactor system block diagram

NBS dilute-phase reactor system block diagram
NBS initial reactor modules
BLACK LIQUOR DROPLET INJECTOR (Model II)

Black liquor droplet injector
IPC TESTING

TEMPERATURE PROFILES
RESIDENCE TIME TESTS
"EQUILIBRIUM" PYROLYSIS TESTS
PYROLYSIS GAS STUDIES
TEMPERATURE PROFILES
Doe Reactor High Medium and Low Profiles w/o SOS

IPC flow reactor temperature profile at center of the heater sections
TEMPERATURE PROFILE
Doe Reactor Medium Profile with SOS

Medium temperature profile which shows temperatures in center of heater sections and SOS sections.
CONCLUSIONS - Temperature Profile Tests

- Significant wall temperature variation at SOS sections
- Improved measurements needed for accurate gas temperature

Residence Time Tests

- $N_2$ flow: 2 - 14 scfm (60 - 400 slpm)
- Gas temperature: 1290 - 1670°F (700 - 910°C)
- Particles solids mass:
  - 78.4%
  - 5 - 30 mg
- Particles solids diameter:
  - 1.9 - 3.4 mm (nominal)
DOE PYROLYSIS
Predicted vs Actual Particle Residence Time

\[ RT = 0.053 + 0.044V - 0.33D + 2.6 \]  

\[ r^2 = 0.73 \]

RT = residence time, seconds
\( N_2 \) = \( N_2 \) upflow, SCFM
\( \bar{V} \) = specific swollen volume, cc/g solids
\( \bar{D} \) = expanded diameter, mm

Predicted particle residence time [Eq. (3)] vs. measured residence time under pyrolysis conditions.
DOE PYROLYSIS

Predicted vs Actual Lost Total Sulfur

\[ LTS = 1.5V - 14.7D + 74.3 \]  \hspace{1cm} (5)

\[ r^2 = 0.65 \]

LTS = lost total sulfur, percent of original sulfur present

V = specific swollen volume, cc/g solids

D = expanded diameter, mm

Predicted lost total sulfur [Eq. (5)] vs. measured sulfur loss under pyrolysis conditions.
CONCLUSIONS: RT Tests

- PARTICLE EXPANSION MAIN FACTOR AFFECTING RESIDENCE TIME
- SULFUR LOSS OCCURS DURING EARLY STAGES OF PYROLYSIS

"EQUILIBRIUM" PYROLYSIS TESTS

N₂ FLOW 3.5 SCFM (100 SLPM)
VELOCITY 4.4 - 8.2 FT/S (1.3 - 2.5 M/S)
GAS TEMPERATURE 570 - 1470°F (300 - 800°C)
PARTICLES SOLIDS 78.4%
MASS 40 MG (NOMINAL)
DIAMETER 3.8 MM (NOMINAL)

Sulfur loss during equilibrium pyrolysis tests in the SPR
DOE SPR


Lost plus fixed carbon measured in chars from equilibrium pyrolysis tests.
CONCLUSIONS: Equilibrium Pyrolysis Tests

- Sulfur loss occurs before substantial carbon loss or fixation

Pyrolysis Gas Studies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Temperature</td>
<td>650 - 1050°F (345 - 565°C)</td>
</tr>
<tr>
<td>Particles solids mass</td>
<td>63 - 99%</td>
</tr>
<tr>
<td>Mass Diameter</td>
<td>5 - 15 MG</td>
</tr>
<tr>
<td>DIAMETER</td>
<td>1.9 - 2.7 MM (NOMINAL)</td>
</tr>
<tr>
<td>Sulfur Addition</td>
<td>0 - 3% ODS (ABOVE ORIGINAL IN LIQUOR)</td>
</tr>
</tbody>
</table>
PYROLYSIS GASES – TEMPERATURE
SULFUR GASES

M MOL/G SOLIDS

650 700 750 800 850 900 950 1000 1050 1100 1150

TEMPERATURE F

Reduced sulfur gases evolved during pyrolysis of a black liquor droplet
Hydrocarbon gases evolved during pyrolysis of a black liquor droplet
The effect of added sulfur content on SO₂ evolved during black liquor droplet pyrolysis.
CONCLUSIONS: PYROLYSIS GAS STUDIES

- Heating rate and final particle temperature significantly influences sulfur release
- High heating rates should enhance sulfur retention in black liquor droplets

NEAR TERM PLANS

IPC
- Metered Flow - Trajectory Tests
- Char Production
- Equipment Update to PI System

NBS
- T, V Profiles
- Initial In-flight Processes
- Equipment Update to PI System
Project 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

W. F. W. Lonsky

Stuart Lebo
FUNDAMENTALS OF BRIGHTNESS STABILITY
OF HIGH-YIELD PULPS

Project 3524

Objective

Elucidate mechanism for brightness loss in high-yield pulps
Schematic Outline of Research

1. SPRUCE MP ASPEN MP
   - BLEACHING \( \text{Na}_2\text{S}_2\text{O}_4; \text{H}_2\text{O}_2 \)
   - HEAVY METAL DETERMINATION
     - EDTA EXTRACTION
     - CONTROLLED HEAVY METAL ADDITION
   - HANDSHEET
     - EXPOSURE TO SIMULATED SUNLIGHT
     - EXPOSURE TO MONOCHROMATIC LIGHT
     - PHOTobleaching (MS Thesis)
     - CHEMISTRY OF COLOR REVERSION
     - STRENGTH LOSS CELLULOSE DEGRADATION
     - IDENTIFICATION OF PRECURSORS
     - AVOID COLOR REVERSION: CHEM. MODIFICATION OF PRECURSORS
       - OPTICAL BRIGHTENERS
     - HIGH BRIGHTNESS STABILITY

2. BRIGHTNESS STABILITY COLOR REVERSION
EXPOSURE TO SIMULATED SUNLIGHT

A set of reflectance difference curves obtained from bleached aspen TMP (8% H2O2/2% dithionite) and exposed to light.
INDOOR - OUTDOOR EXPERIMENTS

8% Peroxide/2% Dithionite (Indoor Experiment)
8% Peroxide/2% Dithionite (Outdoor Experiment)
Bleaching of aspen TMP with alkali/hydrogen peroxide and sodium dithionite.

<table>
<thead>
<tr>
<th>H$_2$O$_2$ Based on</th>
<th>NAOH Based on</th>
<th>Residual H$_2$O$_2$, %</th>
<th>pH Out</th>
<th>Brightness</th>
<th>Reversion</th>
<th>Klason Lignin, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>o.d. Pulp, %</td>
<td>o.d. Pulp, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>--</td>
<td>58.4</td>
<td>56.9</td>
<td>20.8</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.7</td>
<td>0.02</td>
<td>9.3</td>
<td>66.2</td>
<td>65.3</td>
<td>20.0</td>
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<td>0.5</td>
<td>1.5</td>
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<td>9.0</td>
<td>69.2</td>
<td>68.2</td>
<td>20.1</td>
</tr>
<tr>
<td>1.0</td>
<td>1.74</td>
<td>0.22</td>
<td>8.5</td>
<td>72.2</td>
<td>71.0</td>
<td>20.3</td>
</tr>
<tr>
<td>1.5</td>
<td>2.5</td>
<td>0.03</td>
<td>8.6</td>
<td>74.0</td>
<td>72.9</td>
<td>20.3</td>
</tr>
<tr>
<td>3.0</td>
<td>2.9</td>
<td>0.66</td>
<td>8.9</td>
<td>78.0</td>
<td>76.4</td>
<td>19.0</td>
</tr>
<tr>
<td>4.0</td>
<td>3.3</td>
<td>1.2</td>
<td>8.8</td>
<td>79.1</td>
<td>77.3</td>
<td>19.0</td>
</tr>
<tr>
<td>8.0</td>
<td>4.4</td>
<td>3.0</td>
<td>9.4</td>
<td>81.9</td>
<td>79.9</td>
<td>18.7</td>
</tr>
<tr>
<td>3.0/1% Dithionite</td>
<td></td>
<td></td>
<td>6.2</td>
<td>79.9</td>
<td>78.3</td>
<td>19.0</td>
</tr>
<tr>
<td>8.0/2% Dithionite</td>
<td></td>
<td></td>
<td>6.2</td>
<td>82.8</td>
<td>80.9</td>
<td>18.6</td>
</tr>
</tbody>
</table>

NOTE: %-Values based on o.d. pulp - Reaction conditions: 0.05% MgSO$_4$, 3% SiO$_2$; 12% consistency, 40°C, 180 min - Second stage (dithionite): pH adjusted to 6.0; 2.5% consistency, 70°C, 60 min.
Effect of bleaching on the brightness stability of aspen TMP.

\[ \% \text{ Brightness} = k \cdot \log_{10} \text{[time]} + R \]

<table>
<thead>
<tr>
<th>Aspen TMP Bleached With</th>
<th>422_K</th>
<th>422_R(1 hour)</th>
<th>457_k</th>
<th>457_R(1 hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>-9.65</td>
<td>51.15</td>
<td>-8.09</td>
<td>61.64</td>
</tr>
<tr>
<td>1.5% Peroxide</td>
<td>-18.91</td>
<td>48.27</td>
<td>-19.51</td>
<td>61.13</td>
</tr>
<tr>
<td>3% Peroxide</td>
<td>-18.32</td>
<td>48.15</td>
<td>-19.97</td>
<td>61.72</td>
</tr>
<tr>
<td>8% Peroxide</td>
<td>-17.98</td>
<td>48.67</td>
<td>-20.53</td>
<td>62.89</td>
</tr>
<tr>
<td>8% Peroxide/2% dithionite</td>
<td>-17.06</td>
<td>48.29</td>
<td>-18.79</td>
<td>62.19</td>
</tr>
</tbody>
</table>

**REMARKS:**
- 422_k and 422_R(1 hour) calculated from the % reflectance values at 422 nm.
- 457_k and 457_R(1 hour) calculated from the % reflectance values at 457 nm.

**EFFECT OF HEAVY METALS**

(W. Welsh, M.S. 1985)
Metal Analyses of Handsheets Used in the Yellowing Experiments

Heavy metal concentrations in ppm (O.D. basis)

<table>
<thead>
<tr>
<th>Handsheets</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached-untreated</td>
<td>261</td>
<td>24.9</td>
<td>51.0</td>
</tr>
<tr>
<td>Unbleached-heavy metal free</td>
<td>33.6</td>
<td>11.1</td>
<td>0.56</td>
</tr>
<tr>
<td>Peroxide bleached-untreated</td>
<td>446</td>
<td>38.2</td>
<td>1.09</td>
</tr>
<tr>
<td>Peroxide bleached-metal free</td>
<td>28.0</td>
<td>10.6</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Brightness Reversion of
Unbleached — Untreated Spruce TMP

\[ Y = 0.0164545 \times X + 0.251575 \]

n.s.e. = 0.0802314
Brightness Reversion of
Unbleached — Heavy Metal Poor Spruce TMP

\[ Y = 0.0158618 X + 0.241054 \]
\[ n.s.e. = 0.0932805 \]

Brightness Reversion of
Peroxide Bleached — Untreated Spruce TMP

\[ Y = 0.03513 X + 0.18372 \]
\[ n.s.e.: 0.0660787 \]
Brightness Reversion of Peroxide Bleached – Heavy Metal Poor Spruce TMP

![Graph showing the relationship between K/S and ln t (HOURS).]

\[ Y = 0.029691 \times X + 0.183959 \]

n.s.e.: 0.0958437

Brightness Stability of Spruce TMP: Light-Induced Reversion

<table>
<thead>
<tr>
<th>Pulp (Handsheets)</th>
<th>k</th>
<th>B</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached-untreated</td>
<td>-7.53</td>
<td>49.7</td>
<td>0.996</td>
</tr>
<tr>
<td>Unbleached-heavy metal free</td>
<td>-7.36</td>
<td>51.9</td>
<td>0.995</td>
</tr>
<tr>
<td>Peroxide bleached-untreated</td>
<td>-16.2</td>
<td>63.2</td>
<td>0.997</td>
</tr>
<tr>
<td>Peroxide bleached-heavy metal free</td>
<td>-15.7</td>
<td>64.4</td>
<td>0.999</td>
</tr>
</tbody>
</table>
### Brightness Stability of Spruce TMP: Thermally Aged

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Brightness Before Aging</th>
<th>Brightness After Aging</th>
<th>Brightness Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached-untreated</td>
<td>53.1</td>
<td>51.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Unbleached-heavy metal free</td>
<td>56.0</td>
<td>53.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Peroxide bleached-untreated</td>
<td>77.6</td>
<td>71.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Peroxide bleached-heavy metal free</td>
<td>75.4</td>
<td>70.9</td>
<td>4.5</td>
</tr>
</tbody>
</table>

**PHOTOBLEACHING**

(S. Lebo, M.S. 1983; D. Dallos, M.S. candidate)
Identification of the photoactive wavelength regions.

Arrow Number | Objective | Result
---|---|---
1-2 | Stabilization of brightness through additive (dye) | 
1-3-4 | Absorption of ultraviolet radiation by a part of the lignin (A) | 
4-5-6 | Energy transfer from excited lignin (A*) to oxygen yielding singlet oxygen | 
6-7-8 | Interaction of singlet oxygen with part of the lignin (B) yielding chromophores | Now discovered
2-8 | Photobleaching of lignin chromophores by visible light | 

Research outline: color reversion and brightness stability.
OXYGEN INVOLVEMENT

\[ \begin{align*}
\oplus & \quad \otimes \\
\bigcirc - \bigcirc & \quad \leftrightarrow \quad \bigcirc - \bigcirc & \quad \leftrightarrow \quad \bigcirc - \bigcirc \\
\end{align*} \]

IN \equiv NI

Polarizability
Molar Heat Capacities (idealized)

<table>
<thead>
<tr>
<th>GAS</th>
<th>$C_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>$\frac{3}{2}R$</td>
</tr>
<tr>
<td>$N_2$</td>
<td>$\frac{5}{2}R$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>$\frac{5}{2}R$</td>
</tr>
</tbody>
</table>

INJECTOR BLOCK

SAMPLE ($O_2$, $N_2$, or AIR)

GC with TMP column
BRIGHTNESS STABILIZATION BY DYE ADDITION
EXPOSURE TO MONOCHROMATIC LIGHT

(S. Lebo, Ph.D. candidate)

--- arc lamp (power supply not shown)
--- focussing sleeve control
--- water filter
--- secondary focussing lens
--- square aperture
--- heat sink and shutter assembly
--- sample shield
--- monochromator
--- sample mount
--- high stability
--- optical bench
--- biconvex lens
--- 1" aluminum base
--- UV Transmitting Filter
--- base supports

Schematic diagram of irradiation apparatus.
Reflectance Spectroscopy Measurements

1. Perkin-Elmer 320 Grating Spectrophotometer
2. Hitachi Integrating Sphere Attachment
3. Apple III Computer

Reflectance spectra of nonirradiated and four hour irradiated (310 nm) spruce RMP sheets. (Flux = $1.57 \times 10^{13}$ photons/cm$^2$ sec)
Difference reflectance spectra of spruce RMP handsheet irradiated for four hours with 310 nm light.
(Flux = 1.57 x 10^{13} photons/cm^2 sec)

Plot of the change in sheet reflectance at 410 nm as a function of irradiation wavelength.
Plots of the change in sheet reflectance (Roo) as a function of time of exposure to 310 nm light. (Flux = 1.57 x 10^13 photons/cm^2 sec)

Light Saturation

Irradiated: 310 nm
Roo: 410 nm
Humidity: 12 ± 2%

Light saturation of spruce RMP sheets.
CHEMISTRY OF COLOR REVERSION

New Research Outline
Possible light-induced oxidation of lignin to quinones by triplet oxygen.
HARDWOOD vs. SOFTWOOD

Solid State Difference Reflectance Spectra of Aspen and Spruce TMP Handsheets
(Sunlight exposed minus unexposed sheet reflectance)

Position of wavelength used for TAPPI Standard Brightness (457 nm) and the quinone absorption band minimum (422 nm) for two types of pulp.
Fiber Length Distribution
Spruce TMP

<table>
<thead>
<tr>
<th>CHAR</th>
<th>WEIGHTED</th>
<th>ARITHMETIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.25</td>
<td>0.00</td>
</tr>
<tr>
<td>02</td>
<td>0.46</td>
<td>0.54</td>
</tr>
<tr>
<td>03</td>
<td>0.63</td>
<td>0.75</td>
</tr>
<tr>
<td>04</td>
<td>1.40</td>
<td>0.90</td>
</tr>
<tr>
<td>05</td>
<td>2.10</td>
<td>1.56</td>
</tr>
<tr>
<td>AV</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>06 10</td>
<td>4.82</td>
<td>4.82</td>
</tr>
</tbody>
</table>
Fiber Length Distribution

Aspen TMP

WEIGHTED DISTRIBUTION

<table>
<thead>
<tr>
<th>CHARACTERISTICS</th>
<th>TOTAL FIBERS</th>
<th>0303</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHIR</td>
<td>WEIGHTED</td>
<td>ARITHMETIC</td>
</tr>
<tr>
<td>D1</td>
<td>0.25</td>
<td>0.60</td>
</tr>
<tr>
<td>D2</td>
<td>0.44</td>
<td>0.69</td>
</tr>
<tr>
<td>D3</td>
<td>0.68</td>
<td>0.62</td>
</tr>
<tr>
<td>D9</td>
<td>0.93</td>
<td>0.60</td>
</tr>
<tr>
<td>AVG</td>
<td>1.20</td>
<td>0.69</td>
</tr>
</tbody>
</table>

ANALYZED BY KAJAANI FC-100
Possible light-induced oxidation of lignin to quinones by triplet oxygen.
Formation of 3-methoxy-o-benzoquinone from softwood and hardwood lignin radicals.
FTIR multiple internal reflectance spectrum of an unbleached spruce TMP sheet.
SPRUCE BLEACHED
F35241.SAB
6069

FTIR multiple internal reflectance spectrum of a bleached spruce TMP sheet.
FTIR multiple internal reflectance spectrum of a bleached and unbleached spruce TMP sheet.
ASPEN BLEACHED
F3924 .SAB
6070

FTIR multiple internal reflectance spectrum of a bleached aspen TMP sheet.
FTIR multiple internal reflectance spectrum of a bleached and unbleached aspen TMP sheet.
FUTURE WORK

1. Clarification of the Mechanisms of Color Reversion

2. Suppression of Yellowing by Lignin Modification

3. Factors Limiting the Brightness of High-Yield Pulps

1.1 Identification of quinonoid structures
   - Incorporation of oxygen
   - Demethoxylation or demethylation of lignin

1.2 Refinement of IR technique

1.3 Effect of humidity on the color reversion

1.4 Thermal aging effects during the light-induced color reversion

1.5 Development of high-power UV scanning spectrophotometer with integrating sphere

1.6 Other analytical methods:
   - IR, UV, Vis photoacoustic spectroscopy (Cooperative Research with M. Gould, NRRC, Peoria, Illinois)
   - UV flash photolysis
   - ESR
The wavelength dependence of the absorption and scattering coefficient.
FUTURE WORK

1. Clarification of the Mechanisms of Color Reversion
2. Suppression of Yellowing by Lignin Modification
3. Factors Limiting the Brightness of High-Yield Pulps

2.1 Reactions with group specific reagents
   - Blocking of phenols in HYP
   - Reduction of carbonyl groups in HYP
   - Hydrogenation of C-C double bonds in HYP

2.2 Exploration of new bleaching techniques

2.3 Brightness stabilization by addition of dyes
   - Quenching of fluorescence of dyes by lignin in the solid state
FUTURE WORK

1. Clarification of the Mechanisms of Color Reversion

2. Suppression of Yellowing by Lignin Modification

3. Factors Limiting the Brightness of High-Yield Pulps

3.1 Effect of bleaching on K/S

3.2 Accessibility of lignin in the fibers to bleach reagents (related to 2.1)
STAFF

Rebecca Ibach
Hugh Corbett

STUDENTS

Stuart Lebo (Ph.D. candidate)
Gary Furman (Ph.D candidate)
William Welsh (M.S. 1985)
Diane Dallos (M.S. candidate)
Project 3566

SEPARATION OF STRONG, INTACT FIBERS

T. J. McDonough

T. Heazel
ULTRAHIGH YIELD
PROCESSSES
FOR CONVENTIONAL
PRODUCT LINES

OBJECTIVE
-------------
DEVELOP CAPABILITY FOR
REPLACING BLEACHED KRAFT
WITH ULTRAHIGH YIELD PULPS
AT ADEQUATE PRODUCT
PERFORMANCE LEVELS

OBJECTIVE
-------------
SIGNIFICANTLY MORE
EQUIVALENT PRODUCT
FROM THE SAME
AMOUNT OF WOOD
COROLLARY

SIGNIFICANTLY FEWER WOOD FIBERS PER UNIT OF EQUIVALENT PRODUCT

COMPONENT PROBLEMS

STRENGTH
BRIGHTNESS
STABILITY
PROCESS

STRENGTH SUBPROBLEMS

FIBER STRENGTH
INTERFIBER BOND STRENGTH
PRELIMINARY EXPERIMENTS

* To define the state of the art

* To determine factors that limit the strength of high yield pulps

1. Relative to kraft, it is possible to increase white spruce pulp yield by 70%, incurring a strength loss of only 20%.

2. The yield increase is achieved without appreciable reduction in fiber length and with apparent increases in fiber strength and specific interfiber bond strength.
3. Opportunities for eliminating strength penalties associated with very large yield increases are to:

* retain more native fiber strength, or otherwise enhance fiber strength

* make fiber more flexible and conformable

4. There is a need for a better understanding of large differences between species with respect to the dependence of pulp properties on yield.
OBJECTIVE
=========

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

MEDIUM RANGE GOAL
====================

IDENTIFY FACTORS GOVERNING RETENTION OF FIBER STRENGTH, INTEGRITY AND DEVELOP CONTROL METHODS

PLAN
=====

* Determine fiber length and strength in wood and in high-yield pulp made from it

* Determine relationship of strength and length losses to pulping variables
**WOOD ZERO-SPAN TENSILE, km**

<table>
<thead>
<tr>
<th></th>
<th>EW</th>
<th>LW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>20</td>
<td>31</td>
</tr>
<tr>
<td>Spruce</td>
<td>32</td>
<td>46</td>
</tr>
</tbody>
</table>

How does sulfonation *per se* affect fiber strength?

To what extent does sulfonation reduce fiber strength loss in refining?
### AXIAL ZERO-SPAN TENSILE STRENGTH
### OF ULTRATHIN WOOD SECTIONS, km

<table>
<thead>
<tr>
<th>Region</th>
<th>Before Sulfonation</th>
<th>After Sulfonation</th>
<th>Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.0</td>
<td>23.9</td>
<td>-0.1</td>
</tr>
<tr>
<td>2</td>
<td>23.9</td>
<td>22.8</td>
<td>-0.9</td>
</tr>
<tr>
<td>3</td>
<td>22.5</td>
<td>24.5</td>
<td>+2.0</td>
</tr>
<tr>
<td>4</td>
<td>22.7</td>
<td>24.8</td>
<td>+2.1</td>
</tr>
<tr>
<td>5</td>
<td>22.8</td>
<td>24.8</td>
<td>+2.0</td>
</tr>
<tr>
<td>6</td>
<td>21.8</td>
<td>24.4</td>
<td>+2.6</td>
</tr>
<tr>
<td>7</td>
<td>21.6</td>
<td>24.6</td>
<td>+3.0</td>
</tr>
<tr>
<td>8</td>
<td>19.4</td>
<td>21.4</td>
<td>+2.0</td>
</tr>
</tbody>
</table>

Sum: +1.59
AXIAL ZERO-SPAN TENSILE STRENGTH
OF ULTRATHIN WOOD SECTIONS, km

<table>
<thead>
<tr>
<th>Region</th>
<th>Before Sulfonation</th>
<th>After Sulfonation</th>
<th>Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.0</td>
<td>23.9</td>
<td>-0.1</td>
</tr>
<tr>
<td>2</td>
<td>23.9</td>
<td>22.8</td>
<td>-0.9</td>
</tr>
<tr>
<td>3</td>
<td>22.5</td>
<td>24.5</td>
<td>+2.0</td>
</tr>
<tr>
<td>4</td>
<td>22.7</td>
<td>24.8</td>
<td>+2.1</td>
</tr>
<tr>
<td>5</td>
<td>22.8</td>
<td>24.8</td>
<td>+2.0</td>
</tr>
<tr>
<td>6</td>
<td>21.8</td>
<td>24.4</td>
<td>+2.6</td>
</tr>
<tr>
<td>7</td>
<td>21.6</td>
<td>24.6</td>
<td>+3.0</td>
</tr>
<tr>
<td>8</td>
<td>19.4</td>
<td>21.4</td>
<td>+2.0</td>
</tr>
</tbody>
</table>

Increase: +1.59

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Yield, %</th>
<th>CSF, mL</th>
<th>Bauer-McNett, %</th>
<th>Tensile Index</th>
<th>Tear Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMP</td>
<td>n.a.</td>
<td>110</td>
<td>42</td>
<td>38</td>
<td>16</td>
</tr>
<tr>
<td>SCMP1</td>
<td>98</td>
<td>235</td>
<td>38</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>SCMP2</td>
<td>85</td>
<td>325</td>
<td>55</td>
<td>18</td>
<td>19</td>
</tr>
</tbody>
</table>
PINE SINGLE FIBER DATA: 28 MESH FRACTION

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Load, g</th>
<th>C.S.A., $\mu m^2$</th>
<th>Stress, kg/mm$^2$</th>
<th>Modulus, kg/mm$^2$</th>
<th>Strain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMP</td>
<td>32</td>
<td>582</td>
<td>59</td>
<td>1111</td>
<td>7.2</td>
</tr>
<tr>
<td>SCMP1</td>
<td>32</td>
<td>534</td>
<td>62</td>
<td>1196</td>
<td>6.8</td>
</tr>
<tr>
<td>SCMP2</td>
<td>34</td>
<td>588</td>
<td>59</td>
<td>1351</td>
<td>7.8</td>
</tr>
<tr>
<td>KRAFT</td>
<td>15</td>
<td>250</td>
<td>62</td>
<td>580</td>
<td>18.3</td>
</tr>
</tbody>
</table>

SINGLE FIBER DATA

<table>
<thead>
<tr>
<th>LOAD, g</th>
<th>STRESS, kg/mm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 mesh</td>
<td>28 mesh</td>
</tr>
<tr>
<td>48 mesh</td>
<td>48 mesh</td>
</tr>
<tr>
<td>RMP</td>
<td>32  28</td>
</tr>
<tr>
<td></td>
<td>32  59</td>
</tr>
<tr>
<td>SCMP1</td>
<td>32  28</td>
</tr>
<tr>
<td></td>
<td>32  62</td>
</tr>
<tr>
<td>SCMP2</td>
<td>34  28</td>
</tr>
<tr>
<td></td>
<td>34  59</td>
</tr>
</tbody>
</table>
Effect of addition of well-beaten sulfite pulp on zero-span breaking length of coarse southern pine thermomechanical fiber.
Effect of bonding additives on zero-span breaking length of coarse southern pine thermomechanical fiber. Upper curve: polyamide polyamine epichlorohydrin (PAE); middle curve: cationic starch; lower curve: PAE-CMC.
APPROXIMATE FIBER BREAKING LENGTHS, km

PINE WOOD ZERO-SPAN 25
PINE RMP FIBERS 40
PINE TMP ZERO-SPAN 19

---

<table>
<thead>
<tr>
<th>Time in British disintegrator min.</th>
<th>Shive Count</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total shives</td>
</tr>
</tbody>
</table>

- □ <6 fibers (9 obs) + >6 fibers (9 obs)
### SPRUCE FIBERIZATION AT 120°C

<table>
<thead>
<tr>
<th>TIME, min</th>
<th>ACCEPTS, %</th>
<th>BAUER-MCNETT CLASSIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+14</td>
</tr>
<tr>
<td>1</td>
<td>37</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>49</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>63</td>
<td>24</td>
</tr>
</tbody>
</table>

### SPRUCE TMP HANDSHEETS

<table>
<thead>
<tr>
<th>FIBERIZATION TIME, min</th>
<th>CSF, mL</th>
<th>ZSBL, km</th>
<th>TENSILE INDEX, km</th>
<th>TEAR FACTOR</th>
<th>$S$ cm²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>590</td>
<td>8.3</td>
<td>16</td>
<td>53</td>
<td>272</td>
</tr>
<tr>
<td>2</td>
<td>550</td>
<td>8.8</td>
<td>20</td>
<td>64</td>
<td>296</td>
</tr>
<tr>
<td>4</td>
<td>520</td>
<td>9.5</td>
<td>24</td>
<td>74</td>
<td>317</td>
</tr>
</tbody>
</table>

### SINGLE FIBER DATA

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Load, g</th>
<th>CSA, $\mu$m²</th>
<th>Stress, kg/mm²</th>
<th>Modulus, kg/mm²</th>
<th>Strain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole Spruce</td>
<td>12</td>
<td>231</td>
<td>54</td>
<td>1014</td>
<td>7.5</td>
</tr>
<tr>
<td>28 mesh Pine</td>
<td>32</td>
<td>582</td>
<td>59</td>
<td>1111</td>
<td>7.2</td>
</tr>
</tbody>
</table>
## APPROXIMATE FIBER BREAKING LENGTHS, km

<table>
<thead>
<tr>
<th>Material</th>
<th>Pine</th>
<th>Spruce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce Wood Zero-Span</td>
<td>25</td>
<td>39</td>
</tr>
<tr>
<td>Spruce TMP Fibers</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>Spruce TMP Zero-Span</td>
<td>19</td>
<td>25</td>
</tr>
<tr>
<td>Pine Wood Zero-Span</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Pine Pulp Fibers</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Pine Pulp Zero-Span</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>
1. The latewood of spruce and pine is 50% stronger than earlywood.

Spruce is 50% stronger than pine.

2. Sulfonation of pine before fiberization does not affect the strength of the separated fibers.

3. In high-yield pine pulps, the 48 mesh fraction contains fibers that are slightly stronger than those in the 28 mesh fraction.

4. The SCMP process in its present form is not suitable for southern pine.

5. It is likely that kraft fibers from southern pine have only half the load-bearing ability of the corresponding mechanical pulp fibers.
6. The long fibers in pine high-yield pulps have probably undergone little strength loss as a result of fiberization.

7. The zero-span strength of chemimechanical and mechanical pulp sheets from pine or spruce is lower than expected on the basis of either thin wood section or single fiber strength measurements.

8. Relative to the strengths of the woods from which they are made, spruce TMP fibers are weaker than pine RMP fibers. This may indicate that spruce is more susceptible to damage during fiberization.
PLANS

1. Complete data analysis and write reports.
2. Complete study of effects of spruce fiberization variables.
3. Develop zero-span test as a measurement of fiber strength.
4. Determine strength of single fiber fragments.
5. Determine effects of fiberization variables on pine pulp properties.
6. Determine maximum sheet strength currently attainable by artificial bonding.
8. Evaluate fiber models.
9. Evaluate feasibility of improving fiber properties.
10. Plan and initiate prediction of fiberization behavior, alternative separation and biopulping.
11. Collaborate with Engineering Division to study effects of pressing conditions on high yield sheet properties.
Thesis Topic:
Sulfonation to Improve High Yield Pulp Strength:
Effects of Fiber Wall Sulfur Distribution.

Thesis Objectives:
1. To determine the influence of various cooking conditions on the distribution of bound sulfite (sulfur) across the fiber double-walls of sulfonated wood chips.
2. To examine the influence of fiber wall sulfur distribution on fiber and paper properties.

Measurement of Sulfur Distribution:
Linescan data obtained with a STEM-EDS (Scanning Transmission Electron Microscope - Energy Dispersive Spectrometer).

Fiber double-wall of loblolly pine latewood showing the path of a linescan.
Schematic of an observed (top) and hypothetical (bottom) sulfur distribution.

Signals produced by the interaction of the electric beam and sample.
40 minute vapor-phase SCMP cook, 140°C, 20% Na₂SO₃

20 minute vapor-phase SCMP cook, 140°C, 6% Na₂SO₃
Biochemical Applications

J. V. Maxham
CURRENT APPLICATIONS OF BIOTECHNOLOGY TO THE PULP AND PAPER INDUSTRY

Retting and Enzymatic Pulping of Non-Woody Plant Tissue

Enzymatic Conversion of Starch in the Paper Mill

Biological Effluent Treatment

ENZYMATIC CONVERSION OF STARCH IN THE PAPER MILL

Amylase solutions purchased to fit a specific application

Enzymatic conversion claimed to be cheaper than thermochemical conversion

Very little enzyme solution needed (about 50 ml converts 1000 kg starch)

BIOLOGICAL EFFlUENT TREATMENT

Biological processes have a large physical size compared to physio-chemical processes. Nevertheless, biological processes are more economical.
ALKALINE ENZYMATIC PULPING OF PAPER MULBERRY
(Kobayashi et. al., 1983 Int. Sym. on Wood and Pulping Chem.)

Pulping Time: 24 hours
Pulping Temp.: 30 degrees C
Paper Properties Same as Chemical Pulp:
   Tensile strength, breaking length, tear factor, folding endurance
Paper Properties Superior to Chemical Pulp:
   Homogeneity in basis weight, dynamic printing smoothness, brightness

ENZYMATIC PULPING TIMES FOR NON-WOODY PLANT MATERIALS
4 TO 24 HOURS

BIOLOGICAL PULPING TIME FOR NON-WOODY PLANT MATERIALS
4 DAYS
OPTIONS IN BIOLOGICAL/ENZYMATIC WOOD PULPING

Grow microorganisms directly on the wood chips
Grow microorganisms in a separate process and contact the chips with the culture fluid
Purchase concentrated enzyme solutions and add to the pulping liquor

INCENTIVES TO DEVELOP A BIOLOGICAL/ENZYMATIC PULPING PROCESS

High selectivity and activity of enzymes (therefore potentially higher pulp yield, better paper physical properties, and lower amounts of pulping chemicals)
Lower pulping energy requirements (due to pulping temperatures below 45 degrees C)
Renewable catalysts (therefore pulping liquor can be recycled)
Environmental compatibility (no sulfur containing lignin products)
PROBLEMS WITH THE BIOLOGICAL PULPING OF WOOD CHIPS

Excessive Pulping Time (at least 2 weeks)

Difficult and Expensive to Maintain Sterile Conditions

Mutation of the Innoculum

Pulp Mills Will Require a Staff of Biochemical Engineers, Microbiologists, and Technicians

ENZYMATIC PULPING OF WOOD

Enzyme solutions are purchased from biotech companies that offer a variety of products

Enzyme solutions replace conventional pulping chemicals; pulp mills are able to use the old equipment with some modification

Spent pulping liquor is directly recycled with a bleed stream going to an enzyme recovery operation

The enzyme recovery system is a series of membrane separation processes that isolate and concentrate the pulping enzymes

Effluent from the recovery system is handled by state-of-the-art biological treatment processes
ENZYMATIC PULP DIGESTOR

Somewhat larger in comparison to a chemical pulping reactor but probably less expensive due to low temperature, low pressure (atmospheric), and mild chemical environment.

ROLE OF GENETIC ENGINEERING IN ENZYMATIC PULPING

The DNA of delignifying and other pulping enzymes can be isolated from any organism and inserted into the DNA of a fast growing bacteria (e.g. E. coli). Therefore these enzymes can be economically produced in large quantities.
USES OF ENZYME SOLUTIONS IN PULPING

Delignifying Wood Chips

Altering the properties of any type of pulp

Bleaching

ENZYMATIC PULPING SCHEMES

Wood Chips ----> Enzyme Digestion ----> Mechanical Pulping ----> Refining

Roundwood ----> Mechanical Pulping ----> Enzyme Digestion ----> Refining
PLAN OF ACTION TO INITIATE AN IPC BIOPULPING RESEARCH PROGRAM

Make a list of commercially available enzyme solutions and names of suppliers

For each enzyme solution commercially available determine what the enzyme does and possible use in an enzymatic pulping scheme

Test promising enzyme solutions in the laboratory

Establish contacts with biotechnology firms interested in biopulping research

Obtain experimental enzyme solutions from biotechnology firms

Establish contacts with funding agencies (e.g. the Dept. of Energy) interested in biopulping research

Write proposals to obtain research funding

Establish contacts with researchers interested in biopulping research (e.g. Karl-Erik Eriksson of the Swedish Forest Products Laboratory, T. Kent Kirk of the USDA Forest Products Laboratory, and Japanese enzymatic pulping researchers)
Solvent Sequences

S. Aziz
INTRODUCTION

3. Future of Solvent Pulping.
### Historical Development in Solvent Pulping.

<table>
<thead>
<tr>
<th>Researcher</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peter Klason</td>
<td>Dissolution of lignin with ethanol water.</td>
</tr>
<tr>
<td>Hagglund &amp; Urban</td>
<td>Delignified wood using a various alcohols with mineral acid.</td>
</tr>
<tr>
<td>Hibbert &amp; Rawely</td>
<td>Extraction of spruce wood meal lignin using benzene alcohol and glycol solvents.</td>
</tr>
<tr>
<td>Rassow &amp; Gabriel</td>
<td>Extracted lignin by glycol and acidic salts at temperatures of 165-175 C.</td>
</tr>
<tr>
<td>Engel &amp; Wedekin</td>
<td>Dioxane was used with small amounts of hydrochloric acid at temperatures of 100 C.</td>
</tr>
<tr>
<td>Aronowsky &amp; Gortner</td>
<td>Used alcohols, glycols, dioxane etc on aspen wood meal.</td>
</tr>
<tr>
<td>Grondal &amp; Zenczak</td>
<td>Used triethylene glycol with aluminum chloride at temperatures of 115 C.</td>
</tr>
<tr>
<td>Alfred Ogait</td>
<td>Used chloral hydrate and a catalyst as pulping agents.</td>
</tr>
<tr>
<td>Kleinert &amp; Tayenthal</td>
<td>Used aqueous alcohol water as the pulping media with or without the addition of mineral acids.</td>
</tr>
<tr>
<td>April &amp; Bower</td>
<td>Delignified southern yellow pine wood meal using butanol-water and phenol.</td>
</tr>
</tbody>
</table>
### Strength Properties of Ethanol-Water Pulps from Various Wood Species in the Kleinert Process (15)

<table>
<thead>
<tr>
<th></th>
<th>Spruce</th>
<th>Southern Pines</th>
<th>Poplar</th>
<th>Hardwood Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cooking temp., °C</strong></td>
<td>185</td>
<td>185</td>
<td>185</td>
<td>182.5</td>
</tr>
<tr>
<td><strong>Cooking time, min</strong></td>
<td>60</td>
<td>60</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td><strong>Total yield, %</strong></td>
<td>58.5</td>
<td>56.1</td>
<td>57.3</td>
<td>55.9</td>
</tr>
<tr>
<td><strong>Unbeaten</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tear</td>
<td>115</td>
<td>120</td>
<td>58</td>
<td>67</td>
</tr>
<tr>
<td>Burst</td>
<td>76</td>
<td>82</td>
<td>21</td>
<td>28</td>
</tr>
<tr>
<td><strong>Breaking length, m</strong></td>
<td>7,980</td>
<td>6,330</td>
<td>5,040</td>
<td>4,870</td>
</tr>
<tr>
<td><strong>Beaten</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tear</td>
<td>105</td>
<td>112</td>
<td>78</td>
<td>82</td>
</tr>
<tr>
<td>Burst</td>
<td>92</td>
<td>102</td>
<td>39</td>
<td>60</td>
</tr>
<tr>
<td><strong>Breaking length, m</strong></td>
<td>10,830</td>
<td>10,440</td>
<td>7,090</td>
<td>6,990</td>
</tr>
</tbody>
</table>
Acid-Catalyzed Delignification of Lignocellulosics

Principle of recovery in organosolv pulping.

(WHITECELLULOSE SUGARS, SOLUBLE OLIGOLIGNOLS).
Selectivity of ammonium sulfide, sodium sulfide organosolv and kraft pulping of western hemlock.
Comparison of carbohydrate recovery from western hemlock by ammonium sulfide organosolv and kraft processes.
Comparison of Aspen pulp properties of various solvent systems.

<table>
<thead>
<tr>
<th>Property</th>
<th>Sulfite</th>
<th>Biodyne</th>
<th>APR</th>
<th>Pasners</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>44%</td>
<td>64%</td>
<td>53%</td>
<td>60%</td>
</tr>
<tr>
<td>Kappa No.</td>
<td>20</td>
<td>23</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Freeness (CSF)</td>
<td>450</td>
<td>397</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Burst Factor</td>
<td>31</td>
<td>33</td>
<td>29.6</td>
<td>50</td>
</tr>
<tr>
<td>Tensile (km)</td>
<td>5.9</td>
<td>7.1</td>
<td>5.6</td>
<td>9.0</td>
</tr>
<tr>
<td>Tear Factor</td>
<td>47</td>
<td>47</td>
<td>56</td>
<td>72</td>
</tr>
<tr>
<td>Bulk (cm^3/g)</td>
<td>1.36</td>
<td>1.34</td>
<td>1.5</td>
<td>---</td>
</tr>
</tbody>
</table>
Selectivity curve for spruce delignification in kraft and ester (acetic acid/ethyl acetate/water) pulping.
A comparison of Spruce pulp properties of various Ethanol-Water pulping systems.

<table>
<thead>
<tr>
<th>Process</th>
<th>Tear Index</th>
<th>Burst Index</th>
<th>Tensile km.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kleinert</td>
<td>105</td>
<td>92</td>
<td>10.83</td>
</tr>
<tr>
<td>APR</td>
<td>---</td>
<td>69</td>
<td>5.46</td>
</tr>
<tr>
<td>Pazners</td>
<td>65</td>
<td>75</td>
<td>11.30</td>
</tr>
<tr>
<td>Sulfite</td>
<td>---</td>
<td>59</td>
<td>7.73</td>
</tr>
</tbody>
</table>
ECONOMIC COMPARISON: APR PULPING VS KRAFT PULPING
CAPITAL COST PER DAILY TON OF PULP BY CAPACITY

Kraft Pulping examples:
A - 1000 TPD Leaf River mill, Great Northern Nekoosa
B - 1000 TPD conceptual "southern" mill of a major forest products company
C - 920 TPD conceptual estimate, Arthur D. Little, Inc.
D - 750 TPD Quinnesc mill, Champion International Corp.
E - 240 TPD Port Alice mill, Western Forest Products, Ltd.
F - 150 TPD conceptual northern mill of a major forest products company
Comparison of various solvent systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioydne</td>
<td>Produces a variety of pulps.</td>
<td>Process has not been tried with S. Pine.</td>
<td>Recovery system is being evaluated.</td>
</tr>
<tr>
<td>APR</td>
<td>Simple recovery</td>
<td>Process adequate only for pulping poplars to sulfite strengths.</td>
<td>Softwoods and southern hardwoods cannot be delignified to achieve reasonable properties</td>
</tr>
<tr>
<td>Pasners</td>
<td>Claims to delignify softwoods and hardwoods.</td>
<td>Process described in patent and literature cannot be verified.</td>
<td>Results obtained using the salt catalyst do not correspond with those obtained by Pasner.</td>
</tr>
<tr>
<td>Ammonium Sulfide</td>
<td>Pulps softwoods and hardwoods. At least 10% yield advantage over kraft pulps.</td>
<td>Require 30% of sulfur charge leading to complicated recovery system.</td>
<td>Delignify's biomass without degrading carbohydrates.</td>
</tr>
</tbody>
</table>
Sulfur Gas Release

J. Cantrell
Sulfur Gas Release During Black Liquor Burning

Purpose: To gain a better understanding of the kinetic release of sulfur gas in the Recovery Boiler in order to minimize sulfur losses and meet environmental standards of sulfur emissions.

Objective: Develop a kinetic model describing sulfur gas release during black liquor burning.

<table>
<thead>
<tr>
<th>Independent variables:</th>
<th>Particle Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Solids</td>
</tr>
<tr>
<td></td>
<td>% Oxygen in gas stream</td>
</tr>
<tr>
<td></td>
<td>Added sulfur</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dependent variables:</th>
<th>Total sulfur released as SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First order reaction rate constant</td>
</tr>
</tbody>
</table>
RATE OF SULFUR RELEASE VS. TIME
63.3% SOLIDS AND 2.0 MM DIAMETER
% TOTAL SULFUR RELEASED VS. PARTICLE DIAMETER

% TOTAL SULFUR RELEASED AS SULFUR DIOXIDE

- 63.3% SOLIDS
- 71.9% SOLIDS
- 83.1% SOLIDS
- 98.9% SOLIDS

PARTICLE DIAMETER (mm)
% TOTAL SULFUR RELEASED AS SULFUR DIOXIDE

% TOTAL SULFUR RELEASED VS. % SOLIDS

- 1.0 mm Diameter
- 2.0 mm Diameter
- 3.0 mm Diameter
- 4.0 mm Diameter

extrapolated
1ST ORDER RXN CONSTANT VS. % SOLIDS

% SOLIDS

K (1/SEC)

1.0 mm Diameter  *extrapolated
2.0 mm Diameter
3.0 mm Diameter
4.0 mm Diameter

1ST ORDER RXN CONSTANT VS. % SOLIDS
% Total Sulfur Released vs. Added Sulfur
65.1% (1.9) Solids and 2.04mm (.09) Diameter
% Total Sulfur Released vs. % Oxygen
63.3% Solids and 2.04mm (.06) Diameter
Conclusions

• As particle size increases, % total sulfur released and reaction rate decrease.

• As % solids increases, % total sulfur released decreases becoming less prevalent for larger particles.

• Reaction rate appears to go through a minimum at around 85% solids.

• Both reaction rate and % total sulfur released do not appear to be affected by the addition of sulfur (emulsified or Na$_2$SO$_4$) for the range studied.

• % total sulfur released, as SO$_2$, goes through a maximum at an Oxygen content of $\approx$13% in the gas stream.
Alkaline Degradation of Amylose

D. Geddes
ALKALINE DEGRADATION
OF AMYLOSE

A Kinetic Model

---

REDUCING END

PEELING

STOPPING

RANDOM CHAIN CLEAVAGE

SECONDARY PEELING & STOPPING

In Polymer Chain

-- anhydroglucose monomer
+ reducing end group
++ stable acid end group

Eliminated From Polymer Chain

+ acid degradation product
Degradation Studies – Cellulose

Samuelson and Wennerblom (1954)
Franzon and Samuelson (1957)
Richards and Sephton (1957)
Johansson and Samuelson (1965)
Lai and Sarkanen (1967)
Johansson and Samuelson (1974)
Lai and Ontto (1979)
Gentile (1985)

Degradation Studies – Amylose

Machell and Richards (1958)
Lai and Sarkanen (1969)
Ziderman and Bel–Ayche (1979)
Árbin (1980)

Previous studies lack:

Chain cleavage
Kinetic constants
Quantitative use of MWDs
Well characterized substrate
Amylose at 80 °C in M NaOH

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Yield (%)</th>
<th>DPn</th>
<th>DPw</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>100</td>
<td>630</td>
<td>2221</td>
<td>3.53</td>
</tr>
<tr>
<td>0.33</td>
<td>84.8</td>
<td>535</td>
<td>1189</td>
<td>2.22</td>
</tr>
<tr>
<td>1.00</td>
<td>73.8</td>
<td>718</td>
<td>1349</td>
<td>1.88</td>
</tr>
<tr>
<td>2.00</td>
<td>56.8</td>
<td>469</td>
<td>935</td>
<td>1.99</td>
</tr>
<tr>
<td>3.00</td>
<td>253</td>
<td>276</td>
<td>559</td>
<td>2.03</td>
</tr>
<tr>
<td>9.00</td>
<td>254</td>
<td>254</td>
<td>498</td>
<td>1.95</td>
</tr>
<tr>
<td>22.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
THEESIS OBJECTIVES

1. Investigate the alkaline degradation of a well characterized polysaccharide.
   a. MWD versus Time
   b. Rate Constants
      Activation Energies

2. Develop a mathematical model to predict yield loss and MWD shifts based on current understanding of reactions.
   a. Peeling, Stopping
   b. Peeling, Stopping, Chain Cleavage

Modeling Approaches

System of Differential Equations

Statistics of Depolymerization
The peeling and stopping process can be viewed as a series of Bernoulli trials.

"Success" = STOP

"Failure" = PEEL

Geometric Distribution of Peeling Lengths

Mean = \( \frac{K_p}{K_s} \)

\[ \text{Prob(PL}=N) = \frac{K_s}{K_p}(1-\frac{K_s}{K_p})^{*(N-1)} \]
<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>DPn</th>
<th>DPw</th>
<th>PD</th>
<th>WT YIELD</th>
<th>NUM YIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Arbin's Results</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting Material</td>
<td>630</td>
<td>2221</td>
<td>3.53</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Final Material</td>
<td>254</td>
<td>498</td>
<td>1.96</td>
<td>&lt;56.8</td>
<td></td>
</tr>
<tr>
<td><strong>Model Results</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting Material</td>
<td>630</td>
<td>2215</td>
<td>3.52</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Kp/Ks = 200</td>
<td>663</td>
<td>2479</td>
<td>3.74</td>
<td>79.1</td>
<td>75.2</td>
</tr>
<tr>
<td>Kp/Ks = 600</td>
<td>742</td>
<td>2807</td>
<td>3.78</td>
<td>55.9</td>
<td>47.4</td>
</tr>
<tr>
<td>Kp/Ks = 1000</td>
<td>792</td>
<td>3020</td>
<td>3.81</td>
<td>44.5</td>
<td>35.4</td>
</tr>
</tbody>
</table>

**Model Results**

Kp/Ks = 600
F. Arbin
Amylose MWDs

Log(DP)
CONCLUSIONS

1. The MWD should shift toward higher molecular weights if only peeling and stopping are occurring.

2. The polydispersity should increase during degradation. (In contrast, chain cleavage should cause a decrease.)

3. Even at low yield losses, there can be a significant loss of molecules due to complete peeling.

FUTURE WORK

1. Apply model to actual MWD.
2. Conduct kinetic studies.
3. Develop comprehensive model.