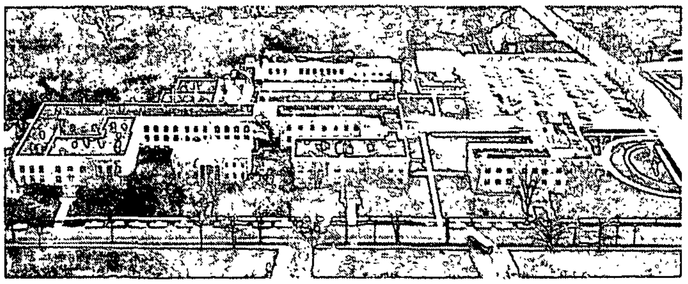

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

APRIL 3-4, 1986

HANDOUTS

TABLE OF CONTENTS

RESEARCH OVERVIEW

E. W. Malcolm

CHEMICAL SCIENCES DIVISION

STAFF (JULY 1986)

10 PH.D. (FACULTY)

25 B.S./M.S.

RESEARCH AREAS

CHEMICAL PULP

KRAFT CHEMICAL RECOVERY

HIGH YIELD PULPS

RESEARCH TYPE

IPC FUNDED

IPC STUDENT

CONTRACT

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

IPC FUNDED

Chemical Pulping		
3288 - Fine Structure of Wood Pulp Fibers	75	
3475 - Fundamentals of Selectivity in Pulping and Bleaching	150	
3474 - Improved Processes for Bleached Pulp	35	
3477*- Development and Application of Analytical Techniques	13	
	273	(-99)
Recovery		
3473-1-Fundamental Processes in Alkali Recovery Furnaces	230	
3456-2-Smelt-Water Explosions	20	
3477* -Development and Application of Analytical Techniques	13	
New -Nodulation of Lime	20	
New -Computer Model of Recovery Furnace	20	
	303	(- 8)
High Yield Pulping		
3566 - Separation of Strong, Intact Fibers	175	
3524 - Fundamentals of Brightness Stability	140	
3521-2-Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue	45	
3477*- Development and Application of Analytical Techniques	13	
	373	(+31)
Other		
3534 - Exploratory Research	70	
3477*- Analytical (Paper)	26	
	96	(+26)
TOTAL IPC FUNDED	1,045	(-50)

CONTRACT RESEARCH

Government Funded		
3473-6-Fundamental Studies of Black Liquor Combustion		
IPC	220	
NBS	205	
3521-3-Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue	50	
New Raman Microprobe	100	
	575	
Nongovernment Funded		
River Survey	210	
Other	122	
	332	
TOTAL CONTRACT RESEARCH	907	

TOTAL FUNDED AND CONTRACT-- 1,952 (46% Contract)
(54% IPC Funded)

Contract Possible Additions - Government - $55,000
Nongovernment - $40,000

* Portion of project budget assigned to this area

EWM/gmk
3/25/86

IPC STUDENT RESEARCH

	PH.D.	M.S.
CHEMICAL PULPING	11	11
KRAFT CHEMICAL RECOVERY	3	7
HIGH YIELD PULP	5	5
	19	23

(1/86)

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

CONTRACT RESEARCH

GOVERNMENT FUNDED		
3473-6-FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION	IPC	220
	NBS	205
3521-3-RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE		50
NEW RAMAN MICROPROBE		100
		575
NONGOVERNMENT FUNDED		
RIVER SURVEY		210
OTHER		122
		332
TOTAL CONTRACT RESEARCH		907

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

IPC FUNDED

CHEMICAL PULPING	273	(-99)
RECOVERY	303	(- 8)
HIGH YIELD PULPING	373	(+31)
OTHER	96	(+26)
TOTAL IPC FUNDED	1,045	(-50)

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

IPC FUNDED

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3477*- DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES	13	
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3473-1-FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES	230	
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NEW -COMPUTER MODEL OF RECOVERY FURNACE	20	
	303	(-8)

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

IPC FUNDED

HIGH YIELD PULPING

3566 - SEPARATION OF STRONG, INTACT FIBERS	175	
3524 - FUNDAMENTALS OF BRIGHTNESS STABILITY	140	
3521-2-RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE	45	
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	373	(+31)

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

IPC FUNDED

OTHER

3534 - EXPLORATORY RESEARCH	70	
3477*- ANALYTICAL (PAPER)	26	
	96	(+26)

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

TOTAL IPC FUNDED	1,045	
TOTAL CONTRACT RESEARCH	907	
TOTAL FUNDED AND CONTRACT	1,952	(46% CONTRACT) (54% IPC FUNDED)

Recovery Summary

T. M. Grace

COMBUSTION RESEARCH

1. Char Burning
2. Fume Formation
3. Black Liquor Burning
4. Sulfur Release

STUDENT RESEARCH

Swelling and Pyrolysis.............Miller
Convective Drying..................Robinson
Pile Burning of Char...............Aiken

Moisture and Combustibility........Moreland
Sulfur Release During Burning......Cantrell
Char Gasification with CO_2.........Goerg
Sulfate Reduction with CO..........Coenen
Model of Particle Burning..........Sumnicht
Cocurrent Burning..................Buehler

SOURCES OF PARTICULATES

1. Physical carryover of burning particles
2. Sparklers during char burnout
3. Vaporization of NaCl and KCl
4. Sodium vaporization-enhanced mass transfer
   A. Smelt oxidation
   B. Char burning

FUTURE WORK

1. SODIUM RELEASE FROM BURNING CHAR - VERRILL
2. BURNING PHENOMENA - COOPERATE WITH HUPA
3. REACTIONS OF HYDROGEN-CONTAINING SPECIES
4. CARBON GASIFICATION REACTIONS - GOERG, AIKEN
5. PREPARE A TEXT ON BLACK LIQUOR COMBUSTION
6. MATHEMATICAL MODEL OF FIREBOX - JONES, WALSH, BURNS, SUMNICHT
7. MECHANISM OF FIRESIDE CORROSION - KULAS

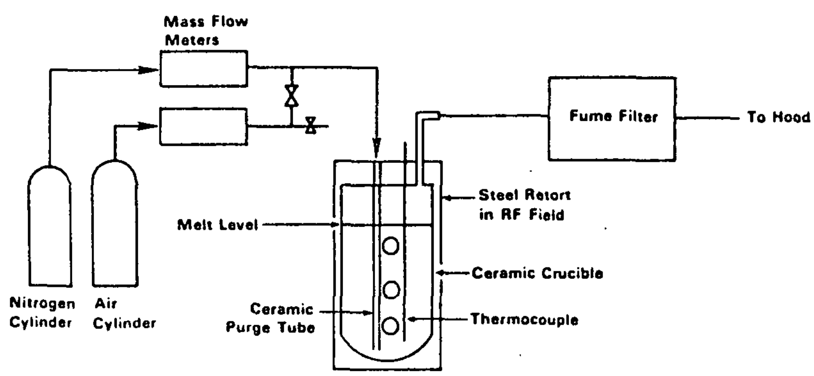
Project 3473-1

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES

Fume Generation - J. H. Cameron

Black Liquor Burning - D. T. Clay

FUME GENERATION



Experimental Apparatus

Effect of purge tube location on oxidative fuming.

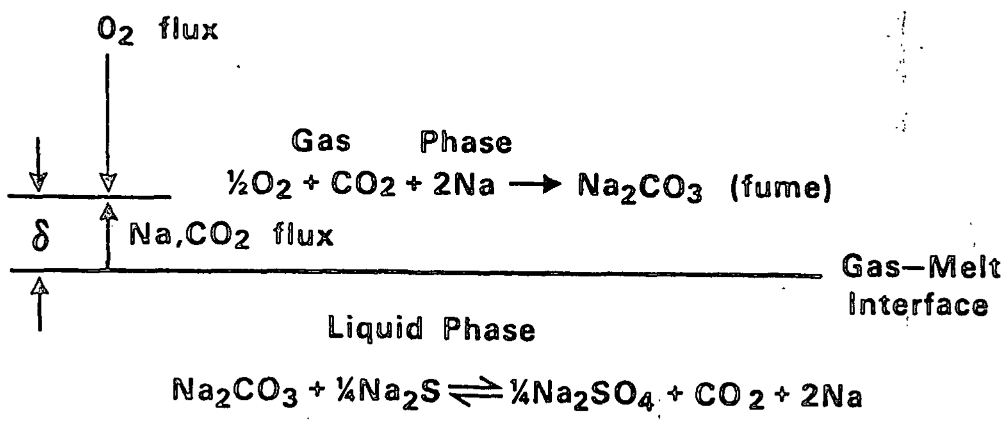
Initial Conditions
Na_2CO_3 = 0.77 mol
Na_2S = 0.03 mol
Temperature = 955°C (1750°F)

Purge Introduced Below Melt's Surface		Purge Introduced Above Melt's Surface	
Oxidation Rate, mol O_2 consumed/min x 10^4	Fume Rate, g/min	Oxidation Rate, mol O_2 consumed/min x 10^4	Fume Rate, g/min
9.38	0.0106	0.84	0.00146
9.46	0.0134	3.88	0.00100
		7.80	0.00115
		12.00	0.00079
		17.70	0.00044

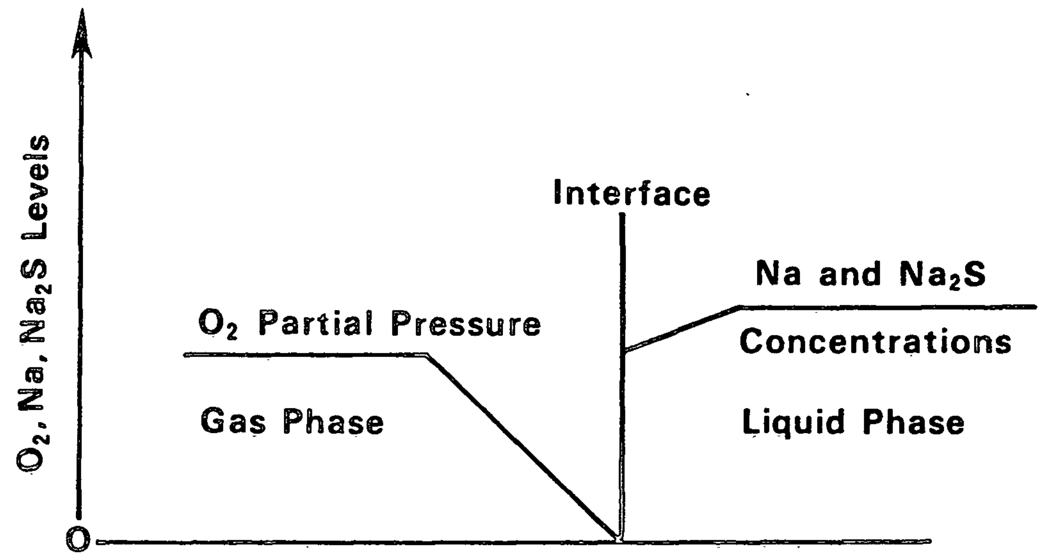
Two Modes of Oxidation

1) N_2-O_2 introduced above melt, Na_2S oxidation is liquid-side mass transfer limited.

2) N_2-O_2 introduced below melt's surface, Na_2S oxidation is gas-side mass transfer limited.



Oxidative Fume Generation



Relative Levels of O_2, Na and Na_2S at Gas-Melt
Interface with Purge Introduced Below Melt's Surface

Rate of O_2 Consumption in Gas Bubble

$$\frac{d(N_{O_2})}{dt} = S\ Pt\ Kg\ \frac{N_{O_2}}{N_{N_2}}$$

N_{O_2} = Moles of O_2
N_{N_2} = Moles of N_2
Pt = Total Pressure
Kg = Gas Phase Mass Transfer Coefficient
S = Bubble's Surface Area

Fume generation rate is constant during O_2 consumption

$$\frac{dF}{dt} = -K\ S$$

Then $$\frac{d\ F}{d\ (N_{O_2})} = -\frac{K\ \ N_{N_2}}{Kg\ Pt\ N_{O_2}}$$

$$\int_o^{Ft} dF = -\frac{K\ N_{N_2}}{kg\ Pt}\int_{N_{O_2I}}^{N_{O_2F}} \frac{dN_{O_2}}{N_{O_2}}$$

Boundary Conditions

1) Moles of O_2 in bubble (N_{O_2}) = Initial moles of O_2 in Purge (N_{O_2I}) and fume generated (F) = 0.
2) Moles of O_2 in bubble (N_{O_2}) = moles of O_2 in bubble where fuming ceases (N_{O_2F}), and fume generated (F) = total fume (Ft)

$$Ft = \frac{K\ N_{N_2}}{Kg\ Pt}\ [\ln\ (N_{O_2I}) - \ln\ (N_{O_2F})]$$

Ft = Fume generation in gas bubble
$N_{O_2}I$ = Initial moles of O_2 fed
N_{O_2} = Final moles of O_2 when fuming stops

APPLICATION OF MODEL TO EXPERIMENTAL RESULTS

(A) Fume generation during sulfide oxidation with the N_2-O_2 purge introduced above melt's surface

1) Fume generation with a N_2-O_2 purge was normally less than under a N_2 purge.

2) Fume generation decreased as O_2 level was increased.

(B) Fume generation during sulfide oxidation with the N_2-O_2 purge introduced below the melt's surface

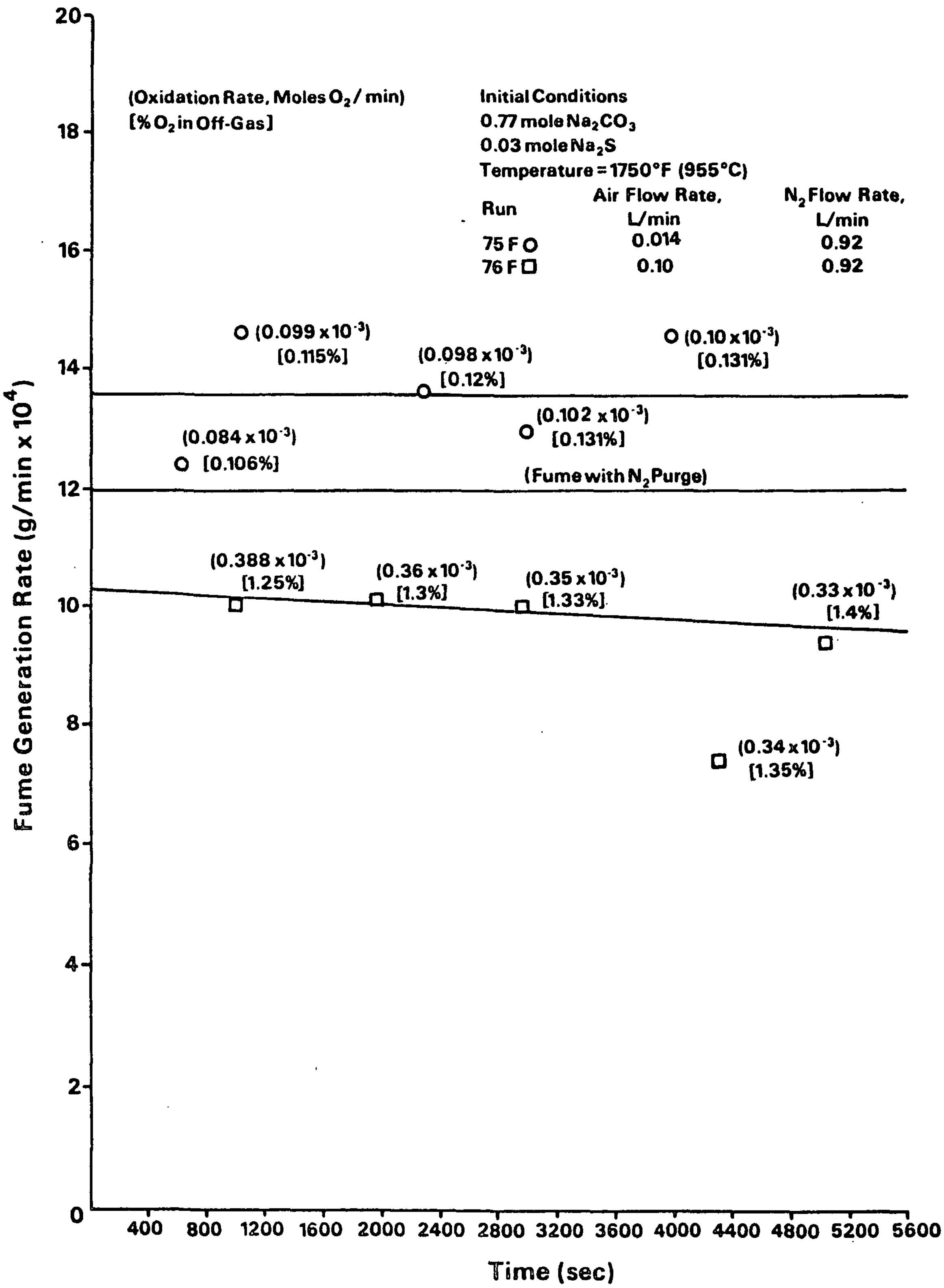
1) Sulfide oxidation in this mode of gas-melt contact produces large quantities of fume.

2) Fume rate is proportional to the N_2 purge rate.

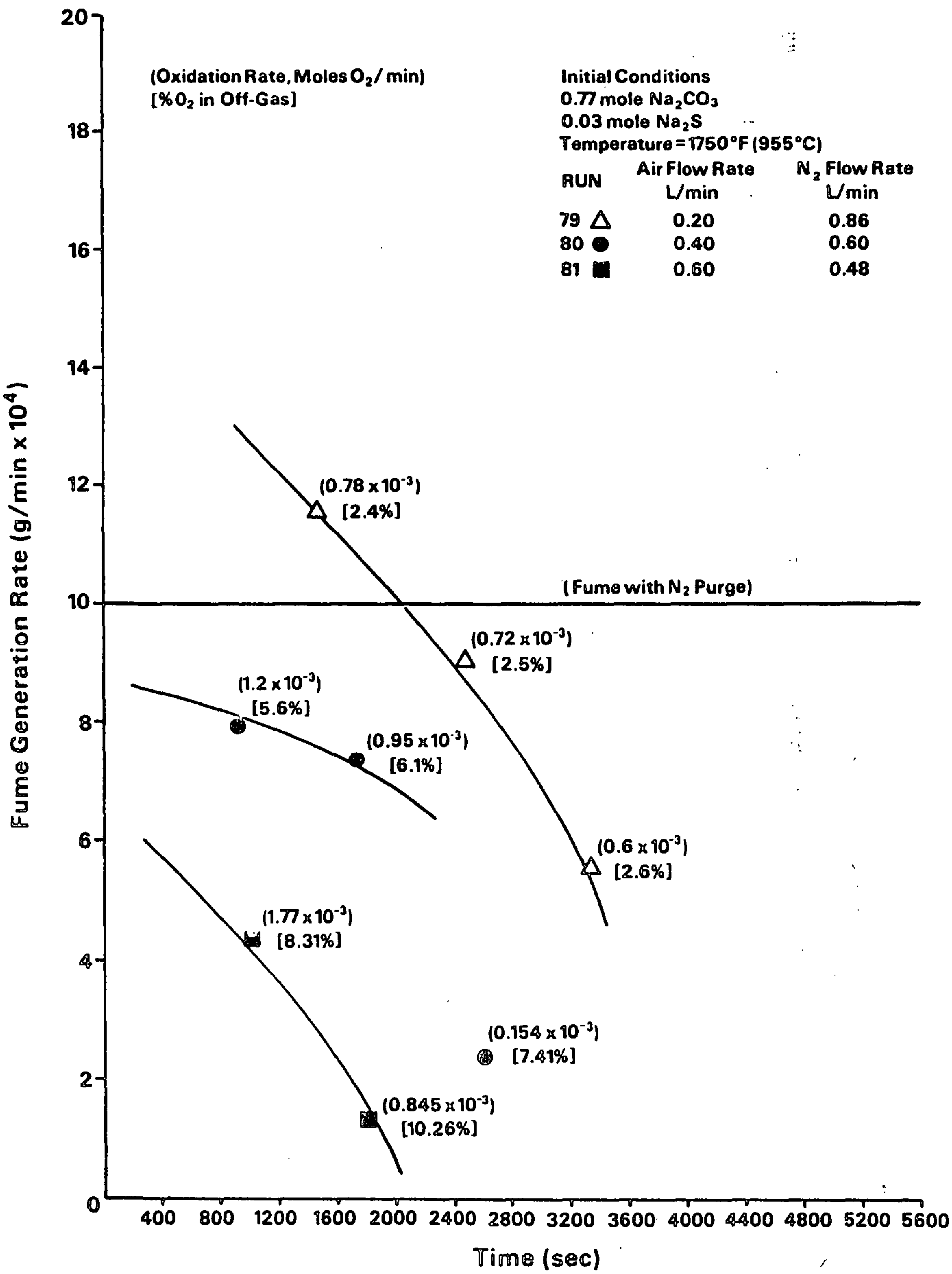
3) The fume generation rate depends logarithmically on O_2 content of the purge.

4) The bubble size and hence surface area has no effect on fume generation rate.

5) Carrier gases with lower interdiffusivities produce lower fume generation rate.



Effect of O_2 on Fume Generation with O_2 Introduced Above Melt's Surface, Low O_2 Levels

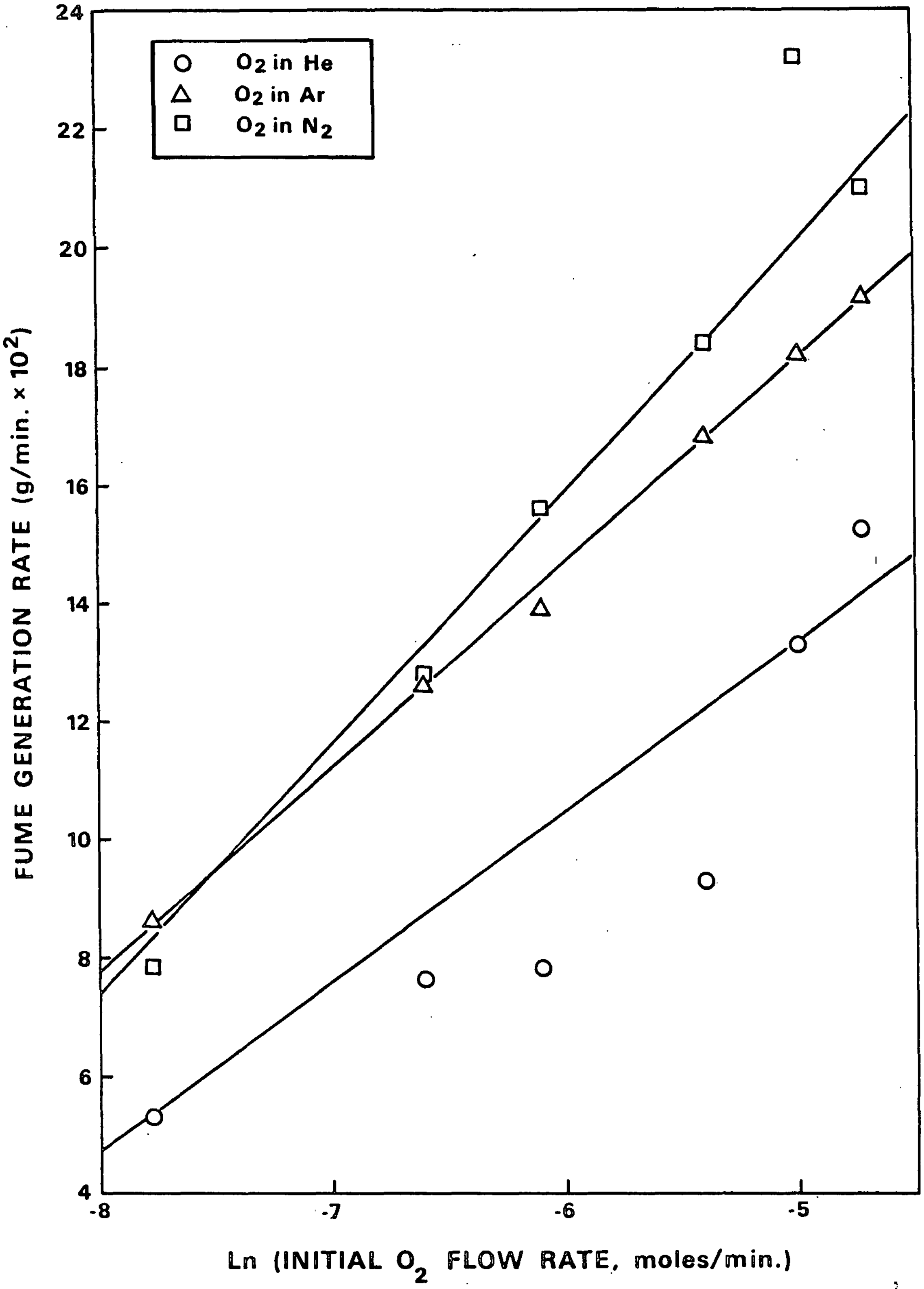


Effect of O_2 on Fume Generation with O_2 Introduced Above Melt's Surface, High O_2 Levels

Effect of N_2 Flow Rate on Fume Generation

Initial Melt Conditions: Na_2CO_3 = 0.77 mol
Na_2S = 0.03 mol
Temperature = 927°C (1700°F)

Run	N_2, L/min	Air, L/min	Total N2, L/min	Fume Generation Rate ± Std. Dev., g/min
50	0.04	0.1	0.48	0.00680 ± 0.00032
51	0.6	0.1	0.68	0.00850 ± 0.00076
52	0.8	0.1	0.88	0.01004 ± 0.00042
38	0.9	0.1	0.98	0.01024 ± 0.00032
53	1.06	0.1	1.14	0.01204 ± 0.00042
54	1.23	0.1	1.31	0.01474 ± 0.00198



Effect of Initial Oxygen Level in Different Carrier Gases

Effect of Two Purge Tubes on Fume Generation Rate

Run No.	Temp °F	N_2 Flow Rate L/Min	O_2 Flow Rate L/Min	Fuming Rate g/Min ± Std. Dev.	Predicted Fuming Rate g/Min
127	1749	1.03	.020	0.0129 ± .001	0.0126
128	1754	1.03	.0426	0.0163 ± .001	0.0156
129	1754	1.01	.0634	0.0156 ± .001	0.0172

MAJOR CONCLUSIONS

1) FUME PRODUCTION IS A DYNAMIC PROCESS DEPENDENT ON MASS TRANSFER PROCESSES AND CHEMICAL REACTIONS.

2) FUME GENERATION RESULTING FROM REDUCTION OF NA_2CO_3 WITH CARBON, H_2 AND CO IS SIGNIFICANTLY LOWER THAN FUME GENERATION DURING SULFIDE OXIDATION IN A WELL-MIXED MELT.

3) EQUILIBRIUM CONSIDERATIONS GOVERN THE VOLATILIZATION OF NACL AND KCL.

4) THE ONLY VOLATILE SPECIES THAT CONTRIBUTE TO FUME FORMATION IN THE KRAFT FURNACE ARE NA VAPOR, K VAPOR, NACL VAPOR AND KCL VAPOR.

FUTURE WORK

DETERMINE APPLICABILITY OF OXIDATIVE FUMING TO COMBUSTION OF BLACK LIQUOR DROPLETS: PH.D. THESIS.

NODULATION OF LIME

OBJECTIVE: DEVELOP AN UNDERSTANDING OF THE PROCESSES INVOLVED IN LIME NODULATION AND EFFECT OF NONPROCESS ELEMENTS ON THESE PROCESSES.

PLANNED ACTIVITY

1) Determine if nodulation behavior is related to sintering.

2) Examine changes in sintering characteristics that occur during calcination-causticizing cycle and effect of impurities on this behavior.

3) Determine the effect of specific nonprocess elements on sintering.

CHEMICAL REACTIONS INVOLVING HYDROGEN-CONTAINING SPECIES (H_2, H_2O, H_2S)

1) Hydrogen Reduction of Sulfate

$$4H_2 + Na_2SO_4 \longrightarrow 4H_2O + Na_2S$$

2) Water Gasification of Char

$$H_2O + C \longrightarrow CO + H_2$$

3) Hydrogen Sulfide Release & Recapture

a) $Na_2S + H_2O + CO_2 \rightleftharpoons H_2S + Na_2CO_3$

b) $H_2S + 2O_2 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

4) NaOH Formation

$$H_2O + Na_2CO_3 \rightleftharpoons 2NaOH + CO_2$$

STUDENT RESEARCH

Gregg Aiken; Ph.D.: A Determination of the Processes Controlling the Carbon Dioxide-Carbon Monoxide Split During Char Combustion.

Kris Goerg; Ph.D.: The Role of the Carbon Dioxide-Carbon Reaction in the Burning of Kraft Char.

John G. Fuller; M.S.: The Effect of Nonprocess on Lime Sintering.

Christopher L. Verrill; M.S.: Sodium Fume Generation During Black Liquor Combustion.

BLACK LIQUOR BURNING
(TASK OF PROJECT 3473-1)

OBJECTIVE

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

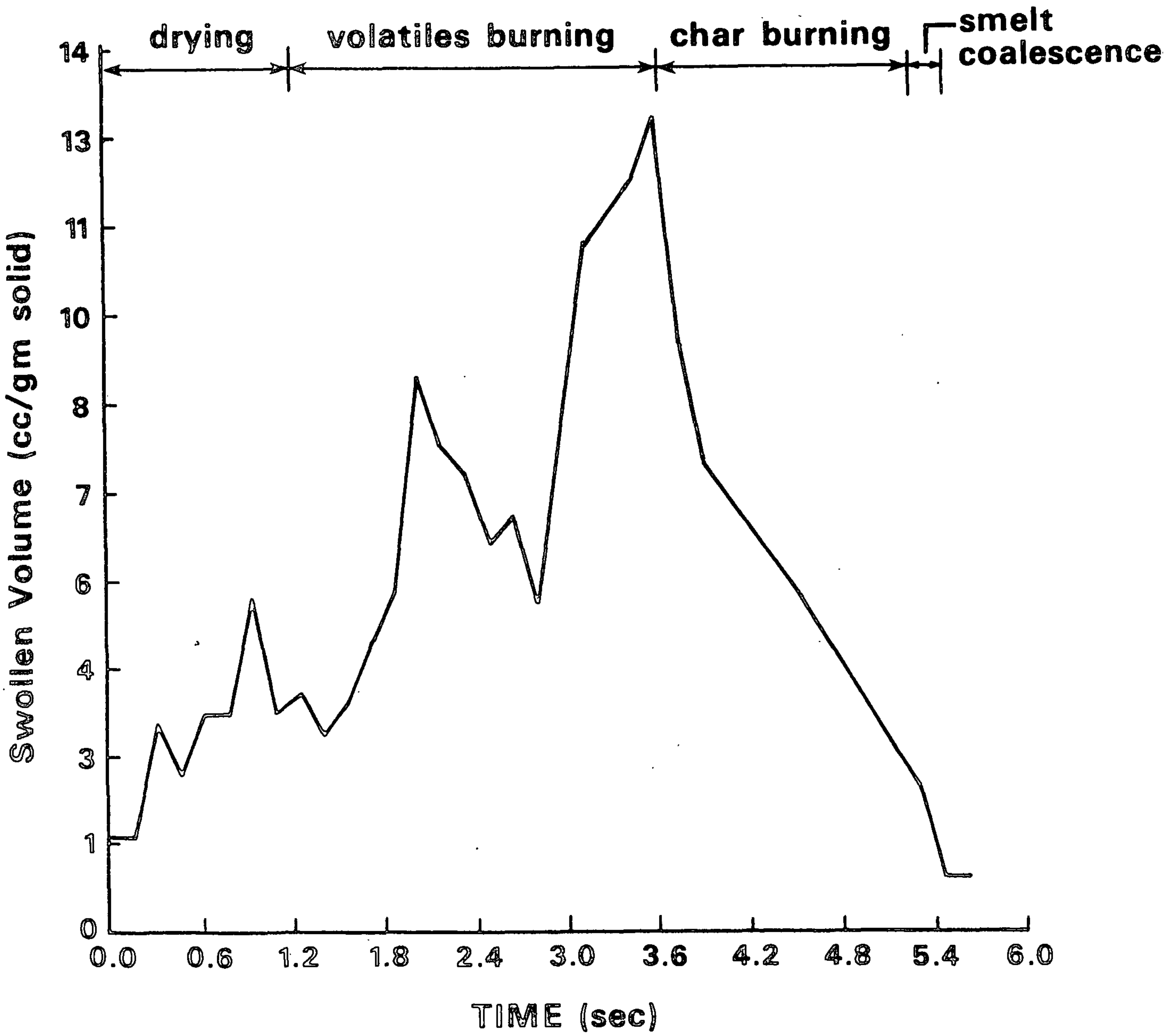
RATIONALE

- MINIMAL FUNDAMENTAL KNOWLEDGE OF THE BURNING PROCESS
- THERMAL EFFICIENCY INCREASES NEEDED
- INCREMENTAL CAPACITY NEEDED
- FOUNDATION FOR FUTURE RECOVERY PROCESSES

APPROACH

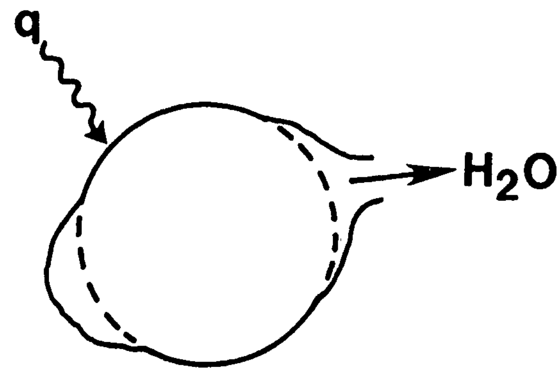
- USE MILL LIQUORS
- CONDUCT CHEMICAL AND COMBUSTION TESTS
- ANALYZE DATA FOR EMPIRICAL INTER-RELATIONSHIPS
- DESIGN CONTROLLED TESTS TO CONFIRM CONTROLLING PHENOMENA

VOLUMETRIC GROWTH OF BURNING LIQUOR PARTICLE



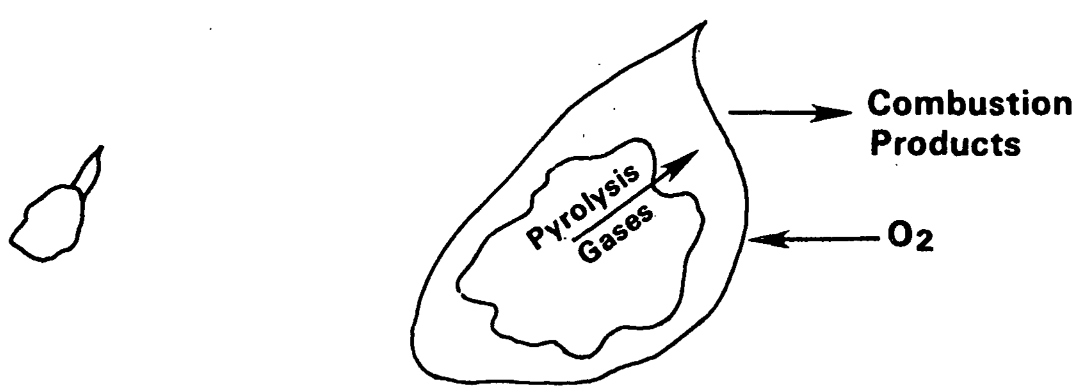
Test 393-30
Air Temperature 800°C
Velocity 2.5 M/S
Initial Solids 69.5%

DRYING



- External heat transfer
- Skin forming tendency
- Rapid expansion/contraction
- Swelling can be significant
- Time for 65%-70% solids N/sec

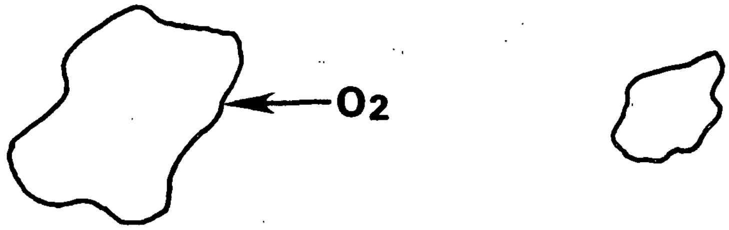
VOLATILES BURNING



Ignition **Maximum Volume**

- Point ignition
- Heat source - pyrolysis gas combustion
- Wide range and variability of swelling
- Liquor composition and O_2 key variables
- Sulfur released
- Nominal time 1.5 sec

CHAR BURNING



- Nominally 50% of original HHV
- Stage for sulfate-sulfide cycle
- Inorganic fuming
- Strong exotherms
- Nominal time 2.5 sec

SMELT COALESCENCE

- Rapid structure collapse @ 2-3% C
- Fluid with strong surface tension
- Will oxidize if exposed to O_2
- Nominal time 0.2 sec

MILL LIQUORS

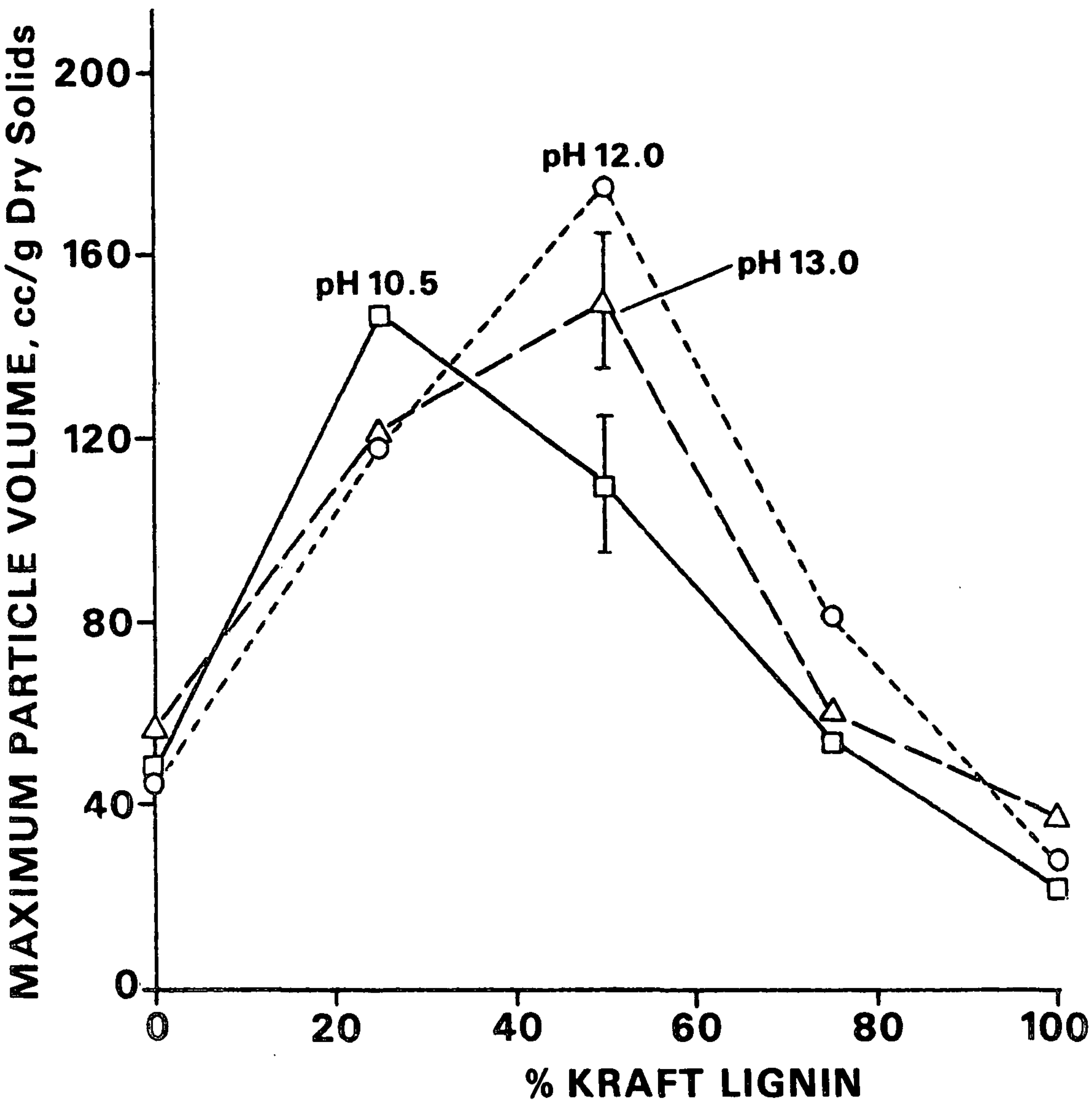
MILL LOCATIONS		20
(U.S.	13)	
(FOREIGN	7)	
MILL SAMPLES		61
(KRAFT	54)	
(SODA	2)	
(SEMICHEMICAL	3)	
(OTHERS	2)	
LAB KRAFT SAMPLES		2

DIRECTION

- EVALUATE EMPIRICAL INTERRELATIONSHIPS
- WORK CLOSELY WITH TWO MILLS HAVING LIQUOR BURNING PROBLEMS
- DESIGN CONTROLLED TESTS WITH SPIKED MILL LIQUORS AND/OR LAB LIQUORS
- COLLABORATE WITH DR. MIKKO HUPPA IN LIQUOR BURNING STUDIES
- INTERTIE WITH STUDENT WORK, E.G., PAUL MILLER AND KATHY CRANE

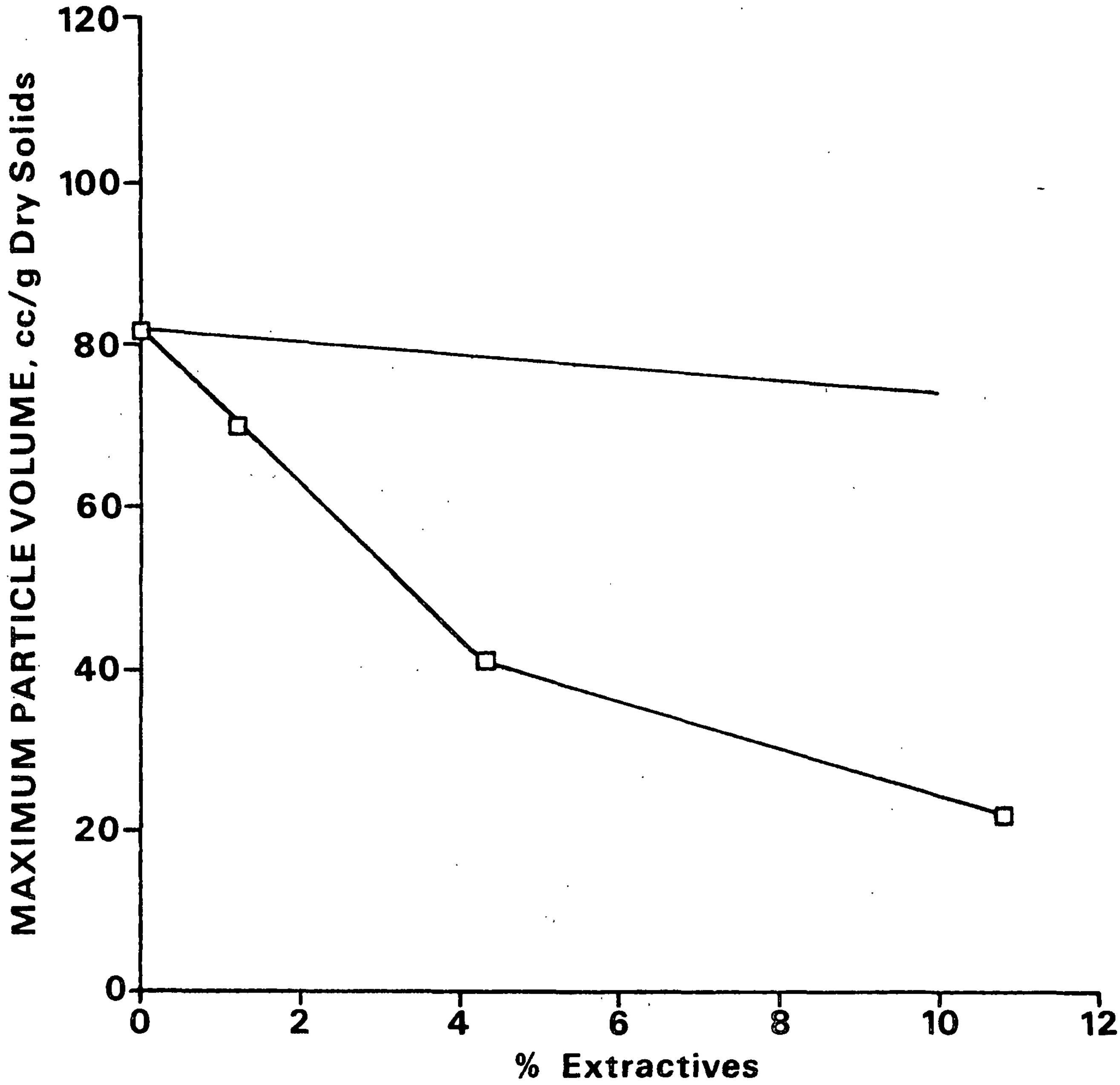
THE INFLUENCE OF HYDROXY ACID/KRAFT LIGNIN RATIO ON THE SWOLLEN VOLUME OF BLACK LIQUOR UNDERGOING PYROLYSIS AT 500°C. THE VARIATION WITH SOLUTION PH IS ALSO SHOWN.

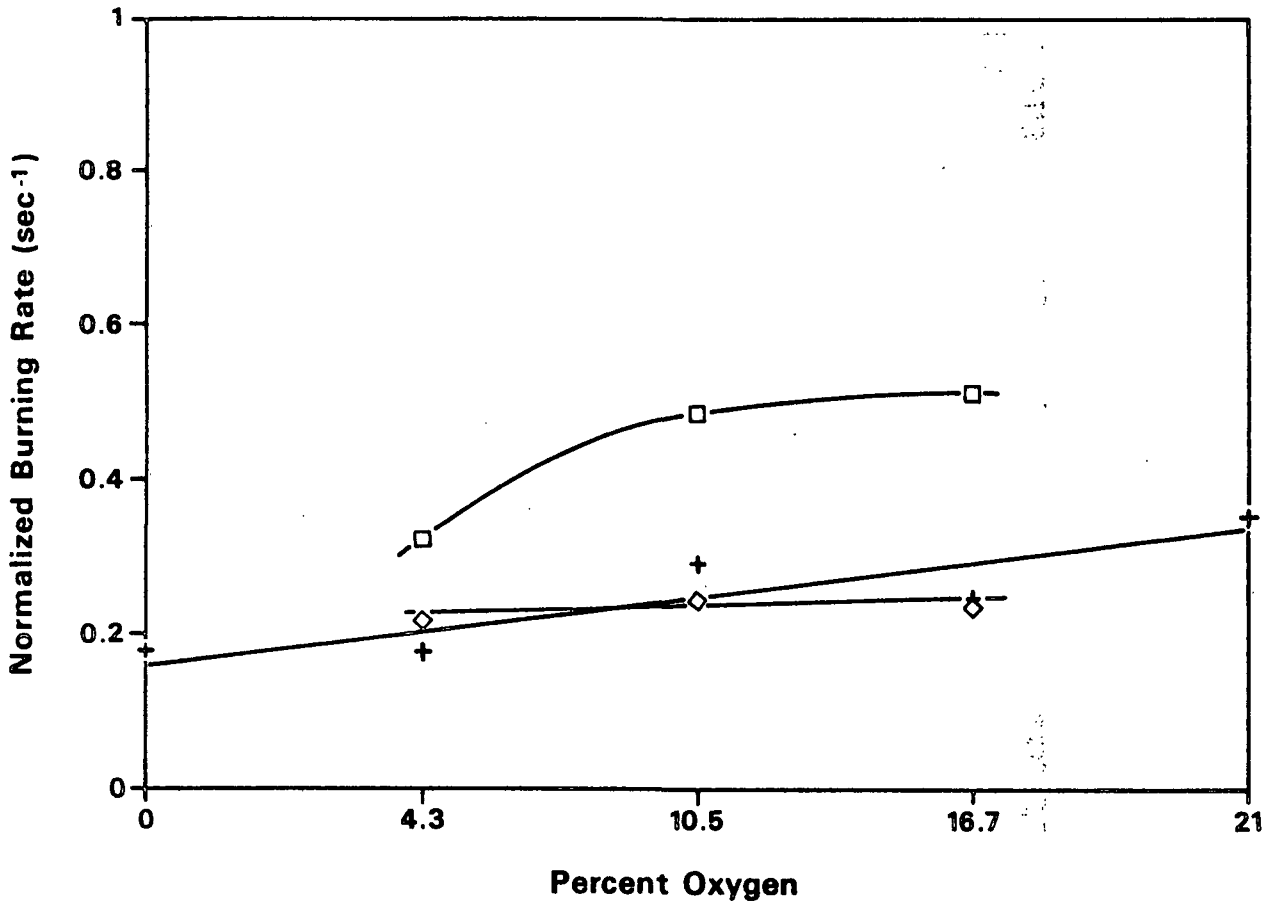
(DATA FROM THESIS WORK OF P. MILLER)



THE INFLUENCE OF EXTRACTIVES ON THE SWOLLEN VOLUME OF BLACK LIQUOR UNDERGOING PYROLYSIS AT 500°C. THE TOP SOLID LINE INDICATES THE RELATIONSHIP IF THE EXTRACTIVES ACT AS ONLY A DILUENT.

(DATA FROM THESIS WORK OF PAUL MILLER)





INFLUENCE OF THE OXYGEN CONTENT ON THE NORMALIZED BURNING RATE OF THREE DIFFERENT SIZE BLACK LIQUOR DROPLETS

INITIAL SOLIDS CONTENT	71.8%
RANGE GAS TEMPERATURE	665-860°C

□	11 MG	2.5 MM
+	22 MG	3.1 MM
◇	33 MG	3.6 MM

(DATA FROM A190 WORK OF KATHY CRANE)

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

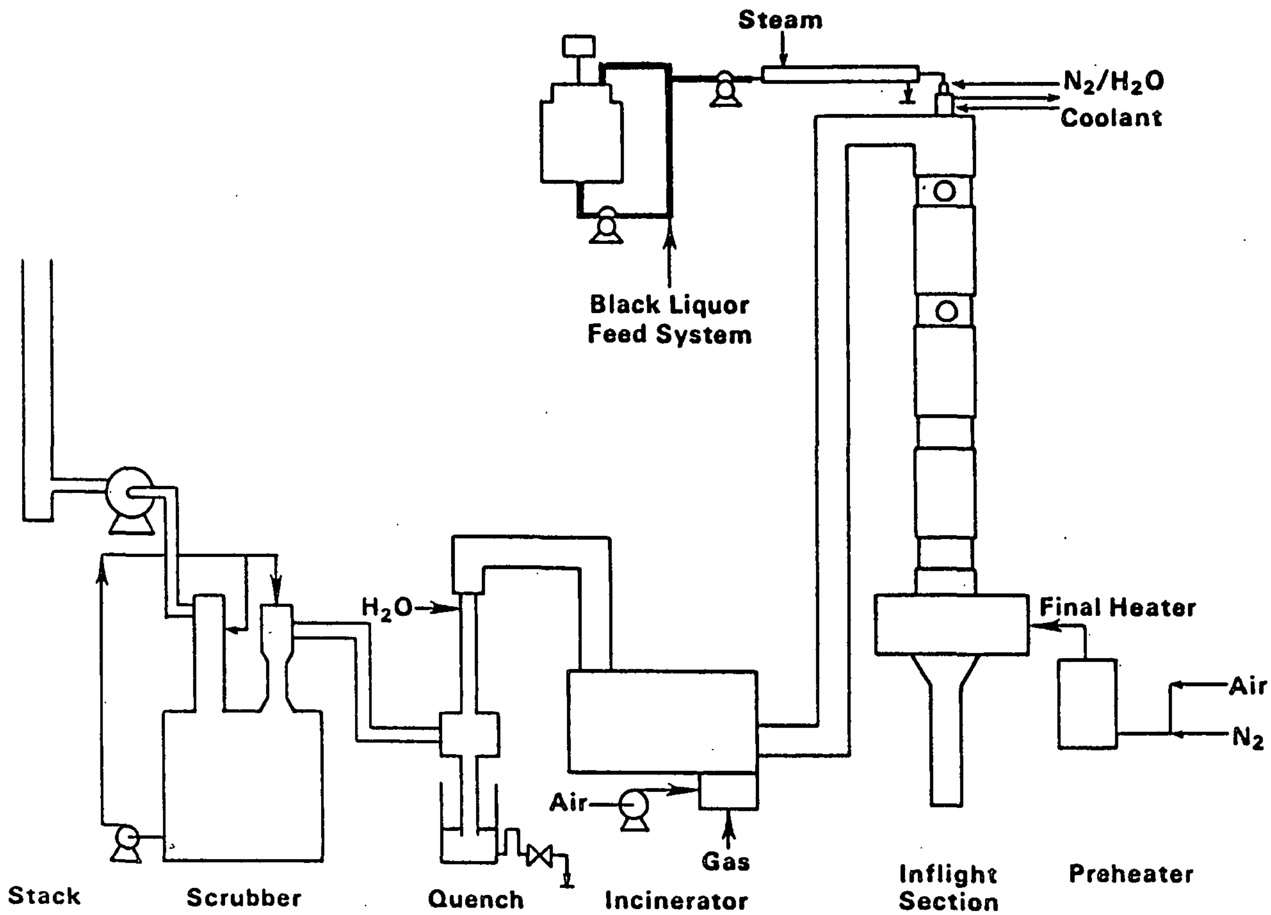
ACCOMPLISHMENTS
(SINCE OCTOBER 1985)

IPC

- FIRST PROGRESS REPORT DISTRIBUTED
- INITIAL TRAJECTORY TESTS COMPLETED
- UPFLOW MODE OF PHASE 1 FLOW REACTOR INSTALLED
- BRIEF TEST AT HIGH LIQUOR FLOWS CONDUCTED

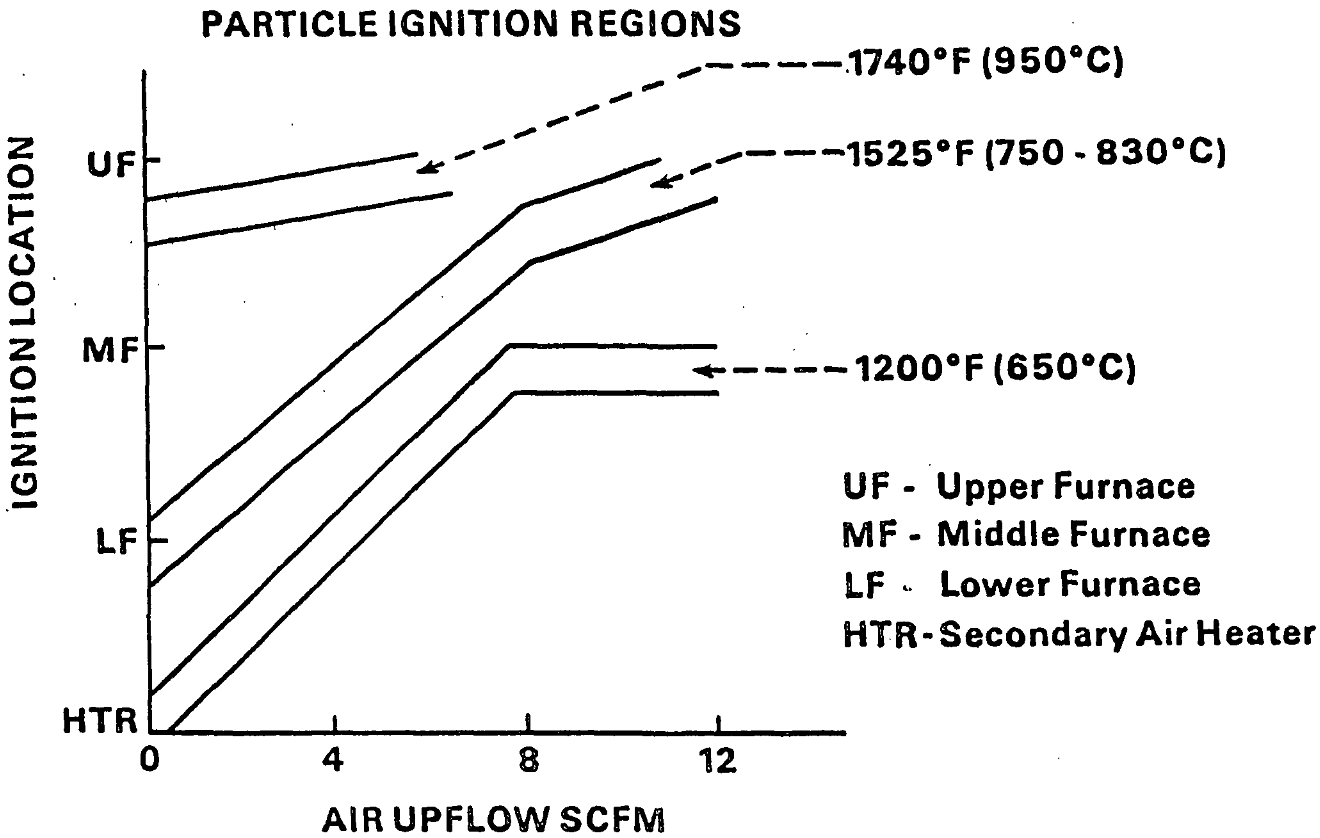
NBS

- VOLUMETRIC DROPLET DIAMETERS MEASURED
- TEMPERATURE PROFILES DETERMINED
- FIRST IN-FLIGHT PROCESSES DOCUMENTED
- DYNAMIC PARTICLE SIZE/VELOCITY MEASURED



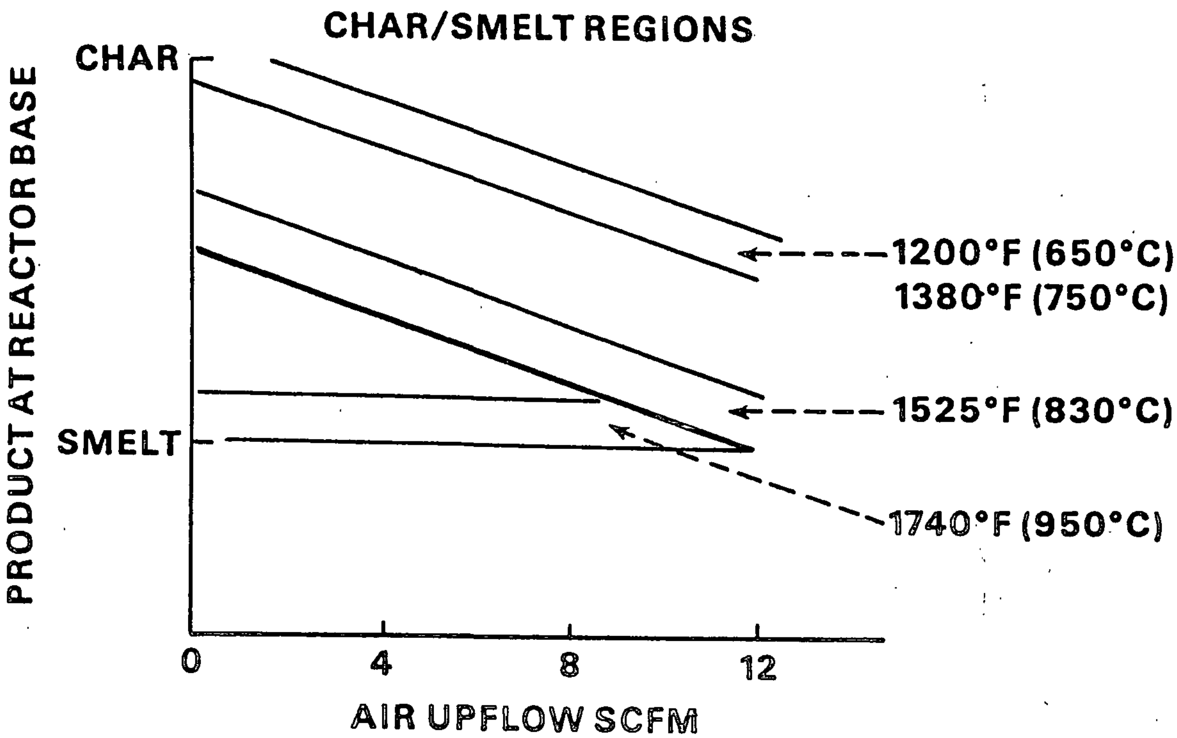
UPFLOW MODE OF IPC PHASE 1 SYSTEM

VERTICAL LOCATION FOR IGNITION



LIQUOR NO. 1
SOLIDS 66.5%
TIP SIZE 0.81 MM ID

PRODUCT CHARACTERISTICS



LIQUOR NO. 1
SOLIDS 66.5%
TIP SIZE 0.81 MM ID

PHASE 1 REACTOR: UPFLOW MODE

STARTUP STATUS

- OPERABLE GAS TREATMENT PACKAGE

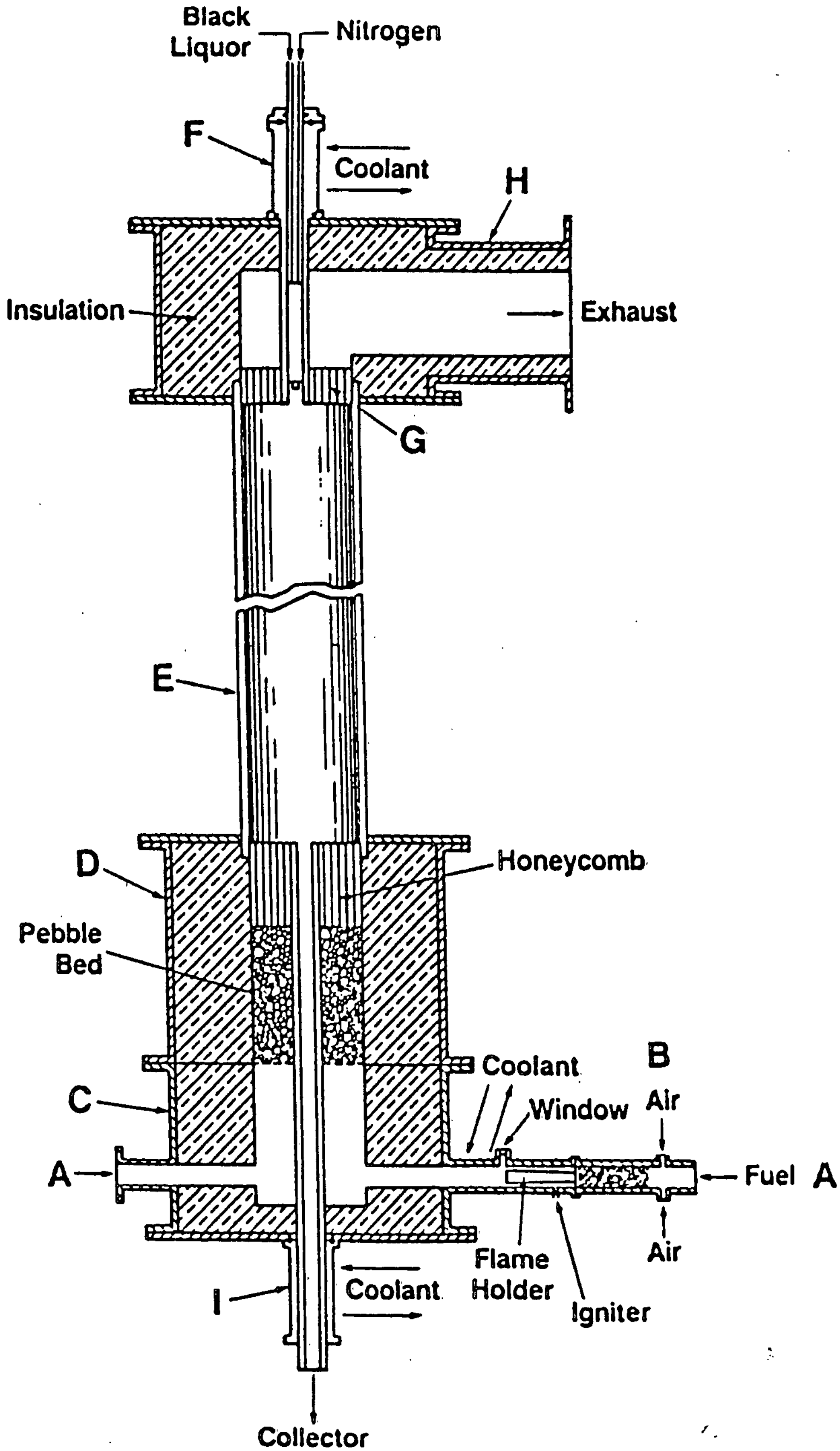
  EQUIPMENT OPERATED AT EQUIVALENT 400,000 BTU/HR CAPACITY

  MINOR MODIFICATIONS REQUIRED TO MEET DESIGN.

- PHASE 1 SYSTEM OPERATED BRIEFLY 0.5 TO 7 LB SOLIDS/HR

  CHAR COLLECTED

  PLUGGED AT BASE



NBS INITIAL REACTOR MODULE

CALCULATED U_T VS. EXPERIMENTAL U_S

$U_T(A)$: ASSUMES SWELLING TO MEASURED D WITHOUT MASS LOSS

$U_T(B)$: ASSUMES COMPLETE DRYING (40% MASS LOSS)

PARTICLE NO.	D (MM)	U_S(CM/S)	U_T(A)(CM/S)	U_T(B)(CM/S)
1	2.6	599	655	466
2	2.6	609	655	466
3	2.9	599	585	418
4	2.3	444	741	527
5	(2.3)*	589	741	527
6	(2.7)*	589	632	449

*NON-SPHERICAL

CONCLUSIONS: PHOTOGRAPHIC DATA

A. EXPERIMENTAL

1. TRAJECTORIES VERTICAL UNTIL SWELLING BY ABOUT FACTOR OF 2 (LINEAR)

2. D_0=1.8 MM, T=900°C, U_G=385 CM/S, ΔH=45 CM

   A. SUBSTANTIAL SWELLING, PARTIAL DRYING

   B. ESTIMATED RESIDENCE: 0.2<T<0.5 SECONDS

B. VAPORIZATION TIME - ROUGH CALCULATION

$$T_V = \frac{M_0 \times 0.4 \times H_W}{N\ \overline{D}\ \overline{N_U}\ K\ (T_G - 110)} = 1.2\ S$$

C. COMPARISON, IPC DATA

$D_0 \sim$ 2 MM, $T_V \sim$ 1 SECOND

NBS TARGETED INSTRUMENTATION
(PRELIMINARY LIST)

- DROPLET INJECTOR
- RESIDENCE TIME MONITOR
- BURNING PARTICLE/GAS TEMPERATURE SENSOR
- COMPOSITION MEASUREMENT OF BURNING PARTICLE FLAMES
- FUME SIZE/CONCENTRATION MEASUREMENT
- BURNING CHAR PILE TEMPERATURE SENSOR

NEAR TERM PLANS
(THROUGH JUNE 1986)

IPC

- OPERATE PHASE 1 SYSTEM AT DESIGN FLOWS
- COMPLETE SYSTEM CHARACTERIZATION
- CONDUCT IN-FLIGHT PROCESS TESTING

NBS

- INSTALL PHASE 1 SYSTEM
- DEVELOP TARGETED INSTRUMENTATION LIST
- MEASURE INDIVIDUAL PARTICLE IN-FLIGHT PARAMETERS

IN-FLIGHT PROCESS TESTING (IPC)

OBJECTIVE STUDY THE FOUR STAGES OF BLACK LIQUOR BURNING UNDER CONDITIONS WHERE THEY OCCUR IN-FLIGHT.

APPROACH
STABLE LIQUOR SOURCE
KEY INDEPENDENT VARIABLES
FINAL AND INTERMEDIATE PARTICLE SAMPLING
SOLIDS CHEMICAL/PHYSICAL CHARACTERIZATION
GAS ANALYSIS

GOAL DATA WHICH SHOWS THE VARIATION WITH TIME OF:

- PARTICLE COMPOSITION/PHYSICAL CHARACTER
- EVOLVED GAS COMPOSITION/QUANTITY AS A FUNCTION OF KEY INDEPENDENT VARIABLES

INDIVIDUAL PARTICLE IN-FLIGHT PARAMETER TESTING (NBS)

OBJECTIVE DOCUMENT THE DRYING STAGE OF BLACK LIQUOR PARTICLE BURNING AND ITS TRAJECTORY.

APPROACH
STABLE LIQUOR SOURCE
STUDY INITIAL DROP SIZE AND OXYGEN CONTENT
MEASURE PARTICLE DIAMETER AND VELOCITY
OBSERVE IN-FLIGHT IGNITION/SWELLING/ TRAJECTORY

GOALS DRYING TIMES, PARTICLE VELOCITIES, AND DYNAMIC DIAMETER CHANGES AS A FUNCTION OF INITIAL DROP SIZE AND OXYGEN CONTENT

Project 3558

INCREMENTAL CAPACITY IN RECOVERY BOILERS

T. M. Grace

Project 3456-2

SMELT-WATER EXPLOSIONS

T. M. Grace

PROJECT 3558

INCREMENTAL CAPACITY IN RECOVERY BOILERS

TERMINATING THE PROJECT

SMELT-WATER EXPLOSIONS

1. NO MAJOR CHANGES IN ACTIVITIES.
2. EXPECTING DRAFT OF SENSITIVITY ANALYSIS FROM UW-MADISON.
3. HAVE SUBMITTED JOINT PROPOSAL WITH CORRADINI.

Project 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

Delignification Reactions - D. R. Dimmel

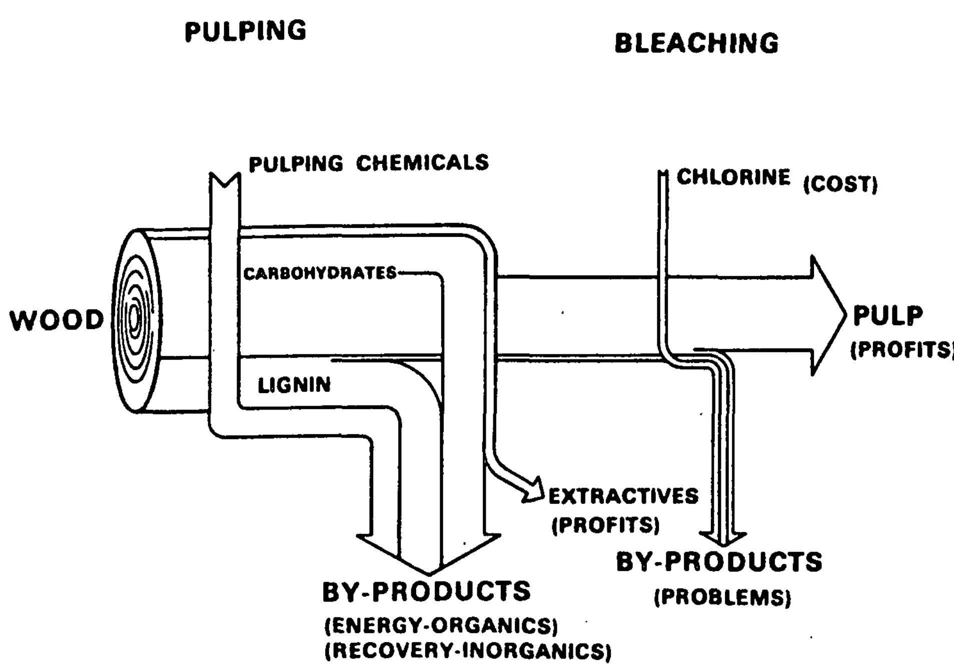
Carbohydrate Reactions - L. R. Schroeder

PROJECT 3475

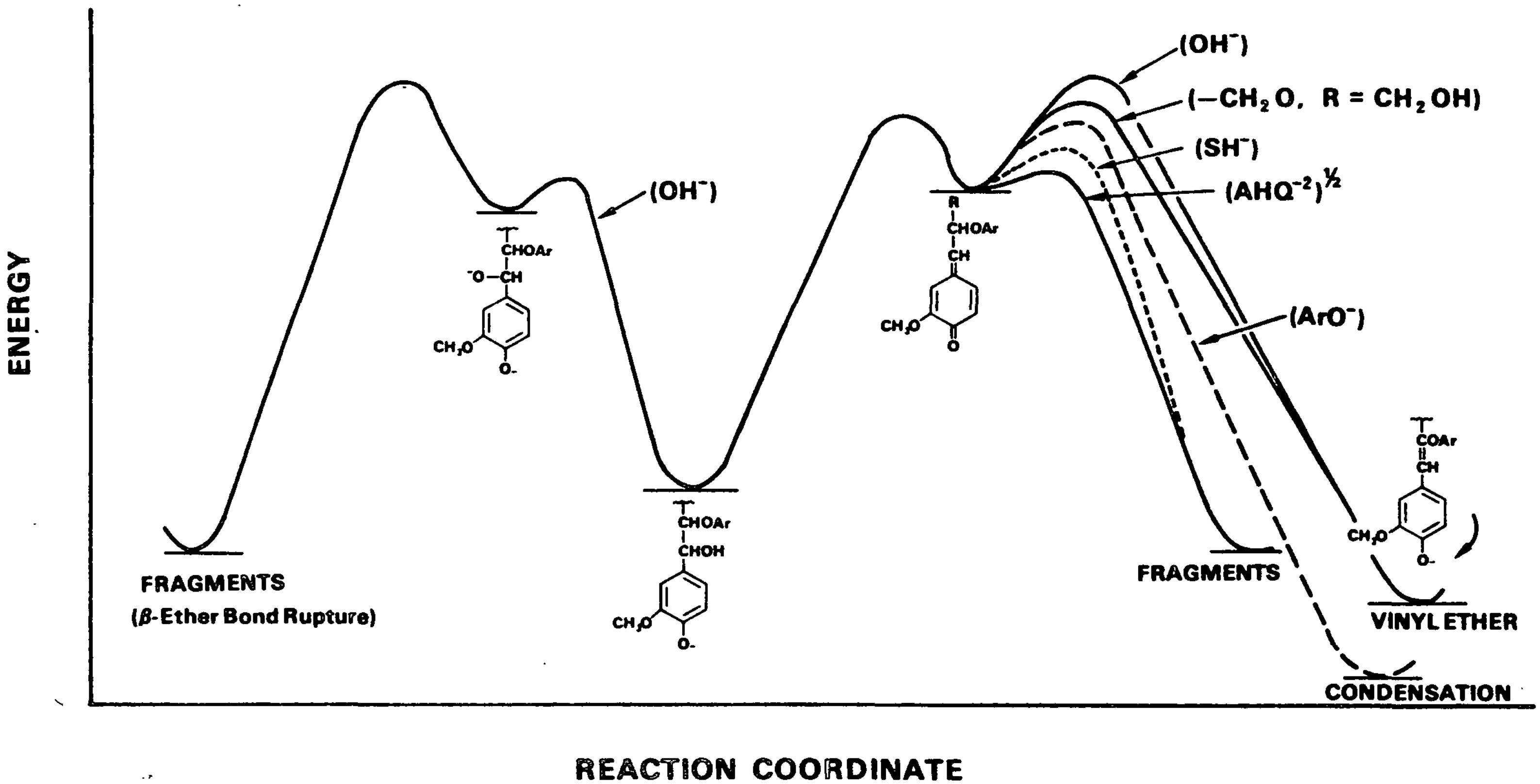
FUNDAMENTALS OF SELECTIVITY
IN PULPING AND BLEACHING

DELIGNIFICATION REACTIONS

CARBOHYDRATE REACTIONS

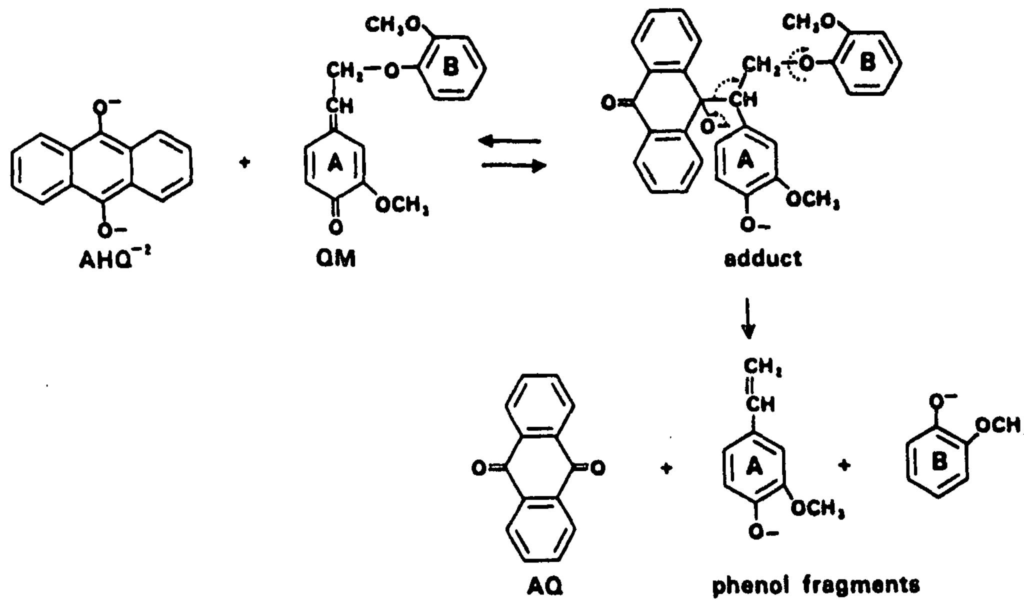


PULPING MATERIAL BALANCES

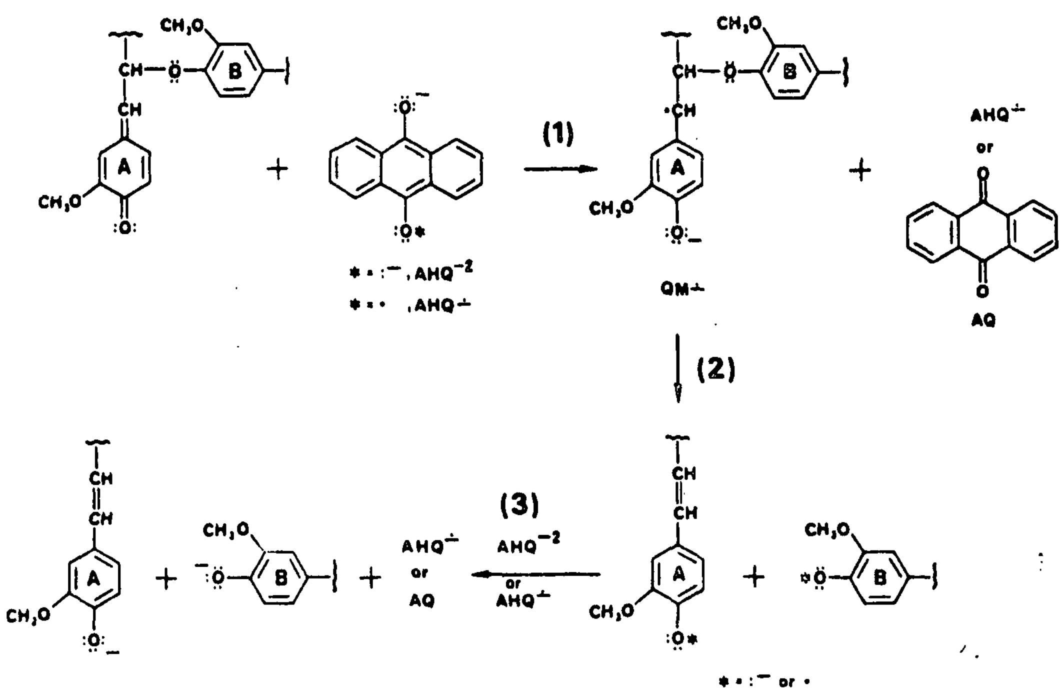


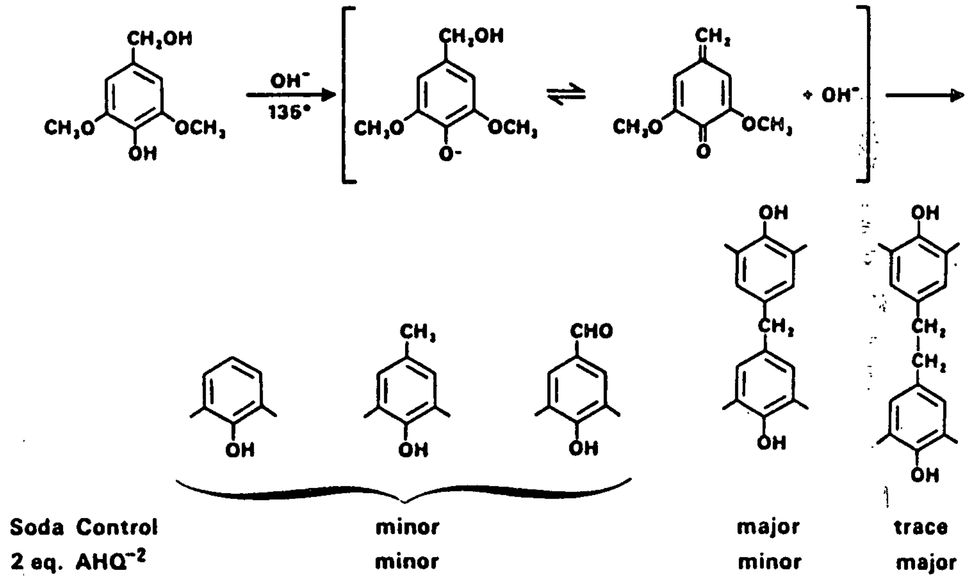
Hypothetical energy diagram for the reactions of phenolic lignin end units.

Delignification via AHQ Adduct Reactions

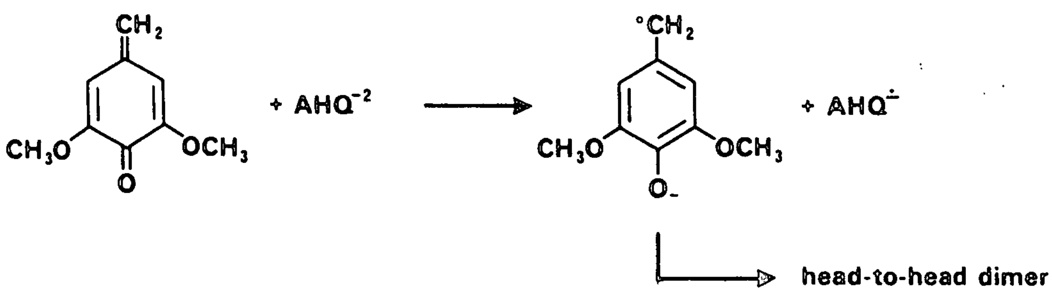


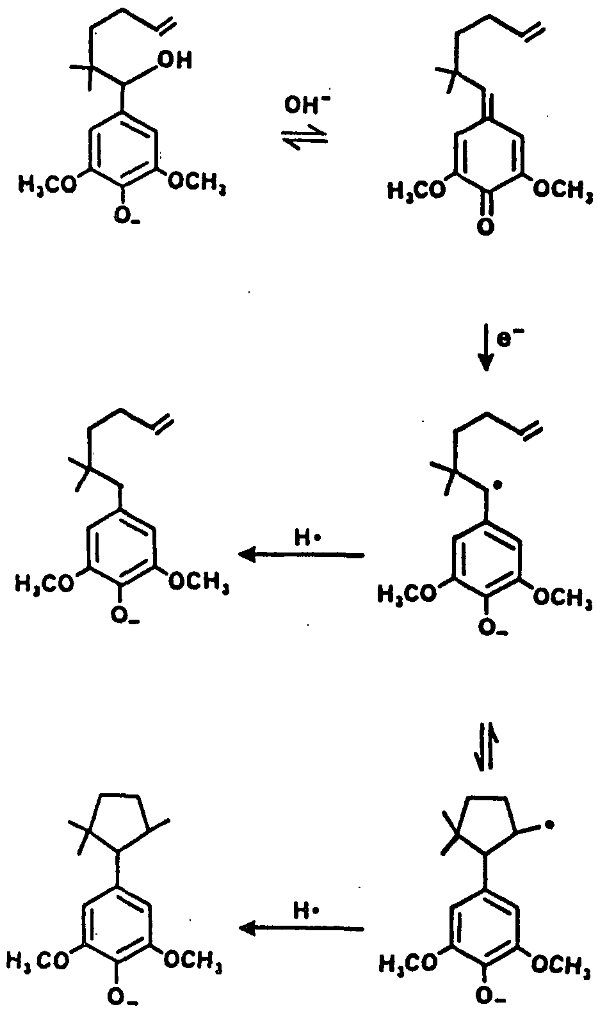
Delignification via AHQ-induced SET Reactions



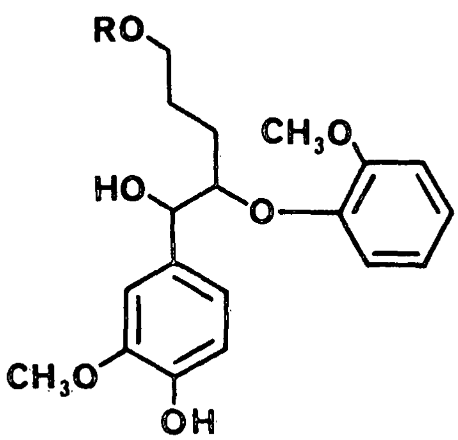


HIGH TEMPERATURE AQUEOUS REACTIONS OF SYRINGYL ALCOHOL
(D. SMITH THESIS)





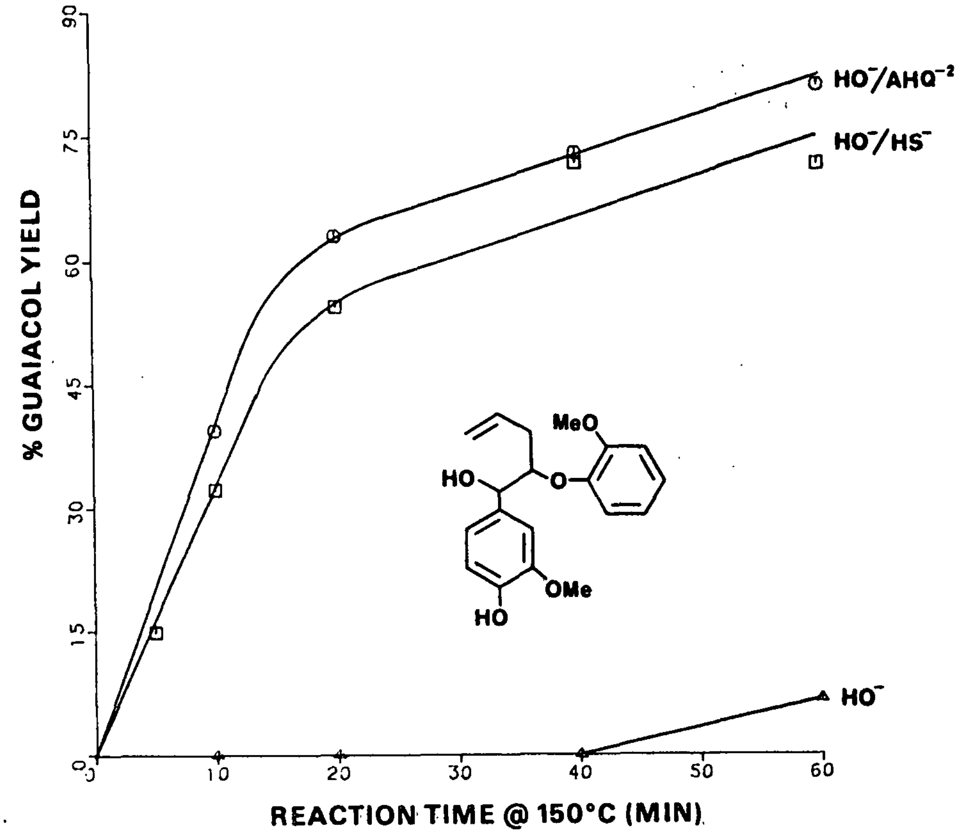
REACTIONS OF A PENTENYL SUBSTITUTED QUINONEMETHIDE (UPPER RIGHT) WHICH SHOW ELECTRON TRANSFER PROCESSES.



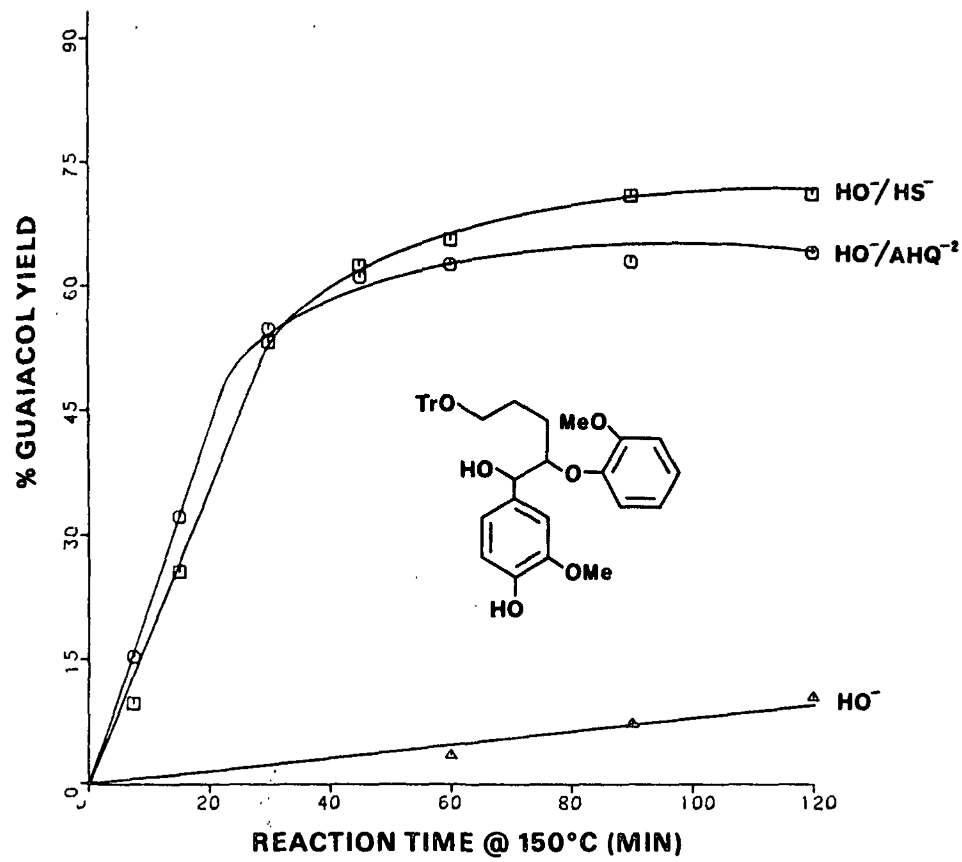
R = H

R = CPh_3

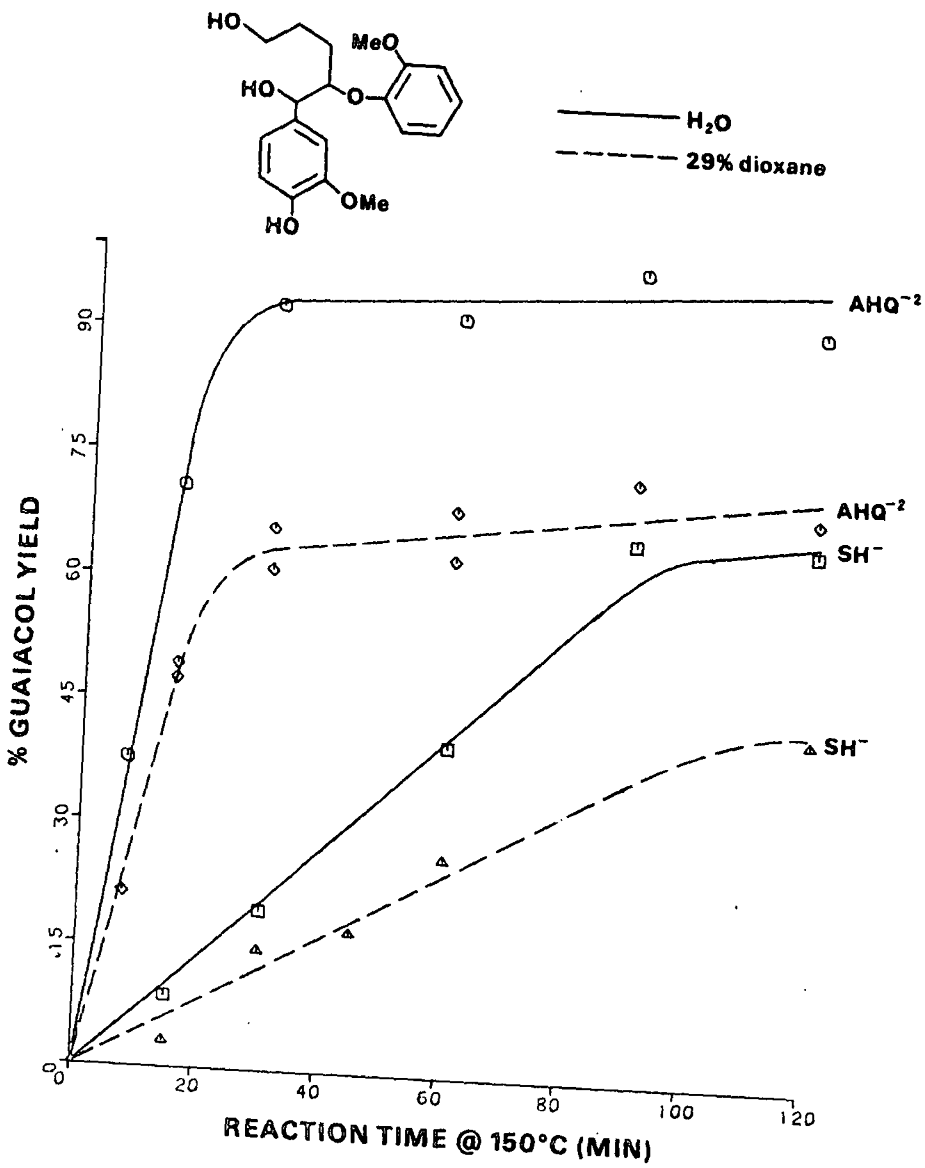
R = CPh_2 –polystyrene



Guaiacol yield as a function of time for the degradation of the indicated model at 150° water in the presence of 25 equiv. of NaOH, and 5 equiv. of NaSH, and 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

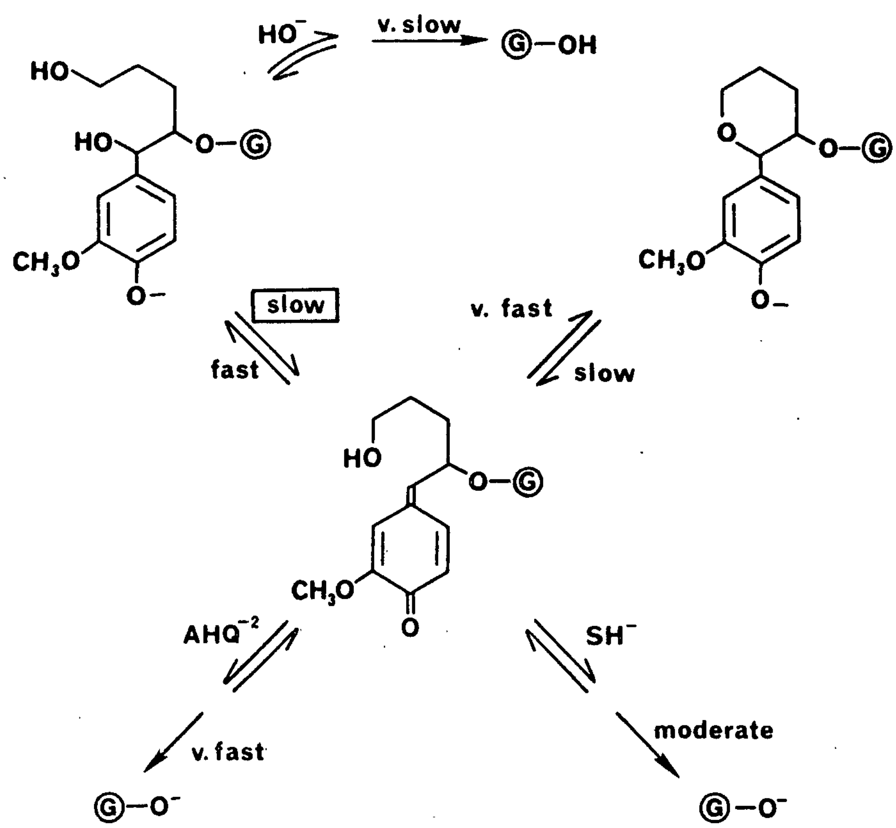


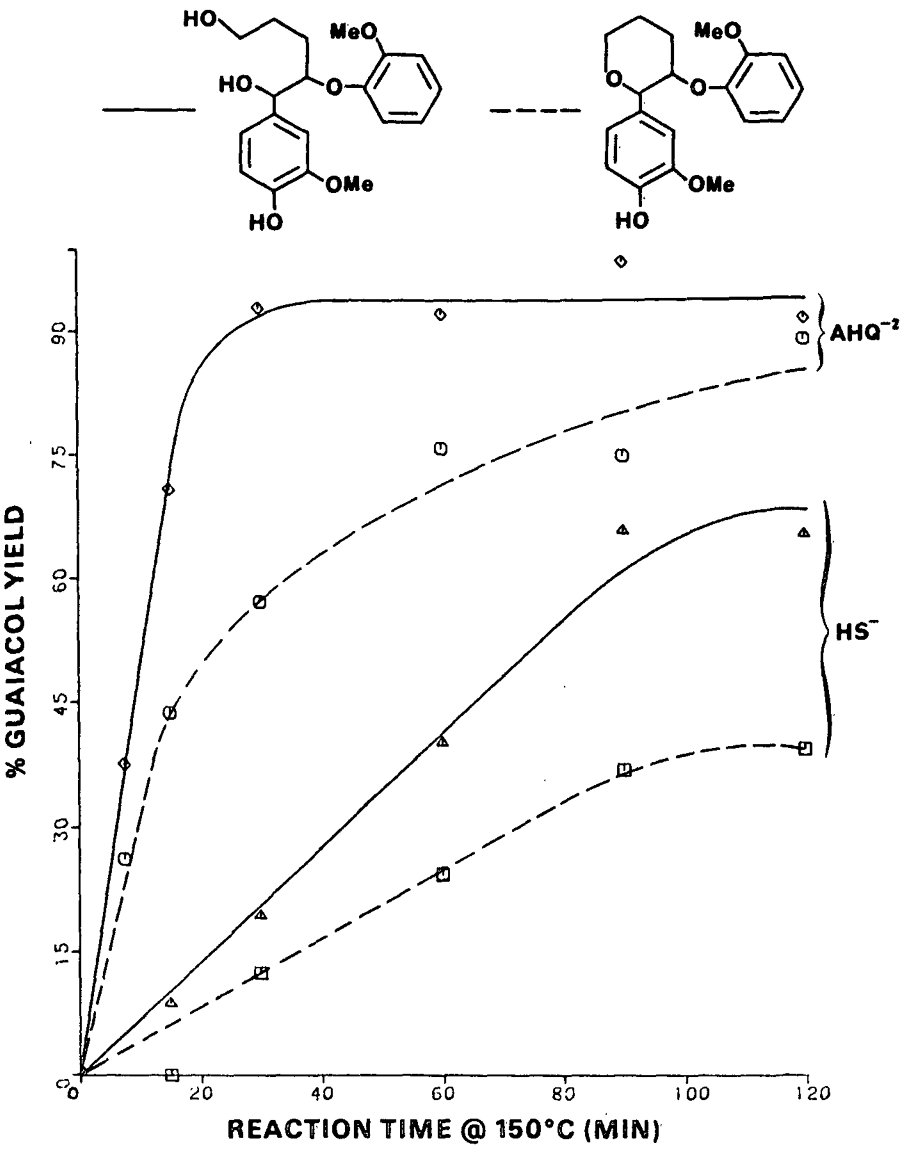
Guaiacol yield as a function of time for the degradation of the indicated model at 150° water in the presence of 25 equiv. of NaOH, and 5 equiv. of NaSH, and 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).



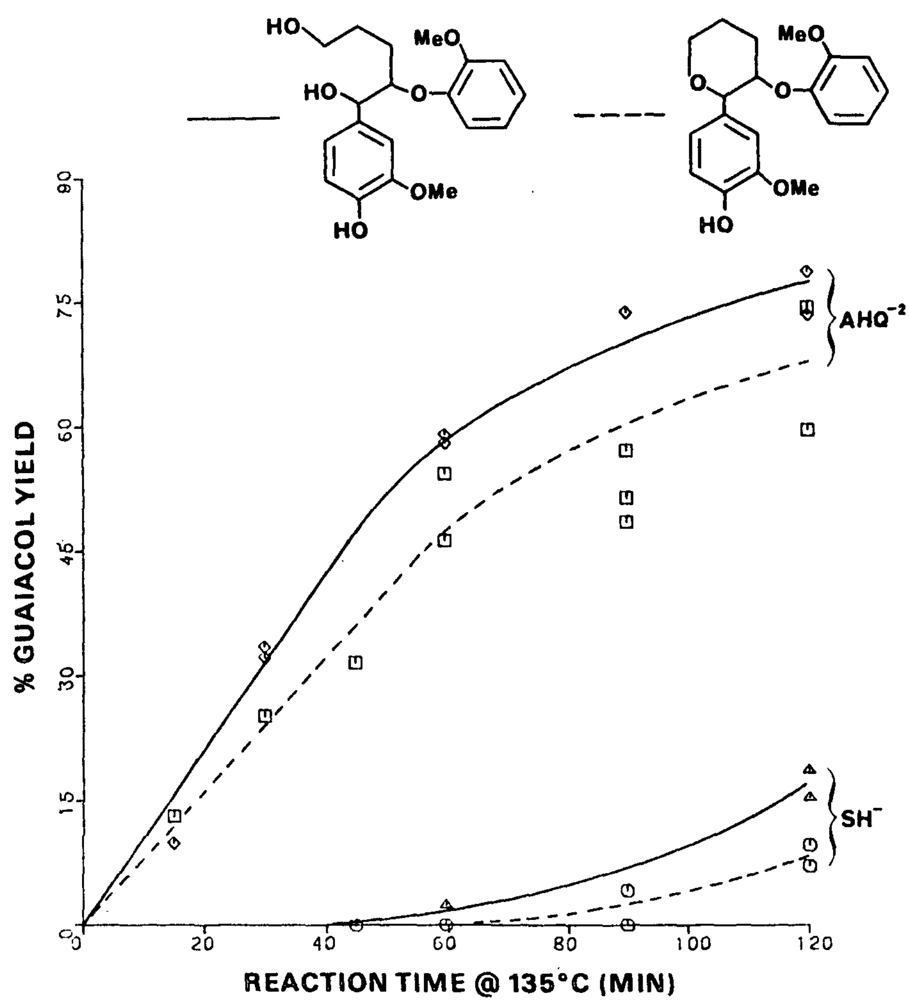
Guaiacol yield as a function of time for the degradation of the indicated model at 150° in either pure water or 29% dioxane-water in the presence of 25 equiv. of NaOH and 5 equiv. of NaSH, or 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

Reactions of the β-(propyl alcohol) model



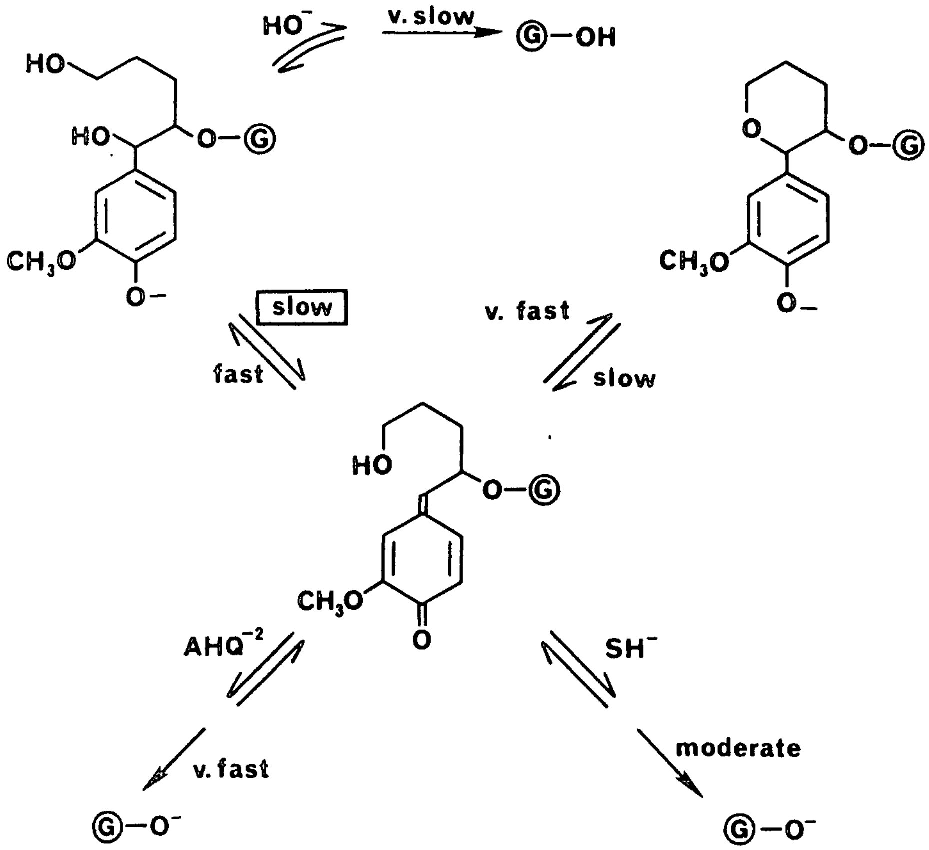


Guaiacol yield as a function of time for the degradation of the indicated models at 150° in water in the presence of 25 equiv. of NaOH and 5 equiv. of NaSH, or 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

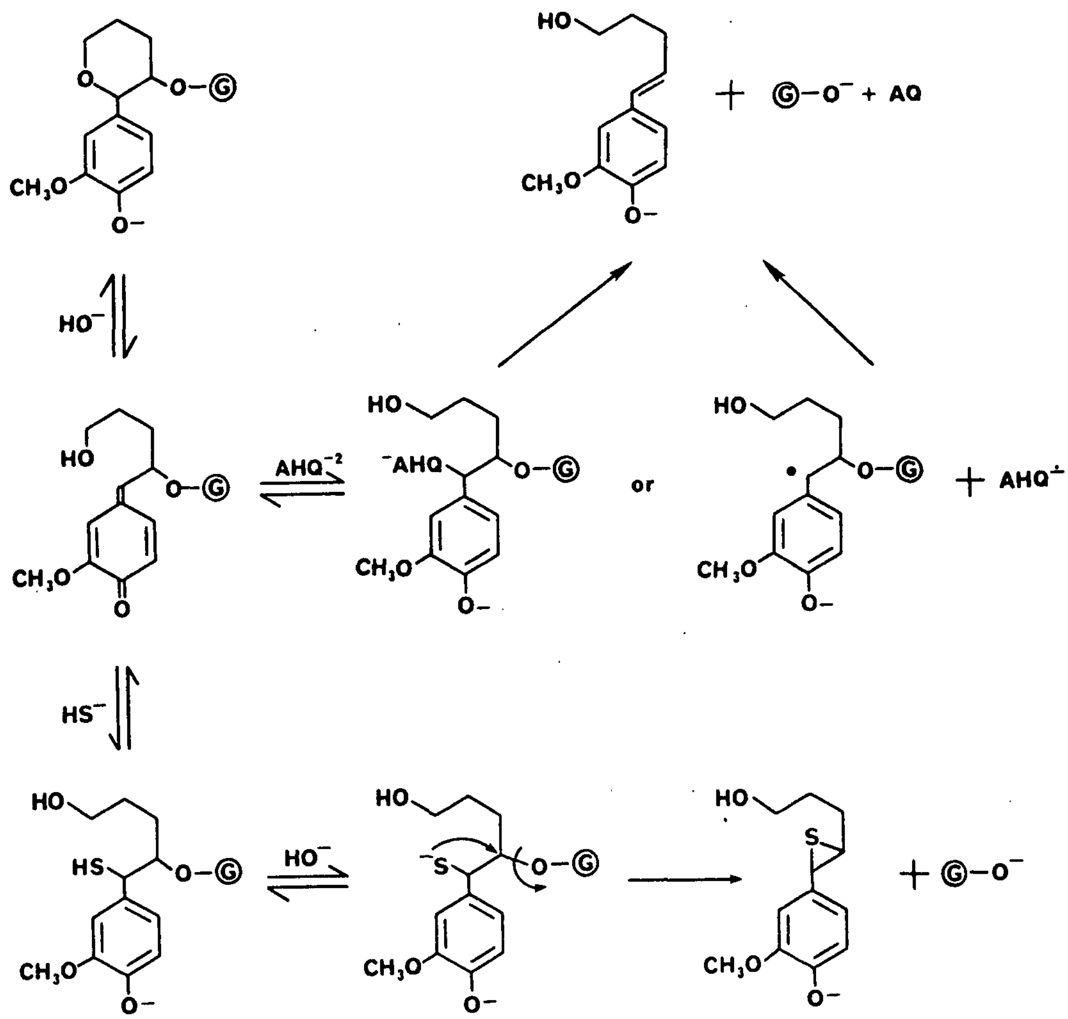


Guaiacol yield as a function of time for the degradation of the indicated models at 135° in water in the presence of 25 equiv. of NaOH, and 5 equiv. of NaSH, or 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

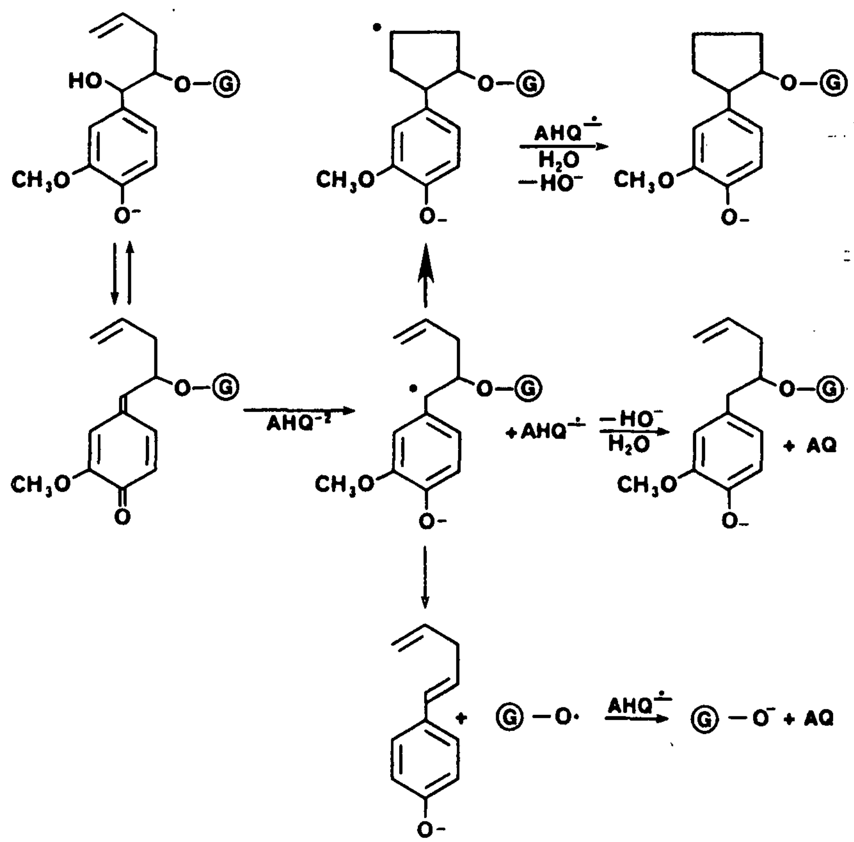
Reactions of the β-(propyl alcohol) model



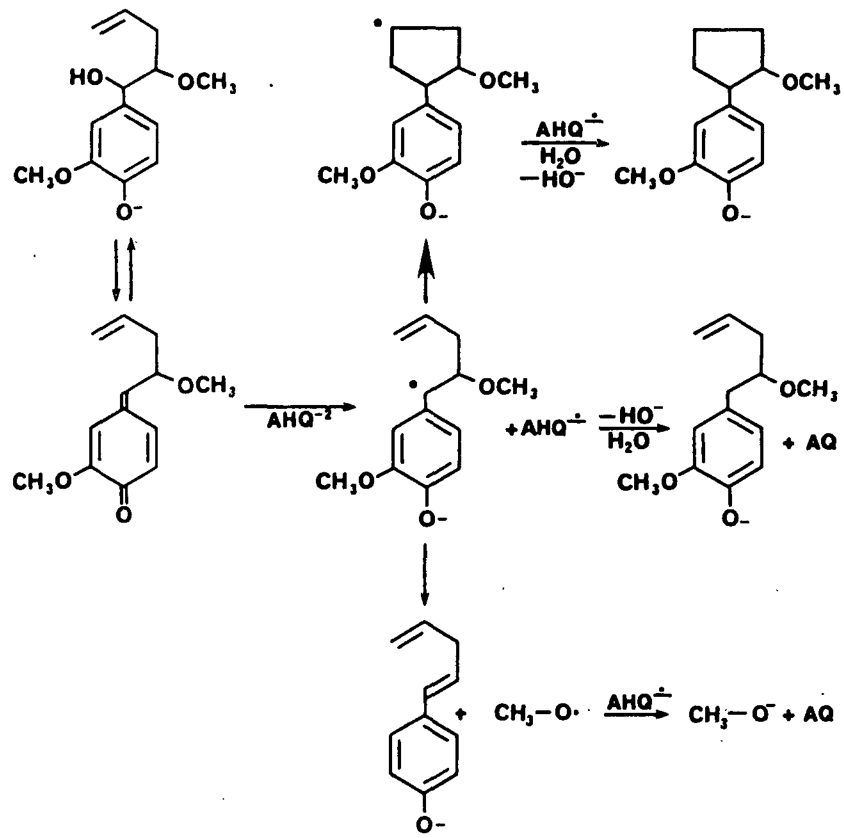
Cleavage Mechanisms of the β-(propyl alcohol) model



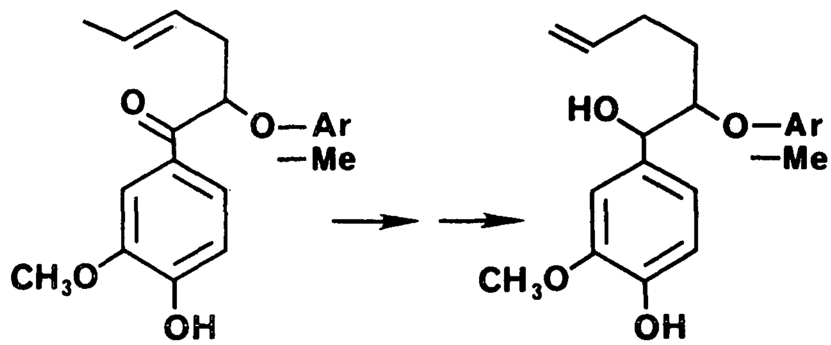
Reactions of a β-allyl - β-ether model



Reactions of a β-allyl - β-ether model



New Model Synthetic Targets



RESEARCH DIRECTIONS

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

Ph.D. STUDENT RESEARCH
The Fundamentals of Chemical Pulp ing

Student	Location	Research Topic
Matthew Bovee	K213	Synthesis and Characterization of Insoluble Cellulose Models
Daniel Geddes	K209	Alkaline Polysaccharide Degradation: Mathematical Modelling
Margaret Henderson	K231	Alkaline Chain Cleavage in Mannans
William Molinarolo	K210	Reactive Intermediates in Alkaline Cellulose Chain Cleavage
Patrick Apfeld	K205	Synthesis and Reactions of Insoluble Lignin Models
Gregg Reed	K232	Sulfide (Kraft) Pulping Chemistry
Dean Smith	K206	Chemistry of Lignin Fragment Recombination Reactions
Robert Barkhau*		Chemistry of Lignin Fragment Recombination Reactions
John Wozniak*		Electrochemical Promotion of Pulping

*Currently working on admission to doctoral candidacy

Project 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

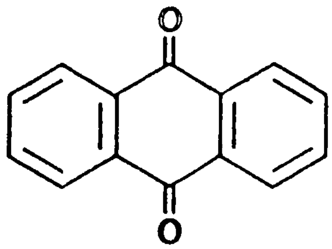
Carbohydrate Reactions

OBJECTIVE

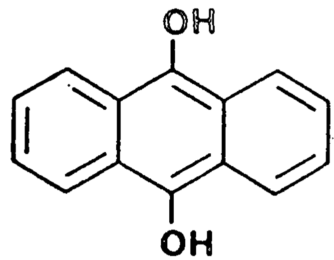
Understand the mechanisms of carbohydrate degradation during pulping and bleaching

CURRENT EFFORT

Effect of anthraquinone on polysaccharide chain cleavage in alkaline pulping

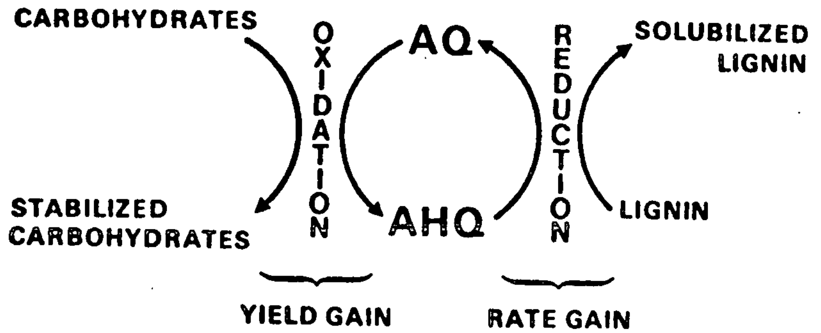


AQ



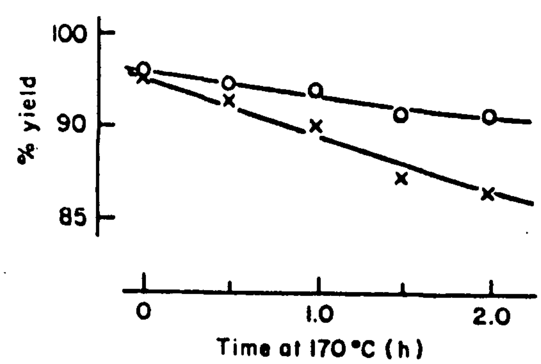
AHQ

REDOX CYCLE



EFFECT OF AQ ON RANDOM CHAIN CLEAVAGE

Polysaccharide	Effect
Amylose	acceleration
Cellulose (Cotton Linters)	little, if any



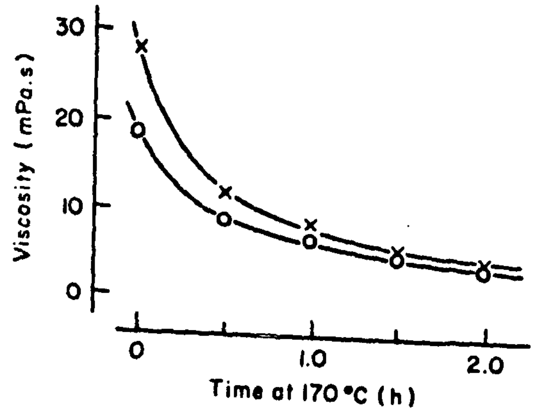
Treatment of cotton cellulose at 170°C with 1M NaOH, without AQ (X) and with 5% AQ addition (O).

WALLIS and WEARNE 1985

Table 1. The effect of anthraquinone (AQ) and yield in kraft and soda cooking of cotton linters.

Temperature, °C	Time, h	Yield, % Kraft[a]	Kraft-AQ[a,c]	Soda[b]	Soda-AQ[b,c]
140	—	96.4	99.5	96.6	99.2
170	0.0	95.3	98.1	95.3	98.7
170	0.5	94.9	95.1	94.4	96.2
170	1.0	92.4	93.0	92.0	94.1
170	2.0	89.5	90.2	90.4	87.5
170	4.0	83.5	83.9	84.4	84.5
170	8.0	73.7	73.6	75.0	75.0

[a]1.0M NaOH, 0.15M Na_2S, 25:1 liquor-to-cellulose ratio.
[b]1.15M NaOH, 25:1 liquor-to-cellulose ratio.
[c]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 1985

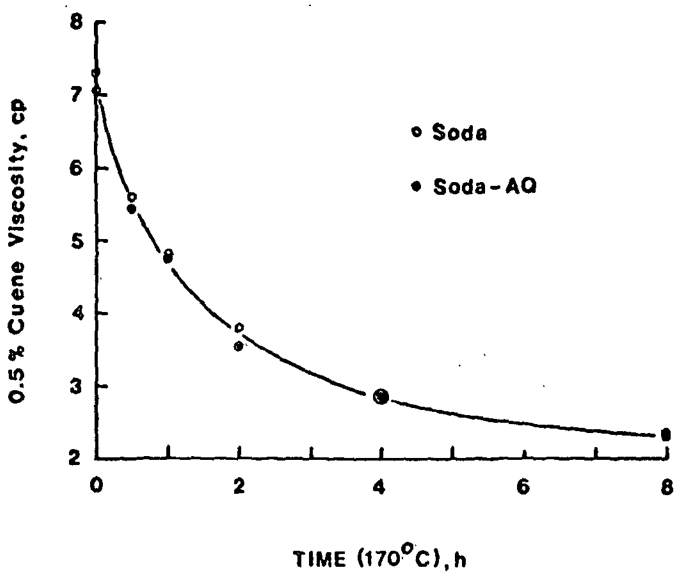


Figure 2. Effect of anthraquinone (0.0048M) on cuene viscosity in soda (1.15M NaOH) cooking of cotton linters.

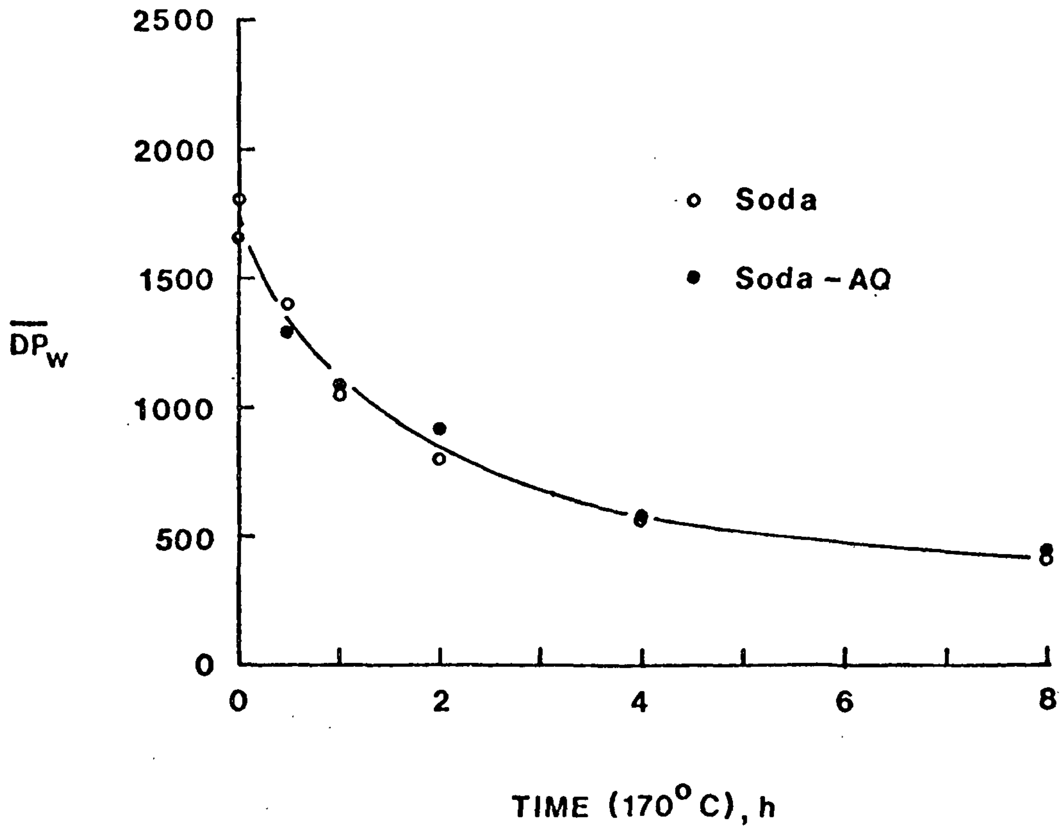
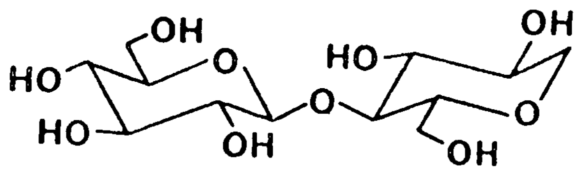


Figure 1. Effect of anthraquinone (0.0048M) on $\overline{DP}_w$ in soda (1.15M NaOH) cooking of cotton linters.

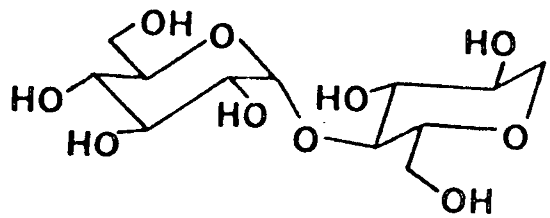
POTENTIAL REASONS FOR DIFFERENT RESPONSE TO AQ

Stereochemical

Physical



1,5-Anhydrocellobiitol



1,5-Anhydromaltitol

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

Additive	$10^6 k_r$, s^{-1}
-	1.12 (0.02)
AQ (0.00480 M)	1.65 (0.06)
AHQ (0.00480 M)	1.20 (0.06)

* ∿ 0.5% at 5:1 Liquor-to-wood

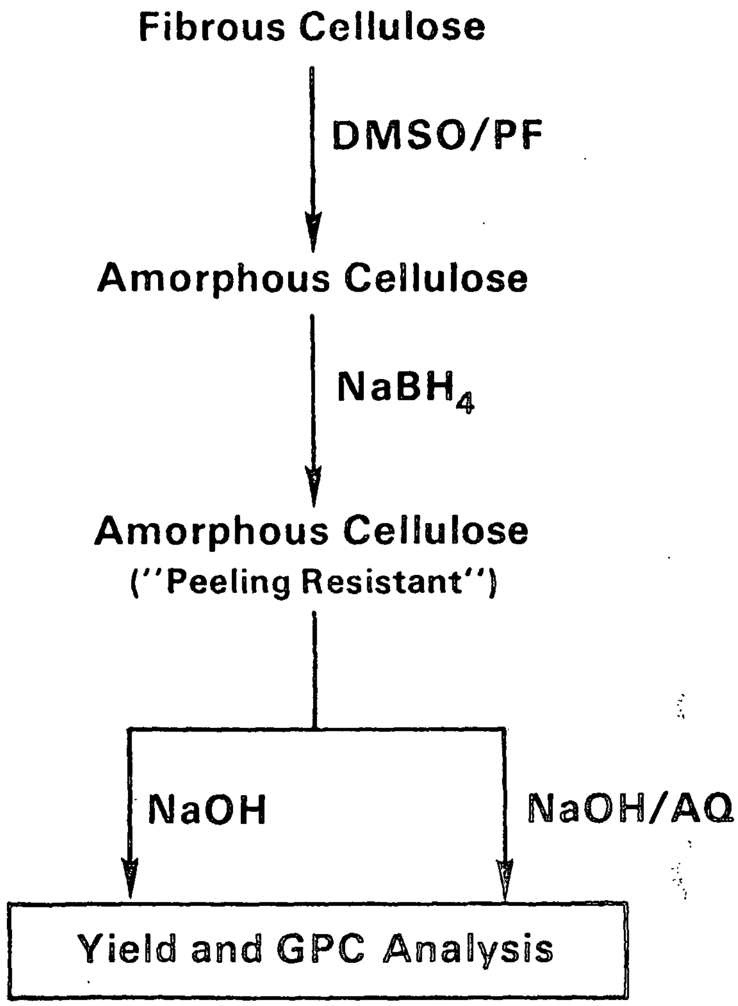
Degradation of 1,5-Anhydrocellobiitol (0.01 M) in 0.985 M NaOH at 169.8° C.

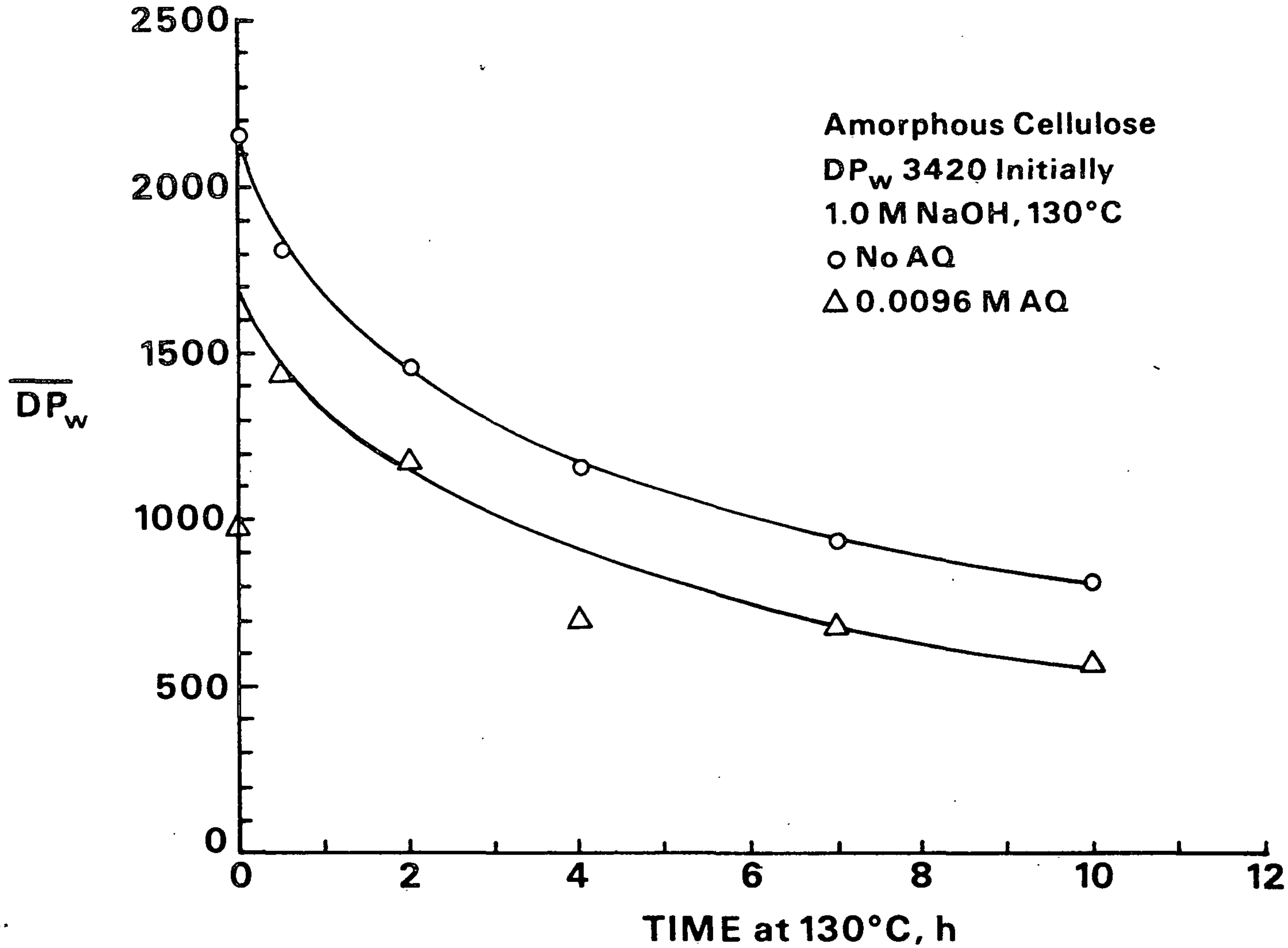
Additive	$10^6 k_r$, s^{-1}
-	6.25 (0.08)
AQ (0.00480 M)*	6.72 (0.08)
AHQ (0.00480 M)*	6.27 (0.06)

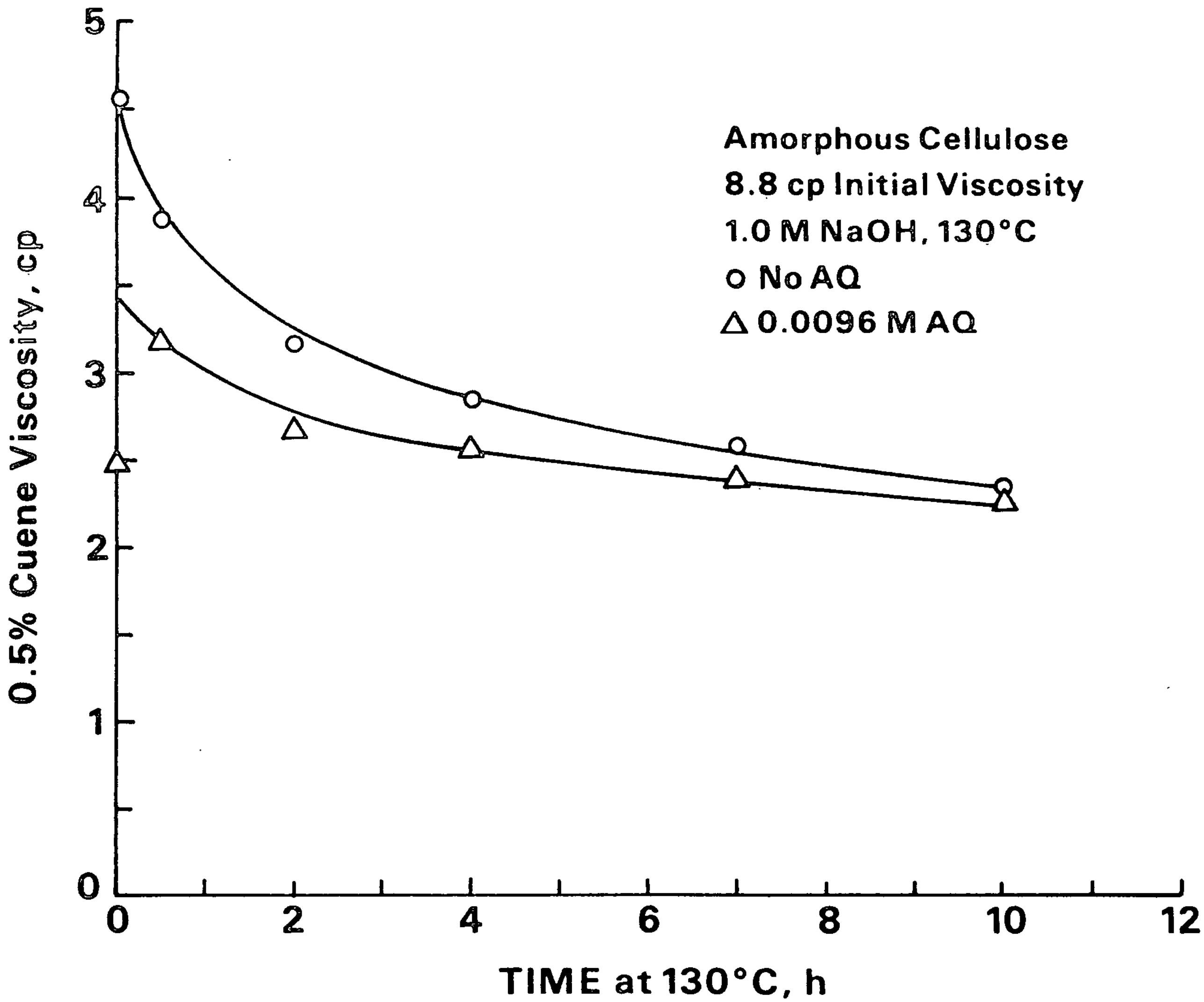
* ∿ 0.5% at 5:1 Liquor-to-wood

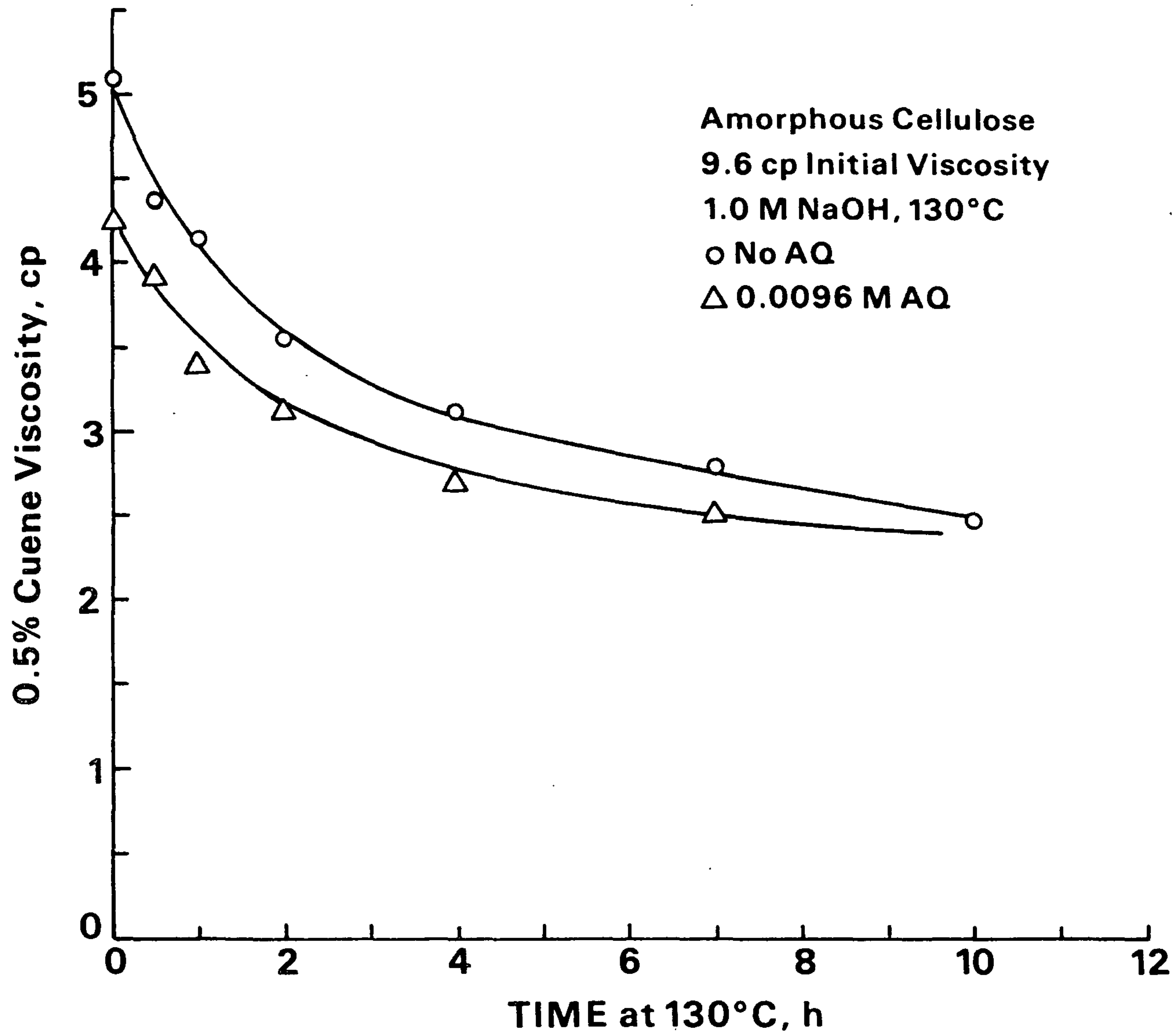
Incremental Effect of Anthraquinone

	$10^6 \Delta k_r$, s^{-1}
1,5-Anhydrocellobiitol	0.47
1,5-Anhydromaltitol	0.53


Fibrous Cellulose
DMSO/PF
Amorphous Cellulose
NaBH4
Amorphous Cellulose
("Peeling Resistant")
NaOH
NaOH/AQ
Yield and GPC Analysis


Amorphous Cellulose
DPw 3420 Initially
1.0 M NaOH, 130°C
o No AQ
△ 0.0096 M AQ
DPw
2500
2000
1500
1000
500
0
0
2
4
6
8
10
12
TIME at 130°C, h


Amorphous Cellulose
8.8 cp Initial Viscosity
1.0 M NaOH, 130°C
○ No AQ
△ 0.0096 M AQ
0.5% Cuene Viscosity, cp
TIME at 130°C, h
0
1
2
3
4
5
0
2
4
6
8
10
12


Amorphous Cellulose
9.6 cp Initial Viscosity
1.0 M NaOH, 130°C
○ No AQ
△ 0.0096 M AQ
0.5% Cuene Viscosity, cp
TIME at 130°C, h
0
1
2
3
4
5
0
2
4
6
8
10
12

Project 3477

DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES

D. B. Easty

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

TAPPI Test Method T 699 pm-83

Analysis of Bleaching and Pulping Liquors
by Ion Chromatography

Intents of IPC investigation:

- evaluate
- supplement
- validate

Ion Chromatographic Analysis of Kraft Black Liquor

Conclusions

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

- sulfite
- sulfate
- thiosulfate
- chloride
- carbonate

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

Studies Needed Before Preparation of T 699 Revision

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

Evaluation of UV Detector

Reservations About Use of Constant Potential Amperometric Detector for Determining Sulfide in Pulping Liquors

1. Extreme sensitivity; extensive sample dilution needed.
2. Narrow useful range: 0.4 - 1 ppm.
3. Need to dilute samples and standards with sulfide antioxidant buffer.
4. Detector maintenance.
5. Simultaneous determination of sulfide and sulfoxy anions is impractical.

Response of UV Detector
to Sulfide in Black Liquor

Added Sulfide, mg/L[a]	Indicated Sulfide, mg/L
None	0
5.0	5.0
10.0	10.0
15.0	14.8
20.0	19.6

[a]Added to oxidized black liquor diluted 1:2000.

Effect of Time on Measured Sulfide Content

Time After Sample Dilution[a], min	Measured Sulfide, %[b]	
	Without Antioxidant	With Antioxidant
<1	1.99	2.05
15	1.55	2.05
30	1.25	2.01
45	1.22	1.97
60	1.13	1.97
90	0.99	1.91

[a]1:1000
[b]Percentage of o.d. liquor solids.

Recovery of Sulfide Added to Black Liquor

Sample	Original, %	Added, %	Total Found, %	Recovery, %
KBL	2.12	1.63	3.75	100
PBL	1.18	0.80	2.01	104
SBL	2.18	1.46	3.63	99

Comparison of Sulfide Determined by
Ion Chromatography and Potentiometric Titration

Sample	Ion Chromatography[a]	Potentiometric Titration[b]
KBL1	2.12	2.06
KBL2	2.05	2.04
PBL	1.18	1.32
SBL	2.18	2.14
ABL	0.69	0.67
KWBL	0.90	0.88

[a]UV detector. Black liquor samples diluted approx. 1:1000. Values are percentage of o.d. liquor solids.
[b]Titration with $HgCl_2$.

Conclusions -- UV Detection of Sulfide

1. Detector is less sensitive than amperometric; range 1 - 20 ppm.

   Less extensive sample dilution:

   Easier manipulation
   Reduced oxidative losses of sulfide

2. Antioxidant recommended for best results.

   Ascorbic acid more concentrated than 1 m<u>M</u> interferes in UV detector.

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

4. Easier detector maintenance

5. Simultaneous determination of sulfide and sulfoxy anions is impractical.

Determination of Sulfate in Green Liquor

Problem reported in literature:

Higher sulfate by IC than by gravimetric method.

Hypothesis:

Oxidation of other sulfur compounds to sulfate.

Proposed solution:

Dilute green liquor with 0.1% HCl.

Effect of Dilution Medium on Sulfate Content
as Function of Time After Dilution

Time After Dilution, min	Sulfate, g/L; Liquor Diluted With 0.1% HCl	Deox. H_2O
<1	6.50	6.49
15	6.38	6.46
30	6.45	6.52
45	6.39	6.65
60	6.36	6.55
120	6.41	6.91
180	6.41	7.12
240	6.46	7.22
300	6.46	7.39

Green liquor diluted 1:1250. Sulfate determined by ion chromatography.

Sulfate Contents of Green Liquors
Diluted With 0.1% HCl and With Deoxygenated Water

Liquor	Sulfate, g/L; Liquor Diluted With 0.1% HCl	Deox. H_2O
1	6.64	6.61
2	5.62	5.66
3	9.55	9.56
4	15.0	14.9
5	9.80	9.80
6	3.46	3.42
7	8.37	8.37
8	0.63	0.63

Liquors were diluted from 1:200 to 1:2000 depending on sulfate content. Samples were injected into the ion chromatograph within 1 min after dilution.

Conclusions -- Sulfate in Green Liquor

1. Dilution with HCl is unnecessary when samples are analyzed promptly after dilution.
2. Liquors diluted with 0.1% HCl and with deoxygenated water gave comparable results.

Future Work

Revise TAPPI Test Method T 699, Analysis of Bleaching And Pulping Liquors by Ion Chromatography.

Complete studies of lignin determination by diffuse reflectance Fourier transform infrared spectrometry.

Expand former exploratory projects:

- Identification of paper additives and contaminants by pyrolysis/GC/MS.
- Interface headspace gas concentrator with GC/MS.

Project 3288

FINE STRUCTURE OF WOOD PULP FIBERS

R. H. Atalla

Project 3521

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

R. H. Atalla

3288

FINE STRUCTURE OF WOOD PULP FIBERS

3521-1

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

OVERVIEW OF PRESENTATION:

1. KEY TOPICS AND PERSPECTIVE WHICH DEFINE OUR PROGRAM.
2. REVIEW OF FALL 1985 PRESENTATION.
3. STUDIES ON CELLULOSE STRUCTURE AND AGGREGATION.
4. STUDIES ON CELL WALL STRUCTURE IN WOOD, AND RESPONSE TO CHEMICAL TREATMENT.
5. FUTURE WORK.

KEY TOPICS CURRENTLY INCORPORATED IN OUR FUNDED, EXPLORATORY, AND STUDENT RESEARCH PROGRAMS:

1. THE DEGREE TO WHICH THE COMPOSITE NATURE OF NATIVE CELLULOSES INFLUENCES THEIR PROPERTIES AND THOSE OF CELLULOSIC FIBERS FROM HIGHER PLANTS (WOOD, COTTON, RAMIE). TWO CLASSES OF PROPERTIES ARE OF INTEREST:

   (A) CHEMICAL REACTIVITY, AND THE RESPONSE TO VARIOUS SOLVATING AND SWELLING ENVIRONMENTS;

   (B) PHYSICAL AND MECHANICAL PROPERTIES.

2. DEVELOPMENT OF METHODS, BOTH EXPERIMENTAL AND CONCEPTUAL, FOR CHARACTERIZATION OF THE STRUCTURES OF NATIVE AND REGENERATED CELLULOSES, WITH PARTICULAR EMPHASIS ON NATIVE STRUCTURES.

3. THE PATTERNS OF AGGREGATION OF CELLULOSE WITH OTHER CELL WALL POLYSACCHARIDES, MAINLY HEMI-CELLULOSES, THE INFLUENCE THESE MAY HAVE ON OUR MEASUREMENT OF ORDER IN CELLULOSE, AS WELL AS THEIR EFFECTS ON PROPERTIES.

4. THE PATTERNS OF ORGANIZATION OF LIGNIN IN WOOD CELL WALLS, AND THEIR INFLUENCE ON FIBER STRUCTURE AND PROPERTIES.

5. THE PHOTOPHYSICS OF ELECTRONIC EXCITATION IN NATIVE LIGNIN, AND THE MANNER IN WHICH THE PATTERNS OF EXCITATION ARE ALTERED BY INTER-ACTION WITH MOLECULAR OXYGEN.

OVERVIEW

3288: FINE STRUCTURE OF WOOD PULP FIBERS

1. STUDIES ON POLYMORPHY IN NATIVE CELLULOSE
2. QUANTITATIVE ANALYSIS OF THE STRUCTURE OF PULP FIBERS ON THE BASIS OF RAMAN SPECTROSCOPY
3. PROTON NMR STUDIES OF THE EFFECTS OF REFINING ON THE MOBILITY OF BOUND WATER

IR

ABSORPTION

$$M + h\nu_V \longrightarrow M^*$$

EMISSION

$$M^* \longrightarrow M + h\nu_V$$

$$50 < \nu_V < 4000\ \text{cm}^{-1}$$

$$200\,\mu \qquad\qquad 2.5\,\mu$$

$$\boxed{\Delta\mu \neq 0}$$

RAMAN

STOKES

$$M + h\nu_0 \longrightarrow M^* + h(\nu_0 - \nu_V)$$

ANTI-STOKES

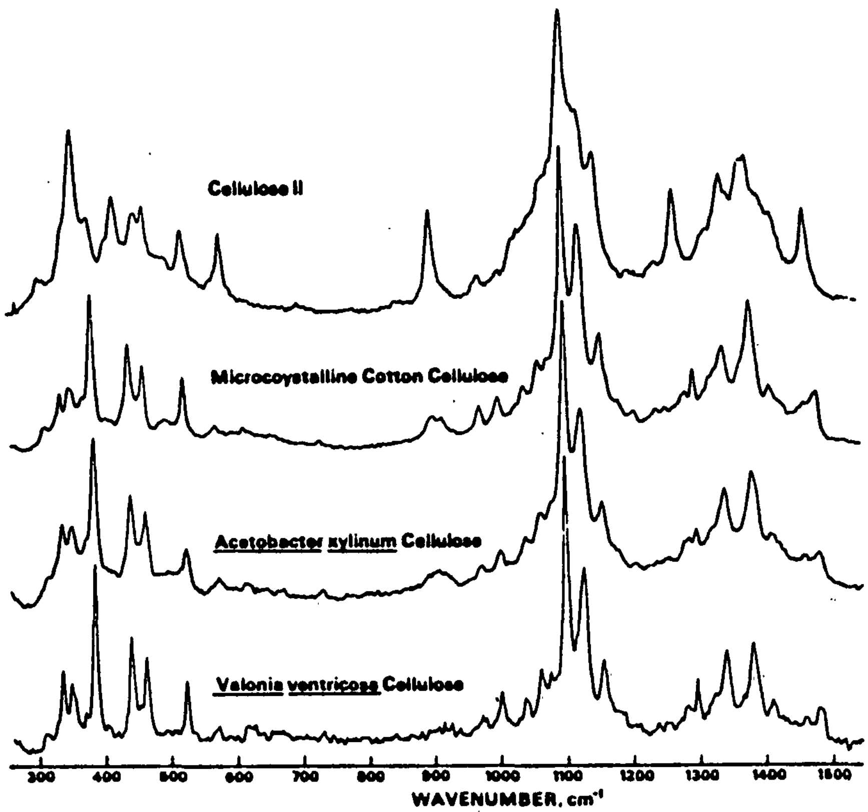
$$M^* + h\nu_0 \longrightarrow M + h(\nu_0 + \nu_V)$$

$$\nu_0 \cong 20{,}000\ \text{cm}^{-1}$$

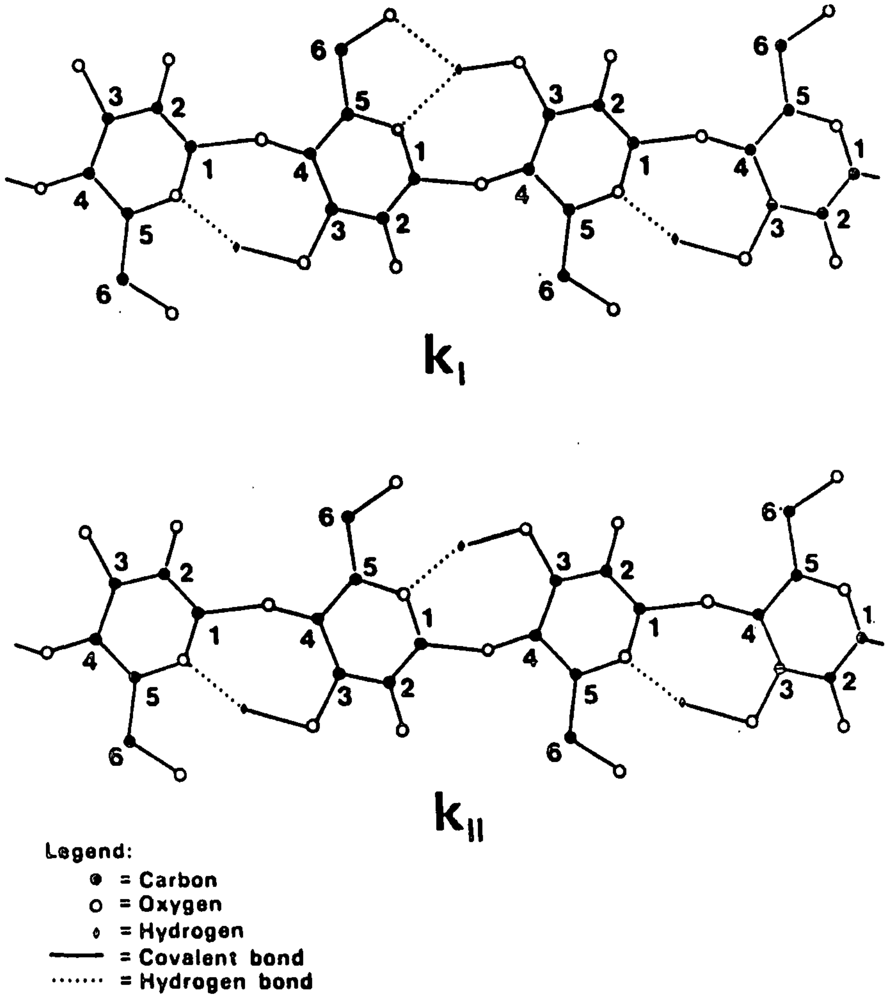
$$5000\ \text{Å}$$

$$\boxed{\Delta\alpha \neq 0}$$

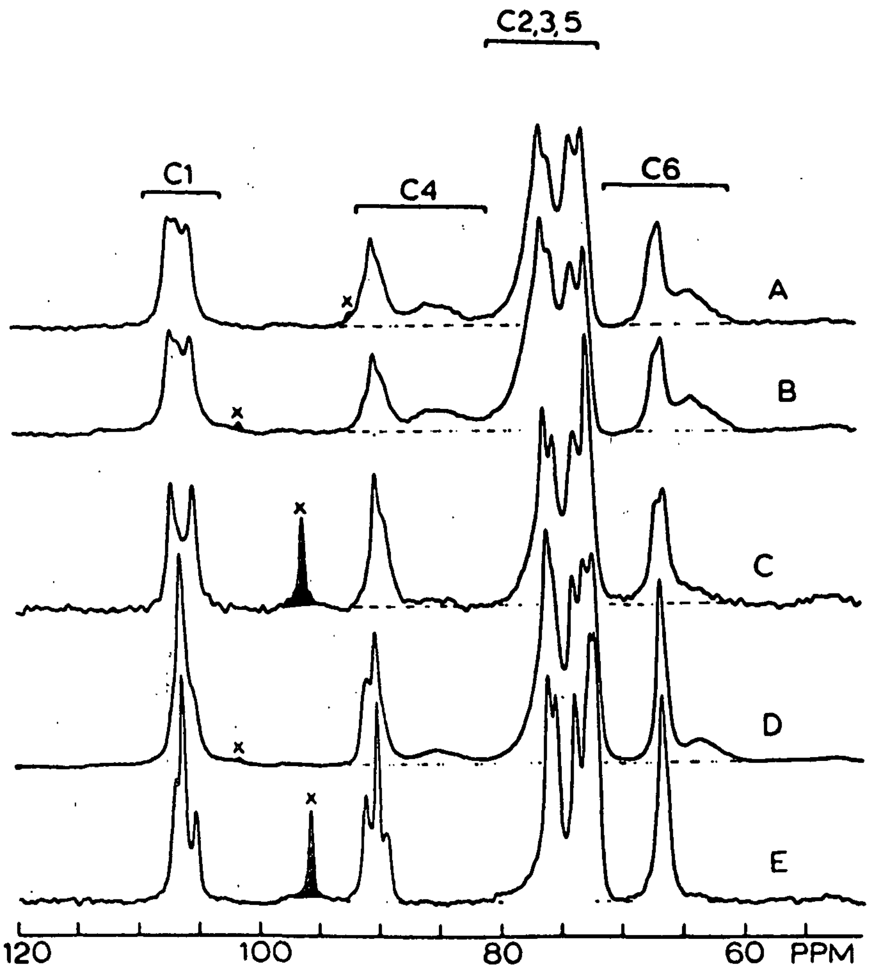
INFRARED AND RAMAN PROCESSES



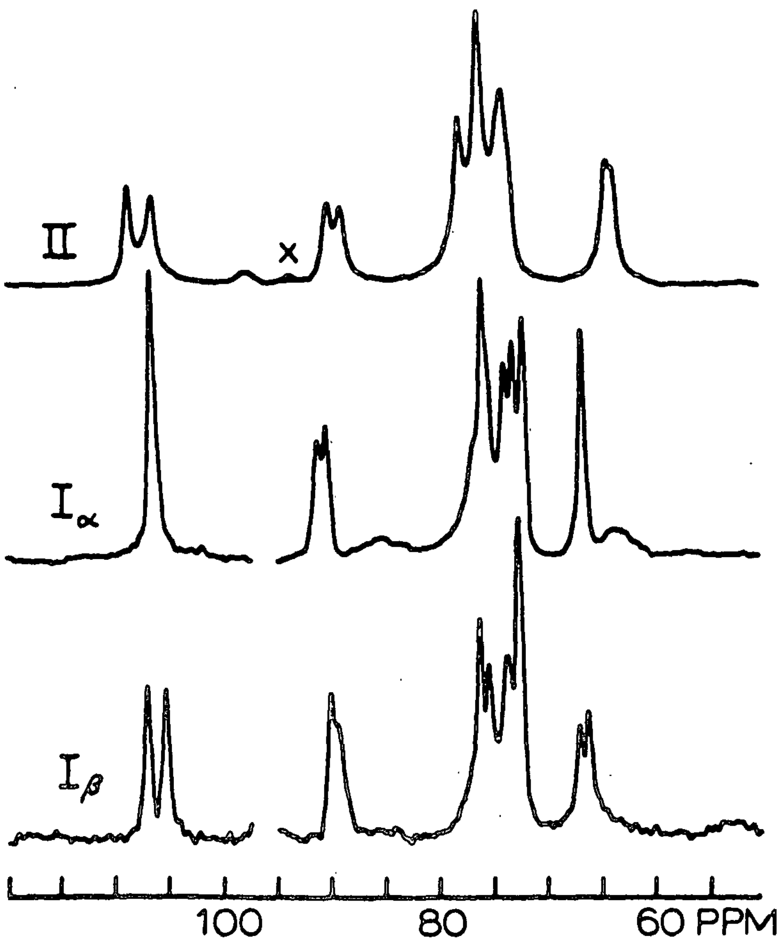
Raman spectra of Valonia ventricosa cellulose, Acetobacter xylinum cellulose, Microcrystalline cotton cellulose, and high-crystallinity cellulose II.



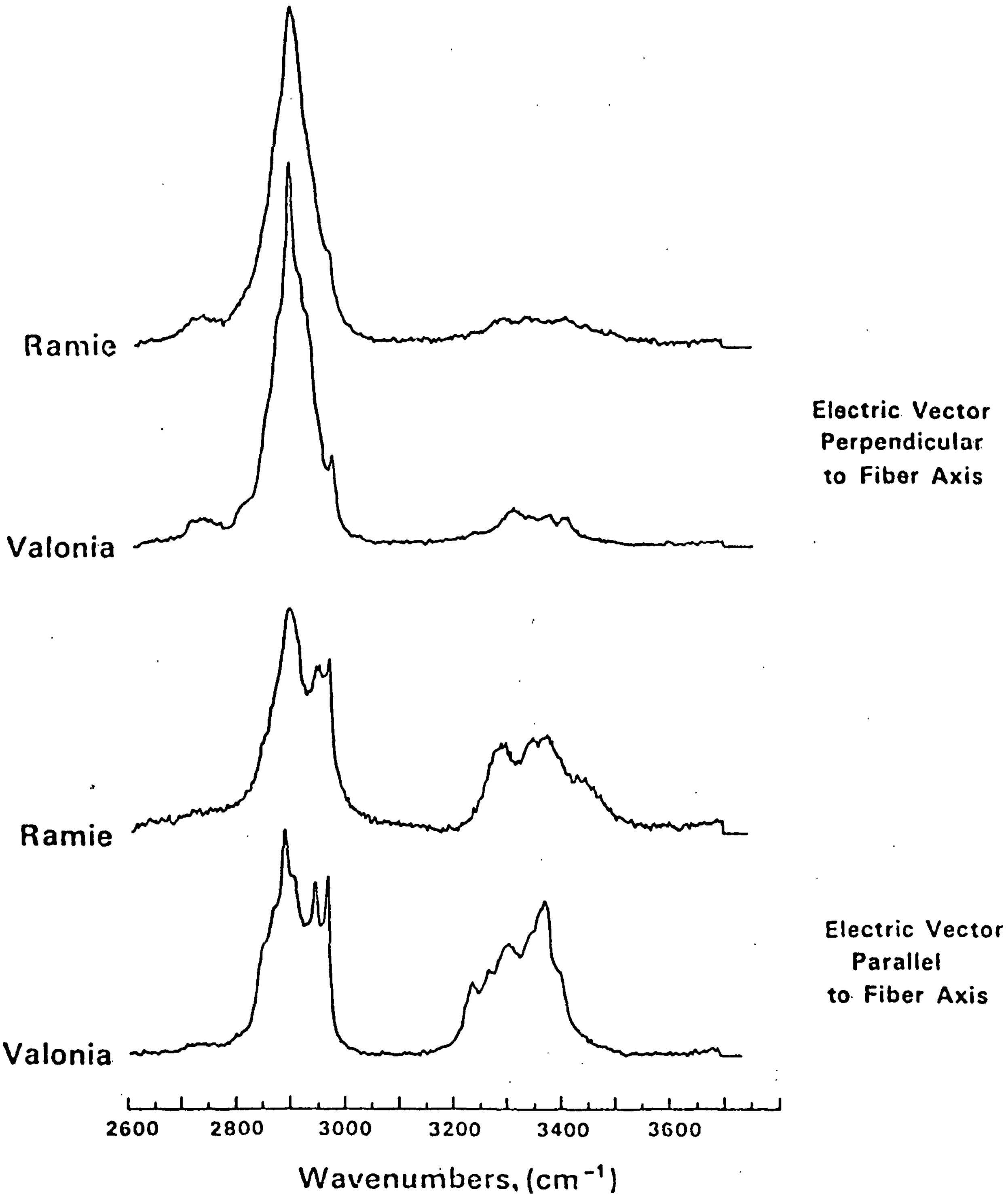
Schematic representation of conformations k_I and k_{II}.



^{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_α, and I_β. An "X" or a gap mark locations of the first spinning sideband of the linear polyethylene chemical shift standard.



Raman microprobe spectra in the CH and OH stretching regions for ramie and Valonia vcentricosa celluloses. The spectra were recorded for fibrillar aggregates of Valonia cellulose and for on individual fiber of ramie.

OVERVIEW

3288: FINE STRUCTURE OF WOOD PULP FIBERS

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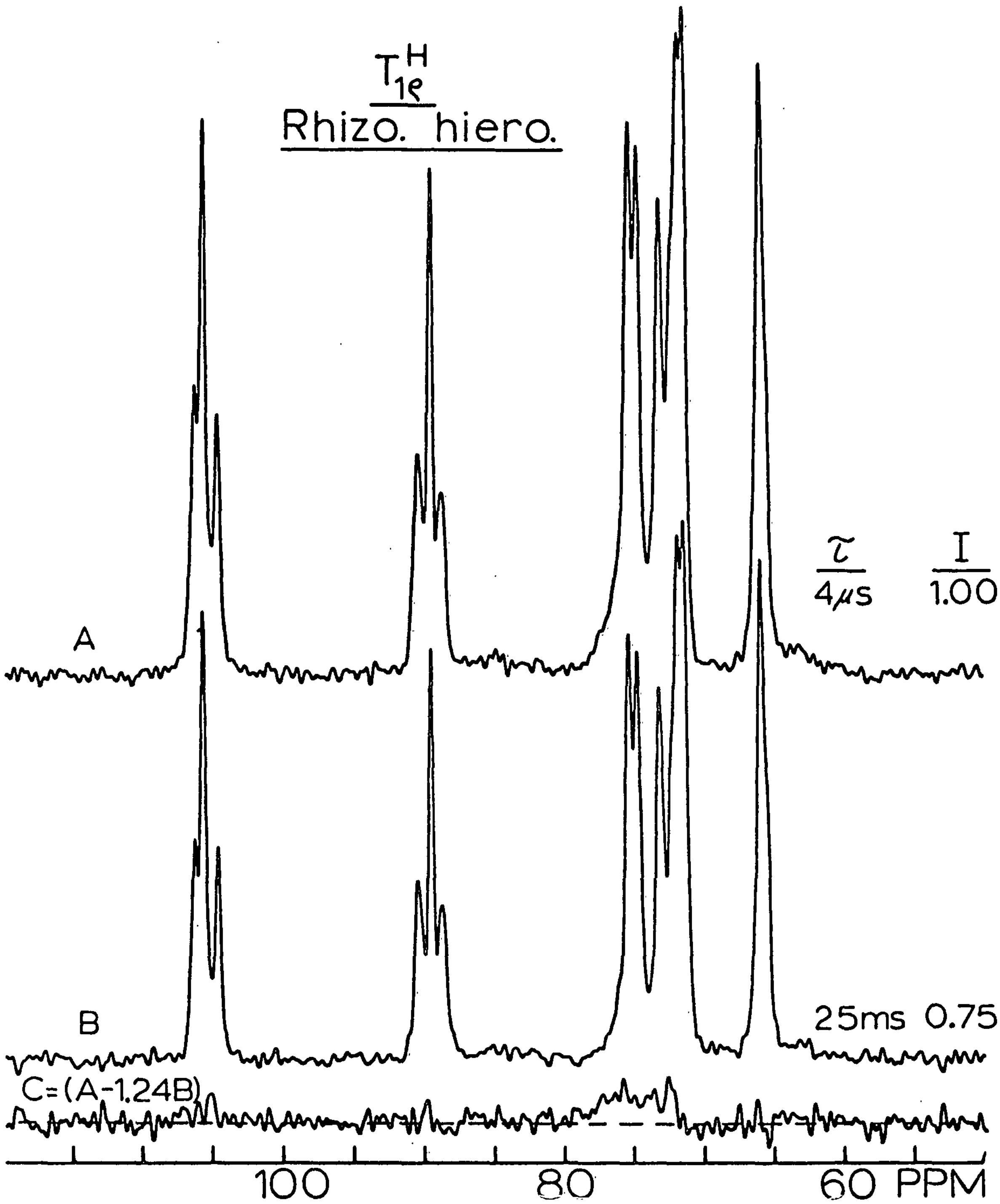
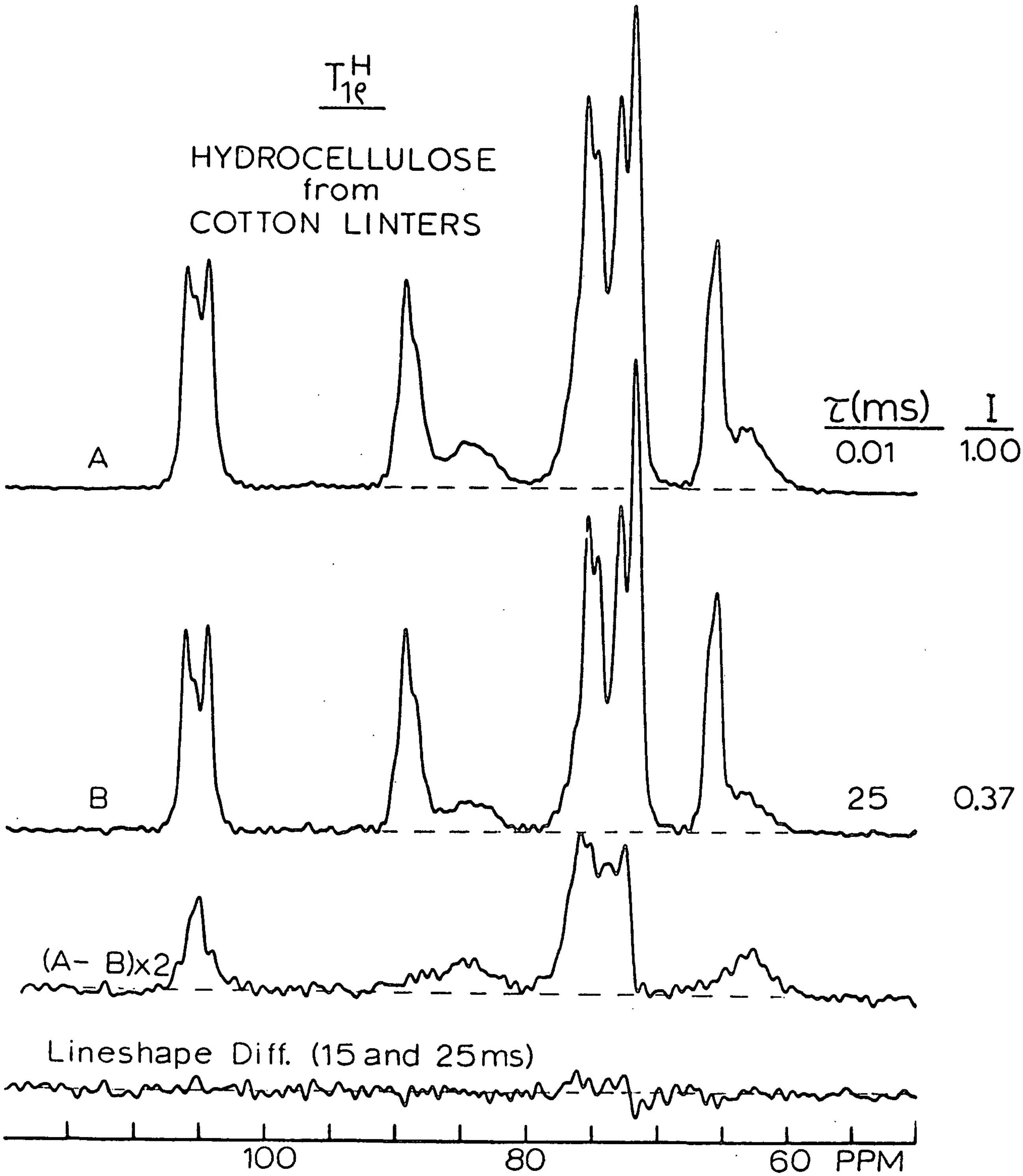
STUDIES ON CELLULOSE

1. VANDERHART - SOLID STATE ^{13}C NMR OF CELLULOSES
2. WILEY - RAMAN MICROPROBE STUDIES OF FIBRILLAR CELLULOSES
3. ISOGAI - REGENERATION AND MERCERIZATION OF DIFFERENT NATIVE CELLULOSES; AMORPHOUS CELLULOSES AND BLENDS WITH OTHER β1-4 LINKED HOMOPOLYMERS
4. WOITKOVICH - CELLULOSE DERIVATIVES DISPLAYING THE MEMORY EFFECT (HAYASHI); CELLULOSES DEGRADED BY WHITE ROT FUNGII (BLANCHETTE)
5. WHITMORE - ALGAL AND BACTERIAL CELLULOSES, CULTURE AND DUETERATION; PREPARATION OF I_β CELLULOSES



CP-MAS spectra of the highly crystalline algal cellulose, <u>Rhizoclonium hieroglyphium</u> as a function of proton spin locking time.



CP-MAS spectra of hydrocellulose following the two indicated periods of proton spin locking; the CP time was 0.5 ms.

STUDIES ON CELLULOSE

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

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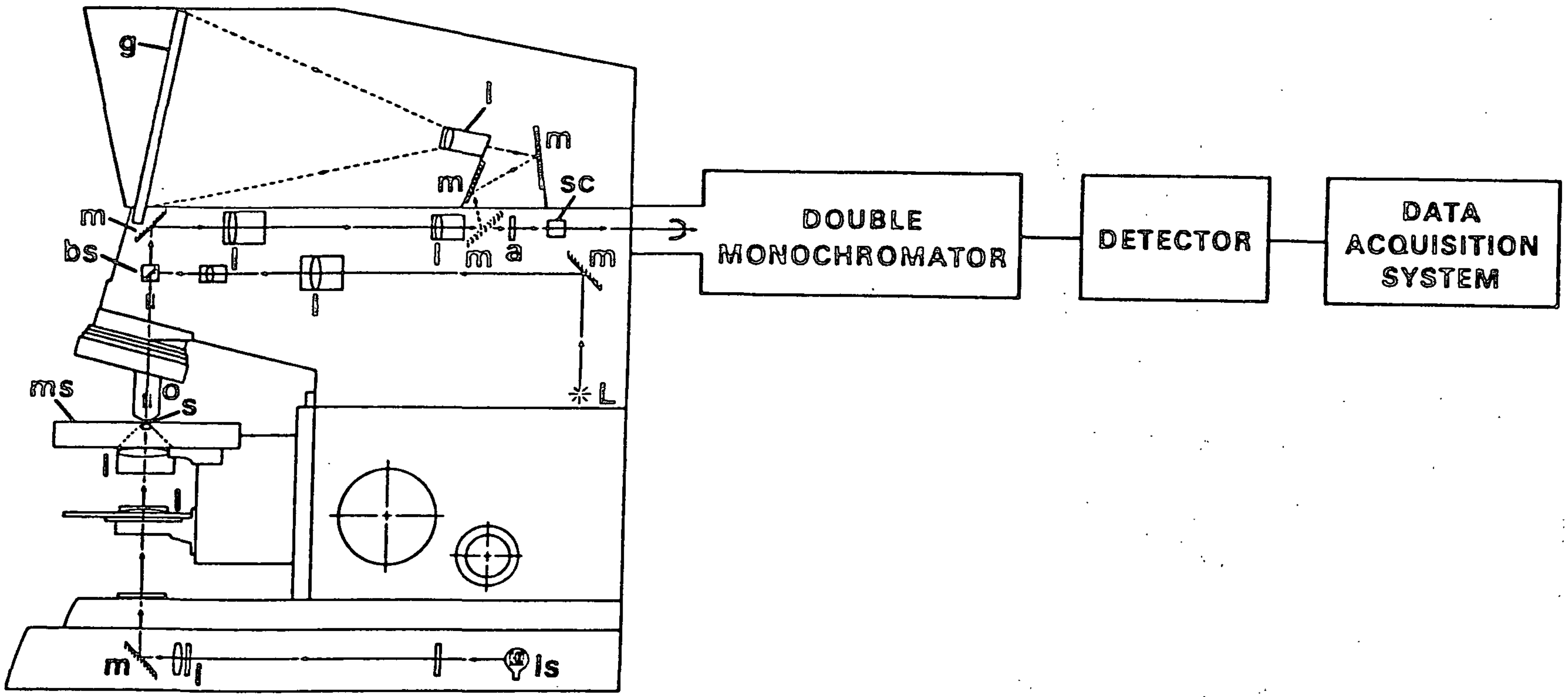
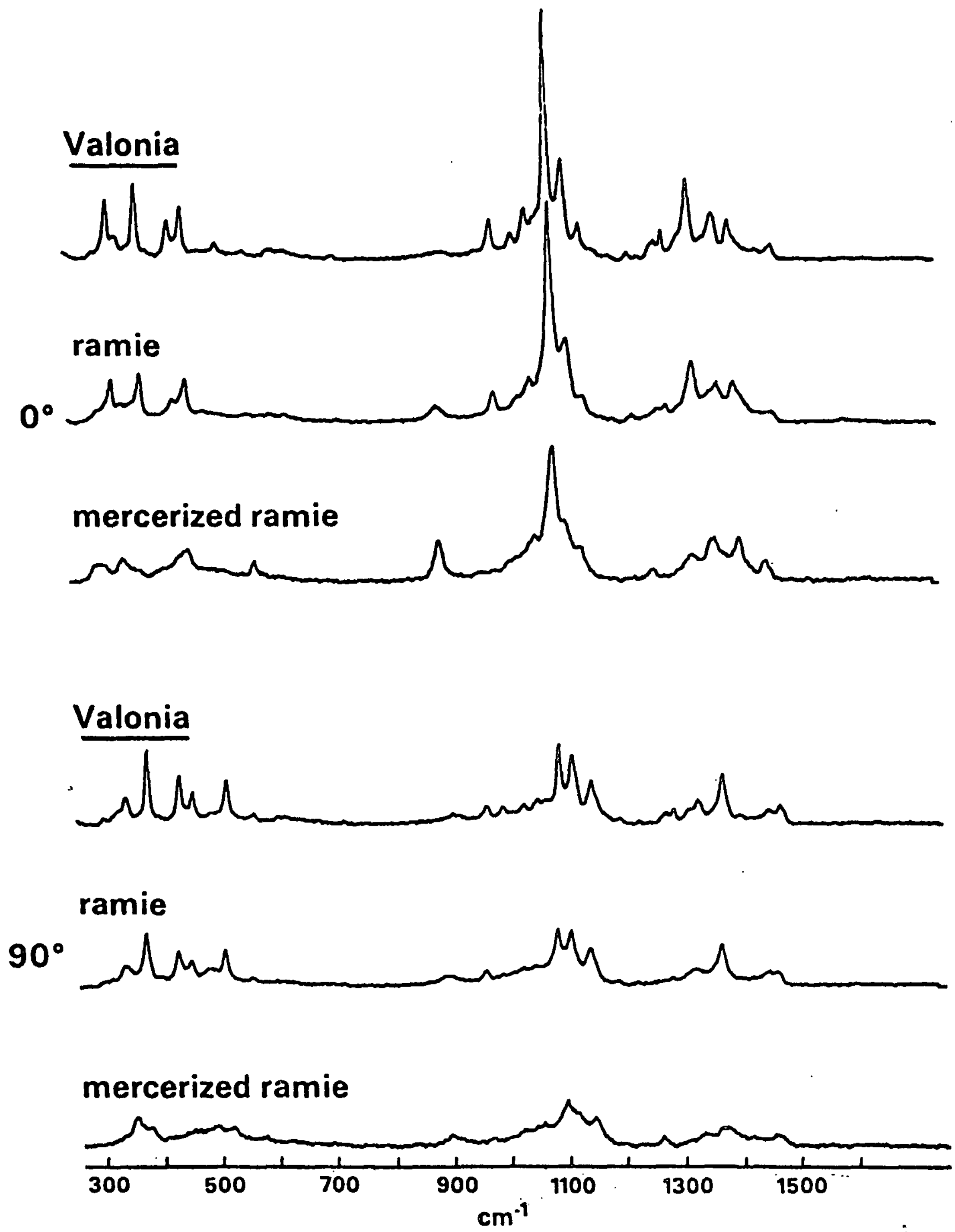
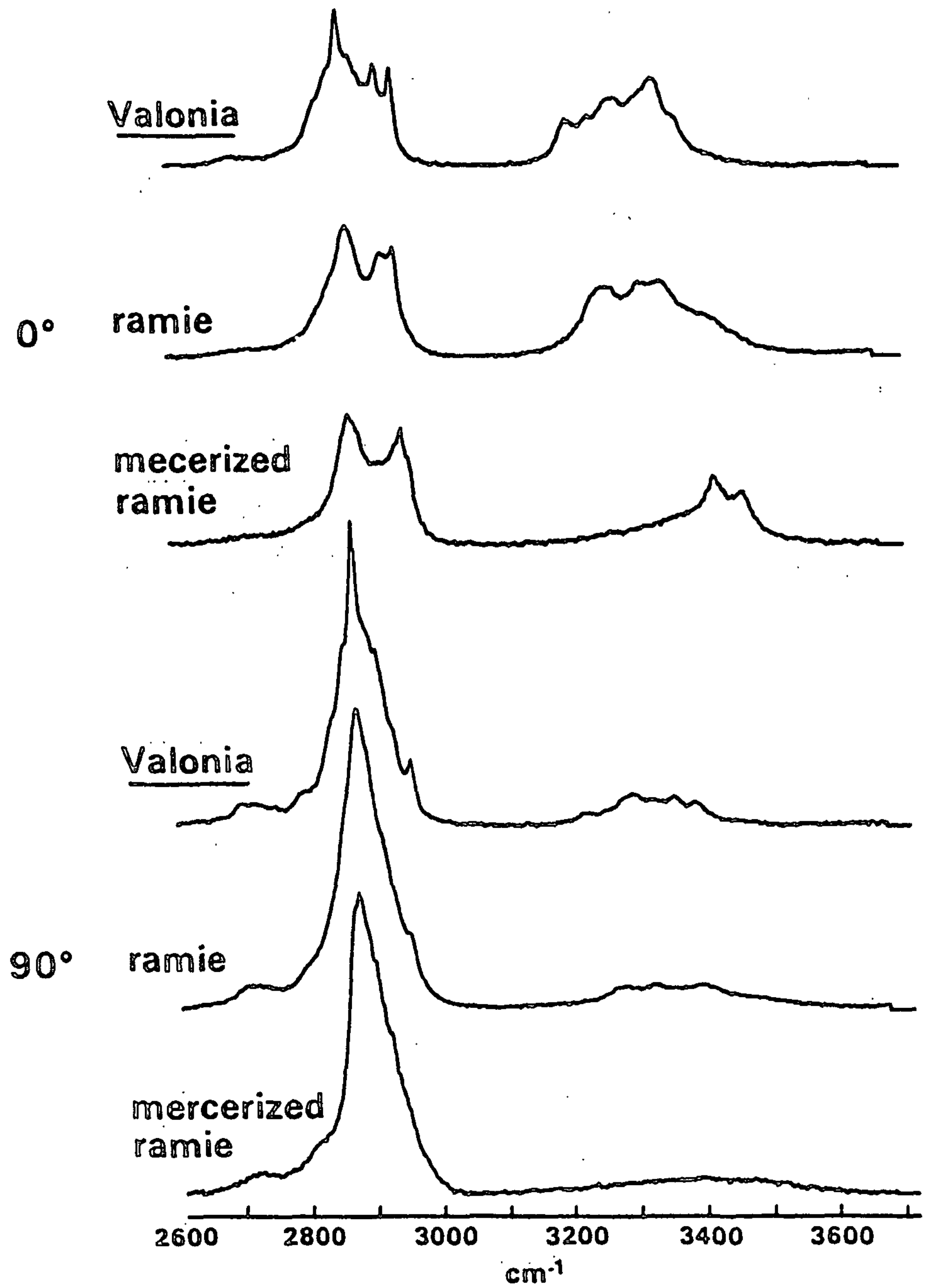


SCHEMATIC DIAGRAM OF RAMAN MICROPROBE SYSTEM



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

STUDIES ON CELLULOSE

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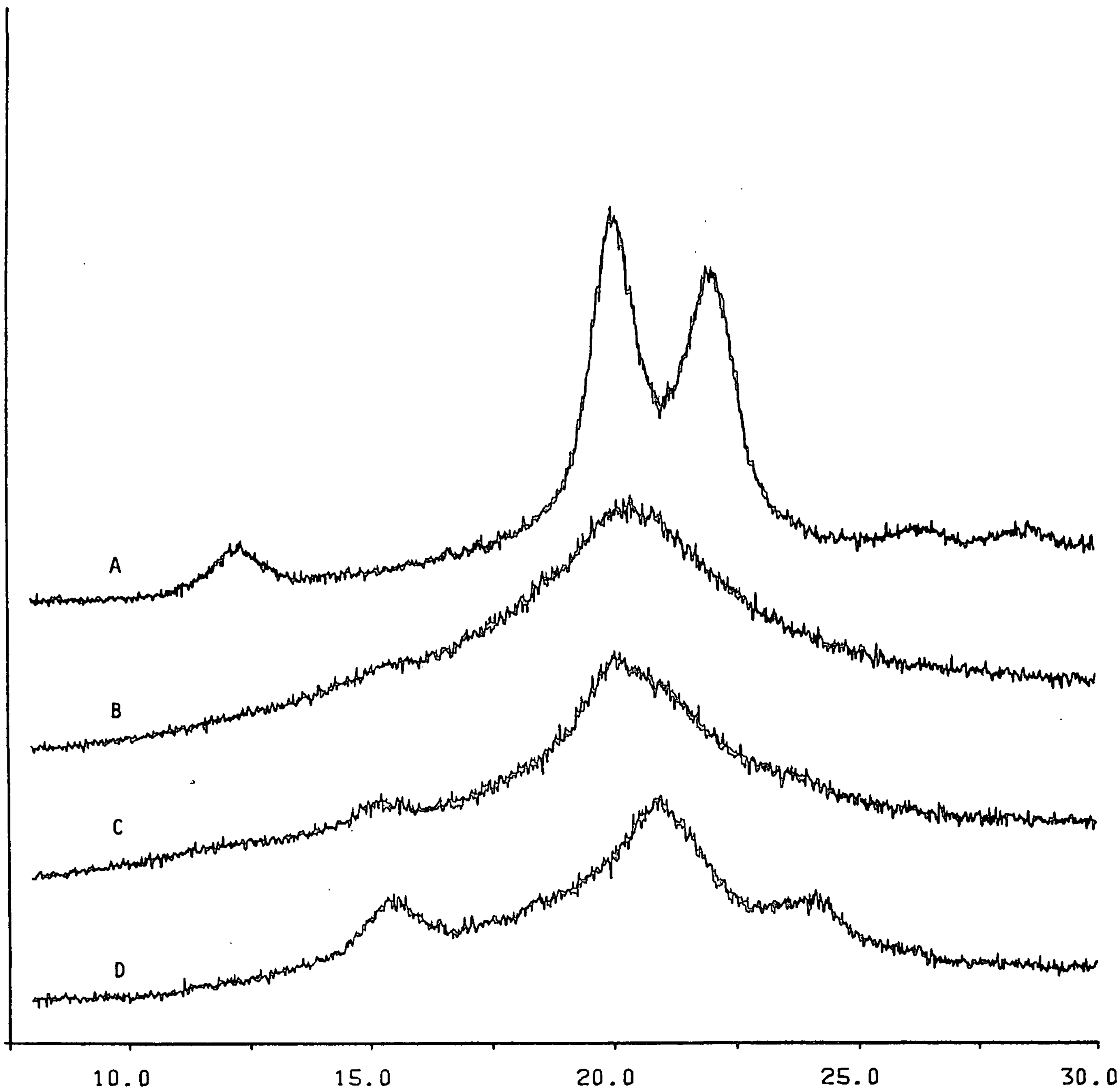
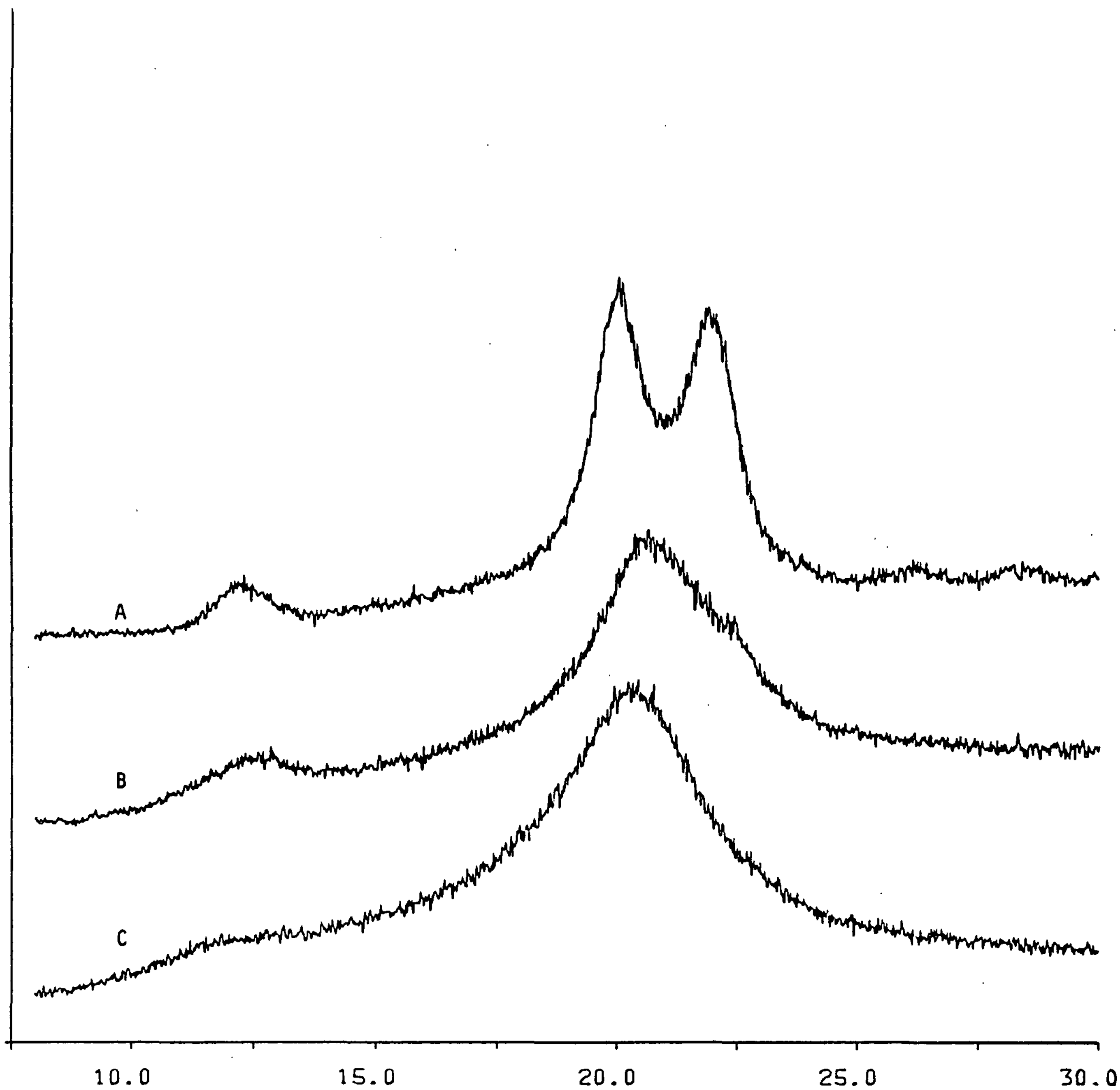


X-ray Diffractograms:
A. High crystallinity Cellulose II
B. Cellulose/Chitosan Blend
C. Cellulose/Chitosan Blend - 20% NaOH treated
D. Chitosan - 20% NaOH treated



X-ray Diffractograms:
A. Cellulose II
B. Cellulose/Chitosan Blend
C. Chitosan

STUDIES ON CELLULOSE

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OVERVIEW

3521-2: RAMAN MICROPROBE STUDIES OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE

I. CURRENT MICROPROBE STUDIES

II. OPPORTUNITIES ARISING FROM THE NEW RAMAN MICROPROBE SYSTEM

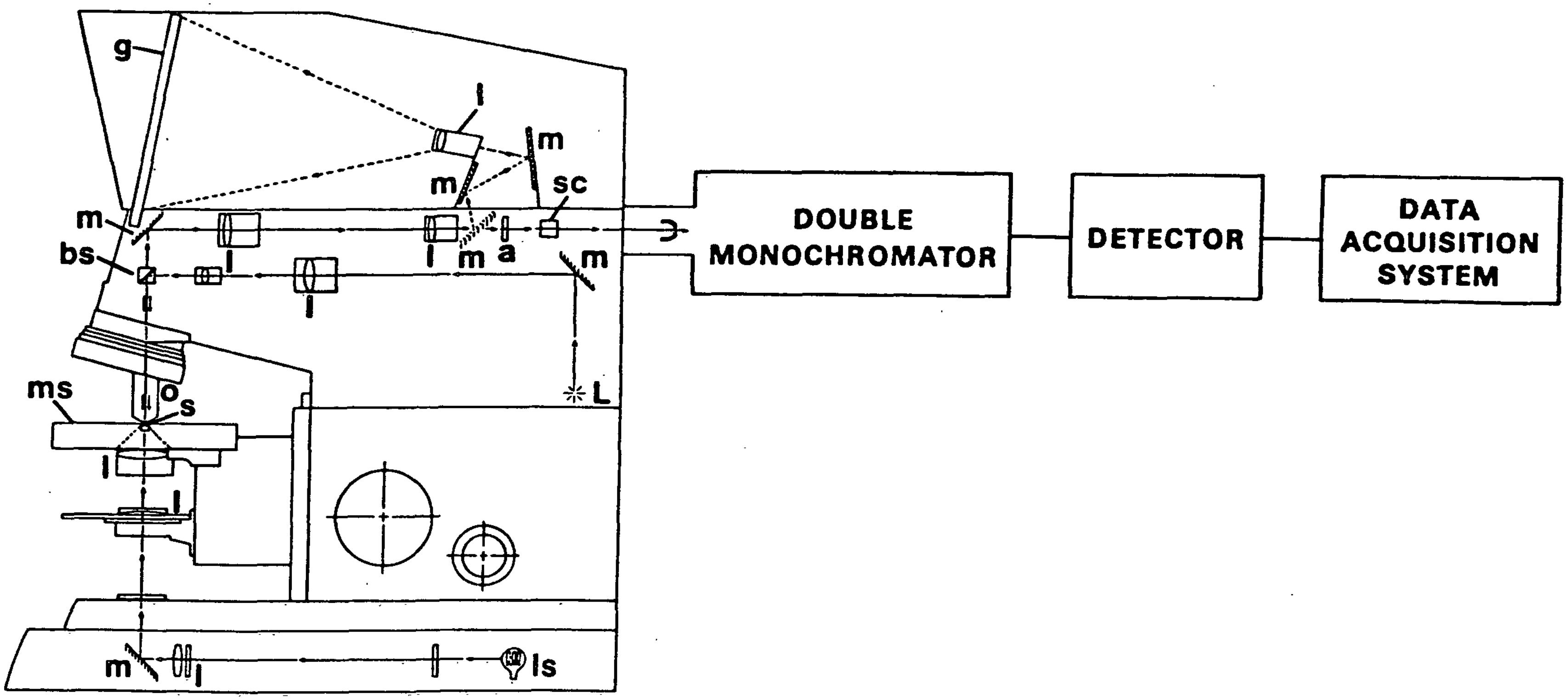
III. STUDIES ON HIGHLY CRYSTALLINE ALGAE

CURRENT MICROPROBE STUDIES:

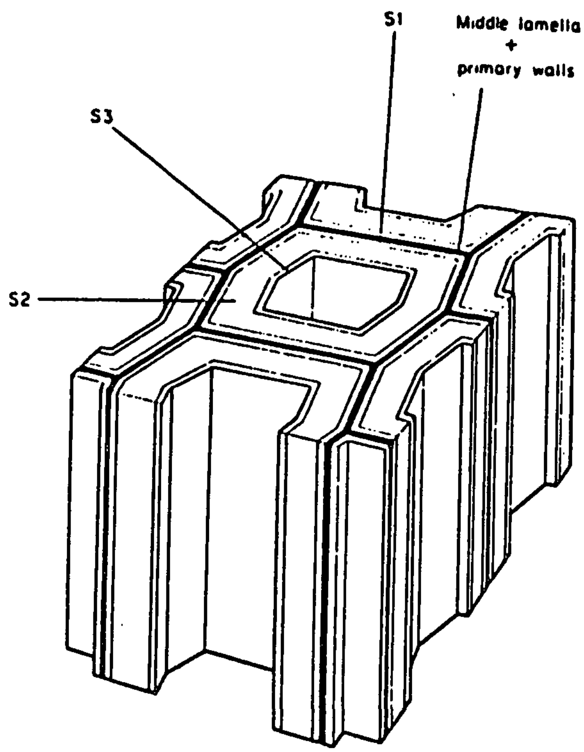
A. MOLECULAR ORIENTATION OF LIGNIN AND CELLULOSE IN NATIVE AND DELIGNIFIED WOODY TISSUE

B. COMPOSITIONAL VARIATION WITHIN CELL WALLS AND BETWEEN ADJACENT CELLS

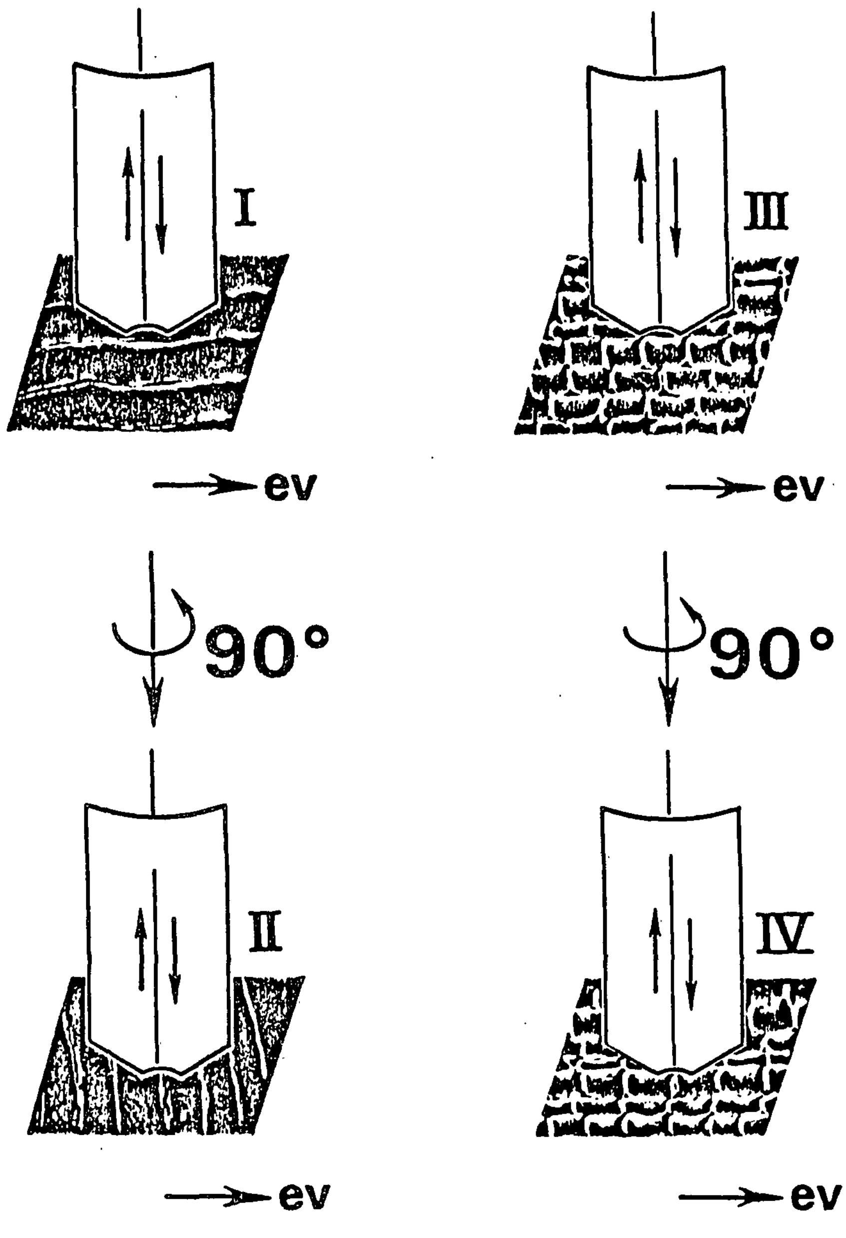
C. STUDIES ON <u>VALONIA</u> AND RAMIE CELLULOSES



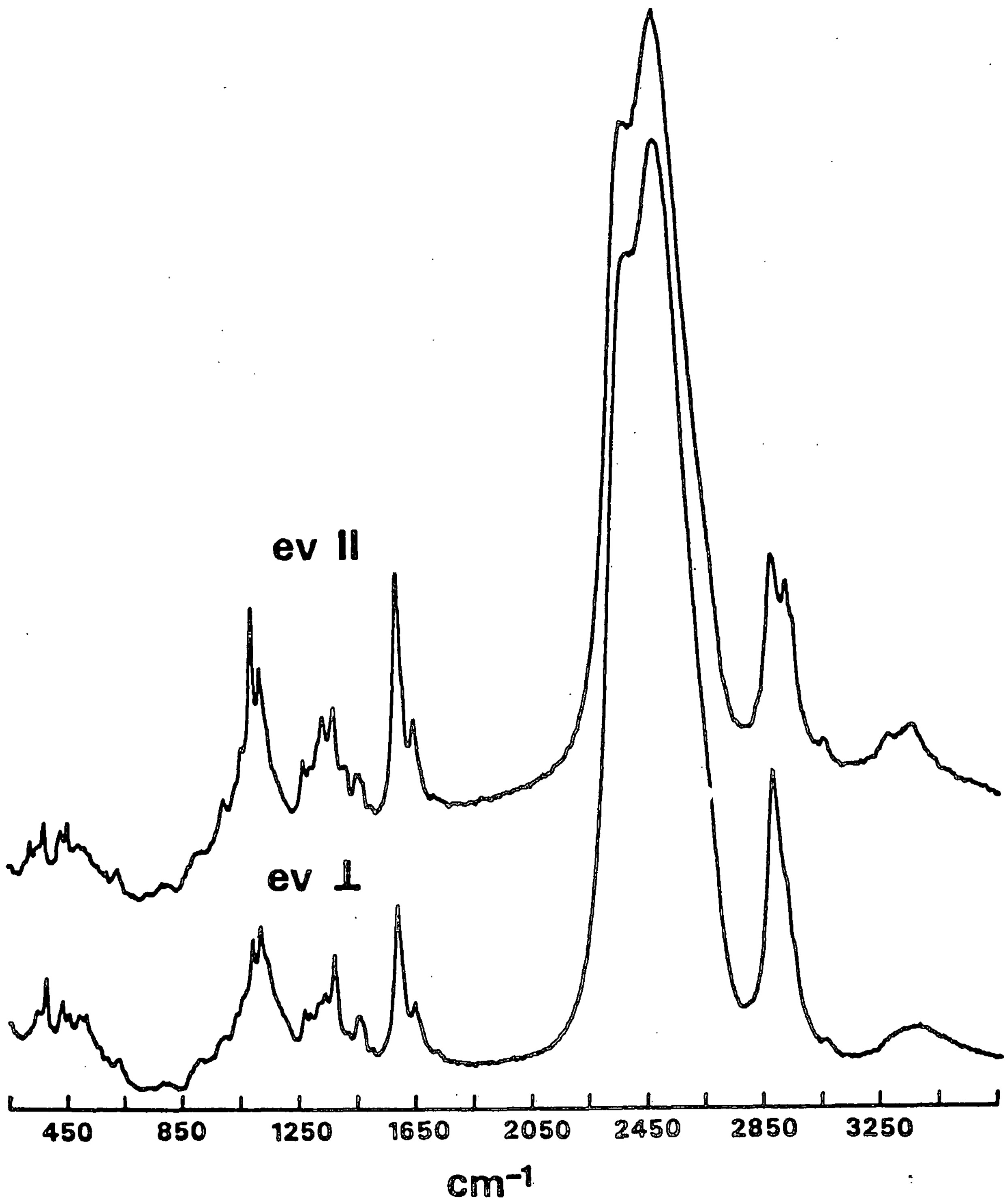
SCHEMATIC DIAGRAM OF RAMAN MICROPROBE SYSTEM



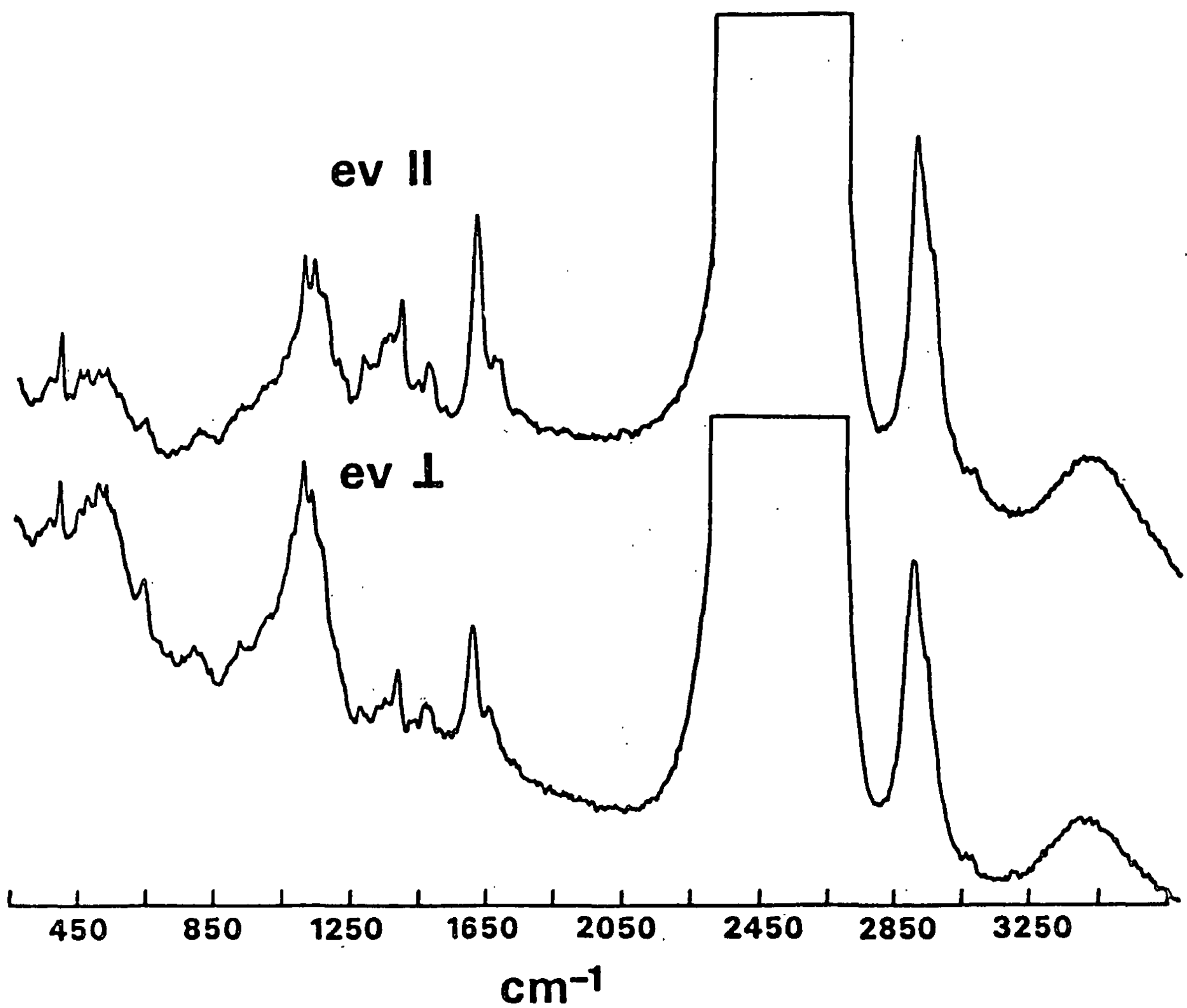
CELL WALL SECTIONS



SCATTERING GEOMETRIES
I - ELECTRIC VECTOR (EV) DIRECTION PARALLEL TO THE CELL WALL SURFACE IN A LONGITUDINAL SECTION;
II - EV PERPENDICULAR TO THE CELL WALL SURFACE (LS);
III - EV PARALLEL TO THE CELL WALL SURFACE IN A CROSS SECTION, AND
IV - EV PERPENDICULAR TO THE CELL WALL SURFACE (CS).



POLARIZED RAMAN SPECTRA OF A SPOT LYING IN THE SECONDARY WALL - LONGITUDINAL SECTION (LS) OF SPRUCE.



POLARIZED RAMAN SPECTRA OF A SPOT LYING IN THE SECONDARY WALL - CROSS SECTION (CS) OF SPRUCE.

CONCLUSIONS

(SECONDARY WALL)

AROMATIC RINGS IN THE LIGNIN STRUCTURAL UNITS ARE OFTEN ORGANIZED PARALLEL TO THE PLANE OF THE SURFACE OF THE CELL WALL.

COMPOSITIONAL VARIATIONS IN THE DISTRIBUTION OF CELLULOSE AND LIGNIN ARE DETECTED.

SUCH DIFFERENCES IN COMPOSITION ARE MORE PROMINENT BETWEEN THE WALLS OF DIFFERENT CELLS THAN WITHIN A PARTICULAR CELL WALL.

LIGNIN & MICROPROBE STUDIES

1. ASSESSING NEW SYSTEM
2. AGARWAL - EFFECT OF MOLECULAR OXYGEN; NEW EXPERIMENTAL METHODS
3. BOND - SEARCH FOR LIGNIN PRECURSURS IN TISSUE CULTURE CELL WALLS; CORRELATIONS BETWEEN RAMAN BANDS OF LIGNIN WITH IR BAND AND KLASSON LIGNIN IN GROUNDWOOD AND PARTIALLY DELIGNIFIED GROUNDWOOD

COMPARISON OF RAMAN MICROPROBE SYSTEMS

CURRENT SYSTEM:

SOURCE -	CONTINUOUS ARGON ION LASER
SPECTROMETER -	DOUBLE MONOCHROMATOR WITH COUPLED GRATINGS, DESIGNED FOR SINGLE CHANNEL DETECTION
DETECTOR -	COOLED PHOTOMULTIPLIER

NEW SYSTEM:

SOURCES -	SOLID STATE/DYE LASER SYSTEM CAPABLE IN THE SUB-PICOSECOND PULSE RANGE; PRESENT CONTINUOUS LASER SYSTEMS
SPECTROMETER -	TRIPLE MONOCHROMATOR OPTIMIZED FOR MULTICHANNEL DETECTION
DETECTORS -	DIODE ARRAY DETECTORS OPERABLE CONTINUOUSLY OR IN GATED MODELS

LIGNIN & MICROPROBE STUDIES

1. ASSESSING NEW SYSTEM
2. AGARWAL - EFFECT OF MOLECULAR OXYGEN; NEW EXPERIMENTAL METHODS
3. BOND - SEARCH FOR LIGNIN PRECURSURS IN TISSUE CULTURE CELL WALLS; CORRELATIONS BETWEEN RAMAN BANDS OF LIGNIN WITH IR BAND AND KLASSON LIGNIN IN GROUNDWOOD AND PARTIALLY DELIGNIFIED GROUNDWOOD

FUTURE WORK

1. QUESTIONS REGARDING NATURE OF CRYSTALLINITY IN WOOD CELLULOSE
2. AGGREGATION STUDIES AND NATURE OF AMORPHOUS CELLULOSES AND CELLULOSE/HEMICELLULOSE BLENDS
3. MICROPROBE MAPPING OF WOOD AND CHEMICALLY TREATED WOOD
4. PHOTOPHYSICS OF LIGNIN

OPPORTUNITIES ARISING FROM THE NEW RAMAN MICROPROBE SYSTEM

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

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

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

D. THE POSSIBILITY OF AN ON-LINE LIGNIN DETECTOR

Project 3474

IMPROVED PROCESS FOR BLEACHED PULP

Low Lignin Pulps - T. J. McDonough

Nonchlorine Bleaching - N. S. Thompson

PROJECT 3474
IMPROVED PROCESS FOR
BLEACHED CHEMICAL PULP

PROJECT 3474

- Modest Recent Effort
- Data Analysis Pending
- Oxygen Delignification Enhancement

PROJECT 3474
RELATED STUDENT ACTIVITY

Kinetics and Modelling of Kraft Pulping
- M. Burazin, Ph.D., 1985
- D. Boyle, M.S., 1987
- K. Sime, M.S., 1986
- J. Rogers, M.S., 1986

Kinetics and Mixing Effects in Bleaching
- S. Pugliese, Ph.D., 1987
- B. Burns, M.S., 1986

Hardwood Pulping Behavior and Pulp Properties
- T. Niemi, Special Student, 1986

PROJECT 3474
PLANS

- Data Analysis and Modelling
- Limited Experiments to Complete Models
- Reporting

PROJECT 3474

OXYGEN DELIGNIFICATION ENHANCEMENT

OBJECTIVE:

MODIFY LIGNIN IN UNBLEACHED PULP TO ENHANCE SUBSEQUENT OXYGEN BLEACHING

NITROGEN OXIDES

OXIDE	PHYSICAL FORM	M.P., °C
NO	colorless gas	-163.6
N_2O	colorless gas	-90.8
N_2O_5	white crystals	30
NO_3	blue gas	decomp.
NO_2,N_2O_4	yellow liquid, brown gas	-11.2
N_2O_3	red brown gas, blue liquid	-102

PREVIOUS WORK

RADICALS IN PULP, DURING BLEACHING

RADICAL CHAIN REACTION THROUGH CELLULOSE

INHIBITION REACTIONS

CONCLUSIONS

MODIFICATION OF LIGNIN

ALIPHATIC

AROMATIC
- MODIFY
- DESTROY

REAGENTS EMPLOYED

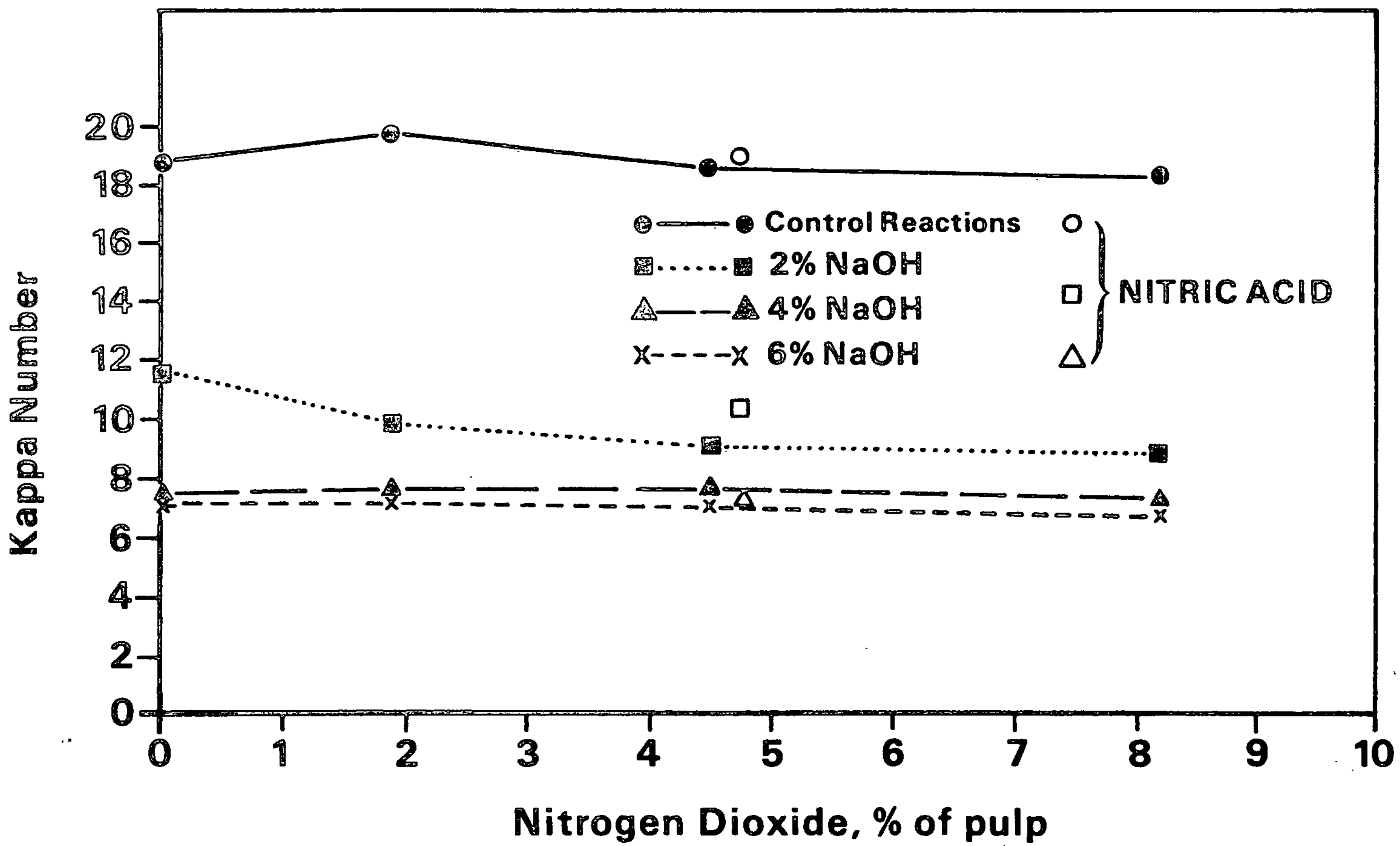
PEROXY ACETIC ACID
NITROGEN OXIDE

CONCLUSIONS

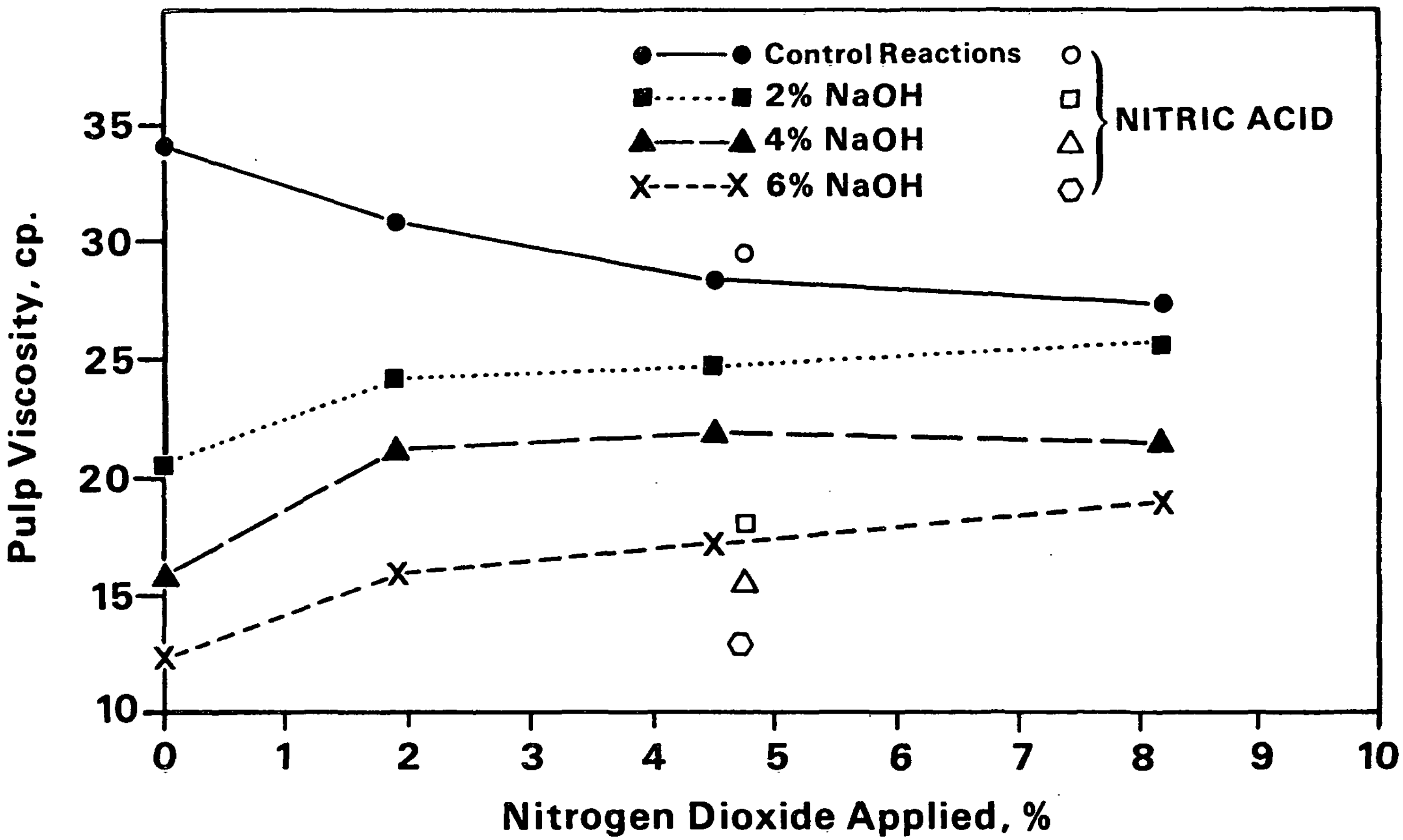
POTENTIAL OF NITROGEN OXIDES

MECHANISM OF STABILIZATION

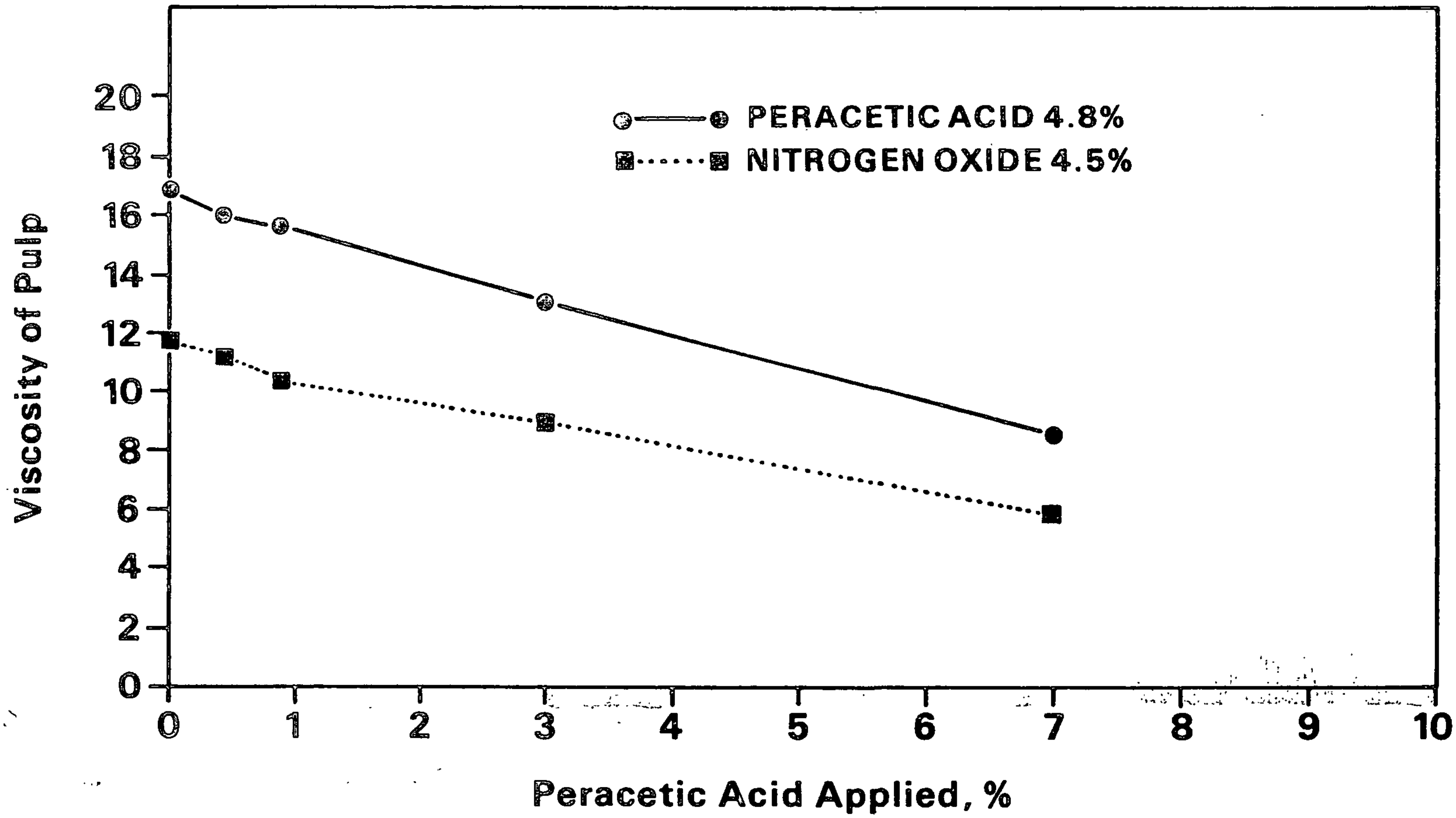
The Effect of NO_2 Pretreatments on Oxygen Bleaching—Kappa Content



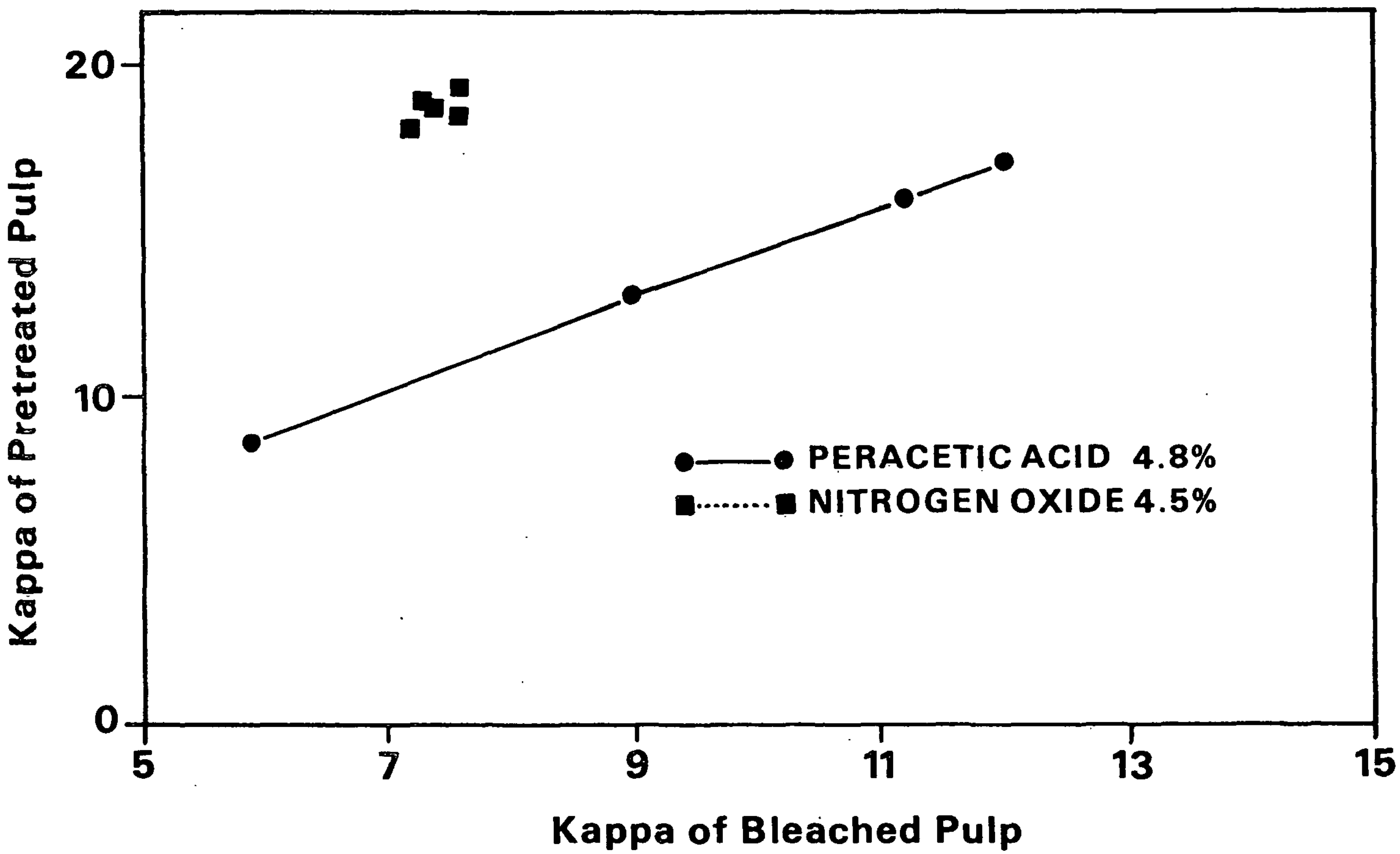
The Effect of NO_2 Pretreatments on Oxygen Bleaching—Pulp Viscosity



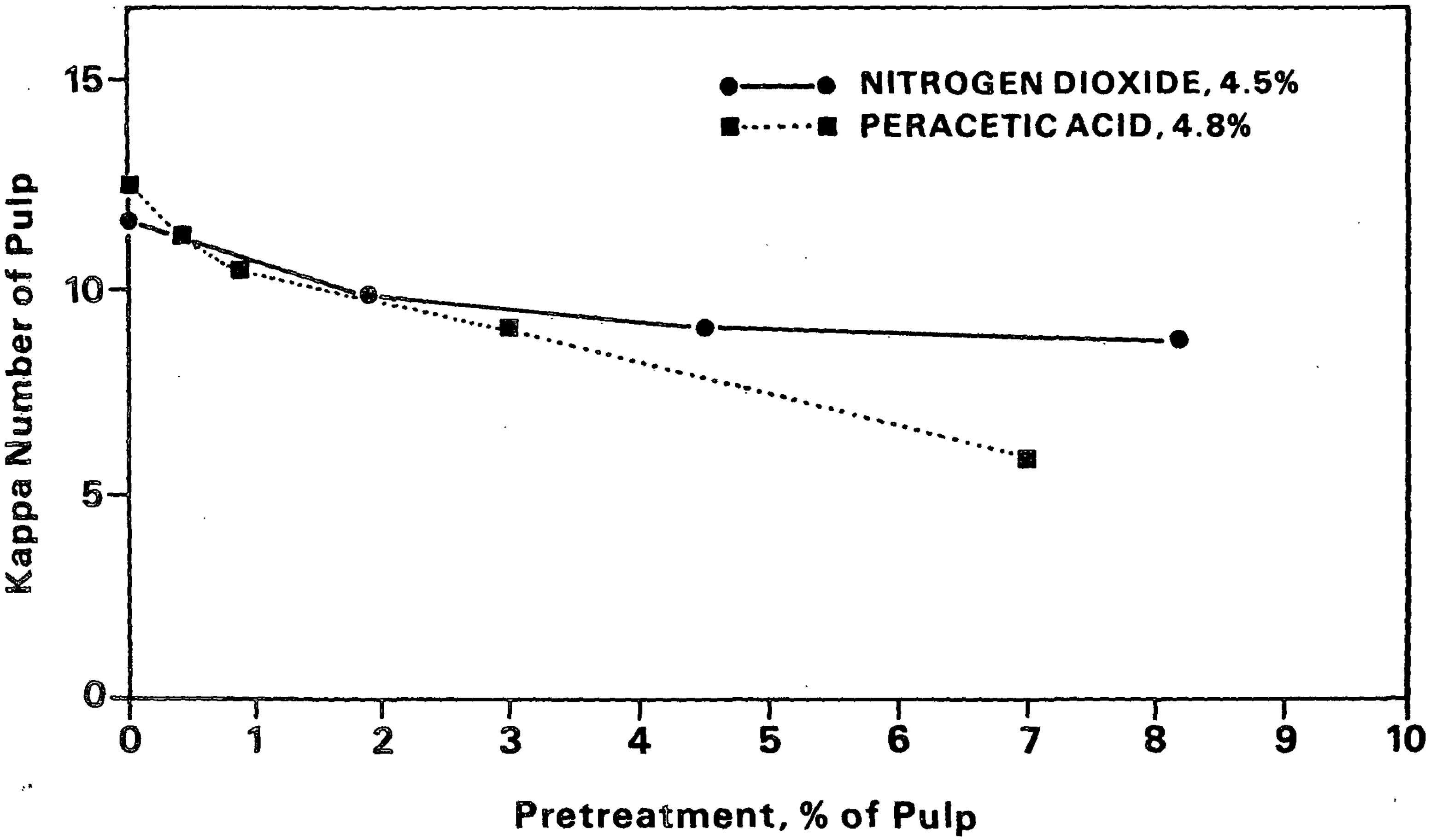
The Effect of Peracetic Acid Pretreatment on Bleached Pulp–Viscosity



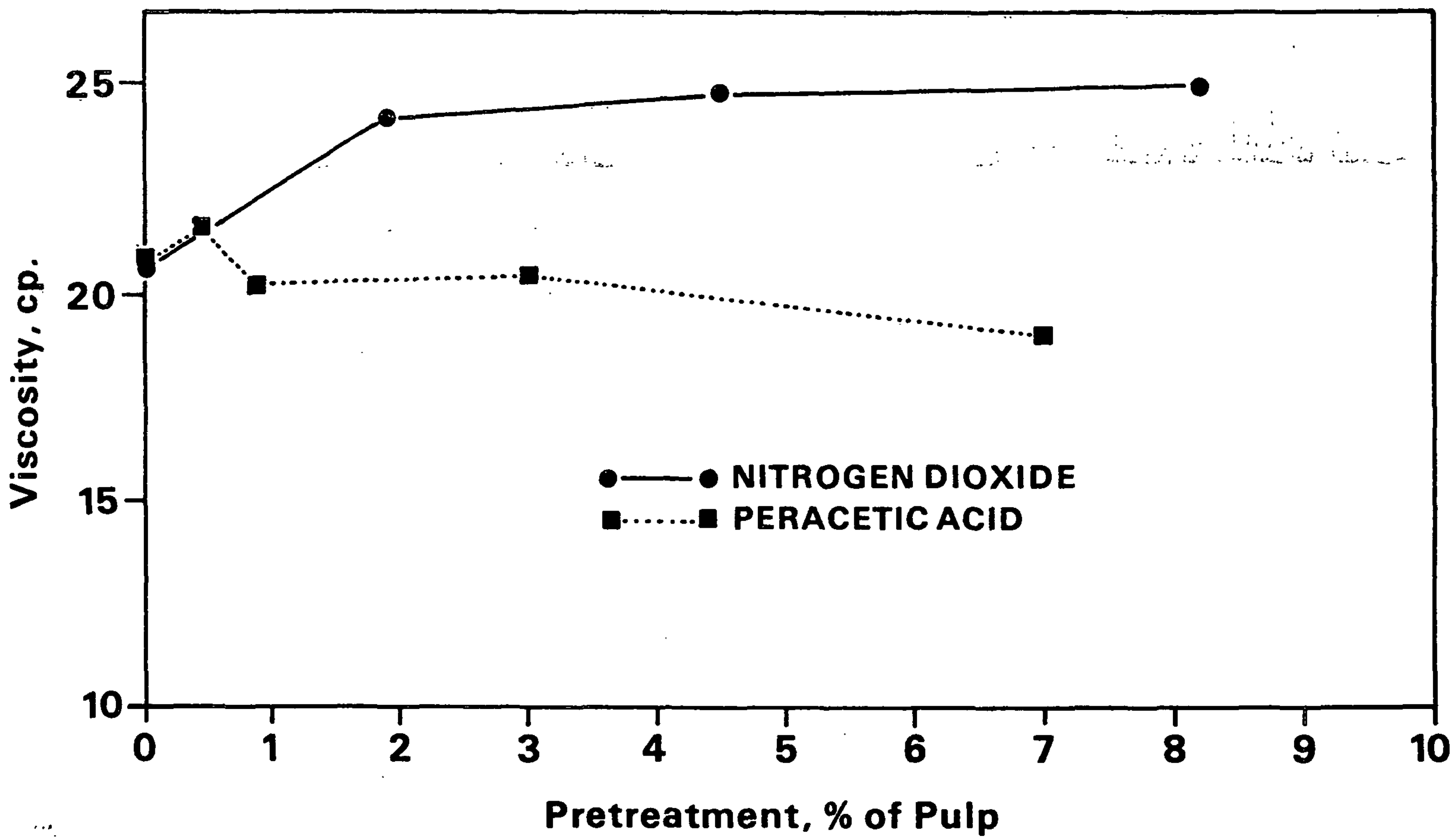
The Effect of Pretreated Kappa on Bleached Kappa



The Effect of Different Pretreatment on Oxygen Bleaching—Kappa



Comparison of Different Pretreatments on Oxygen Bleaching—Viscosity



Project 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

W. F. W. Lonsky

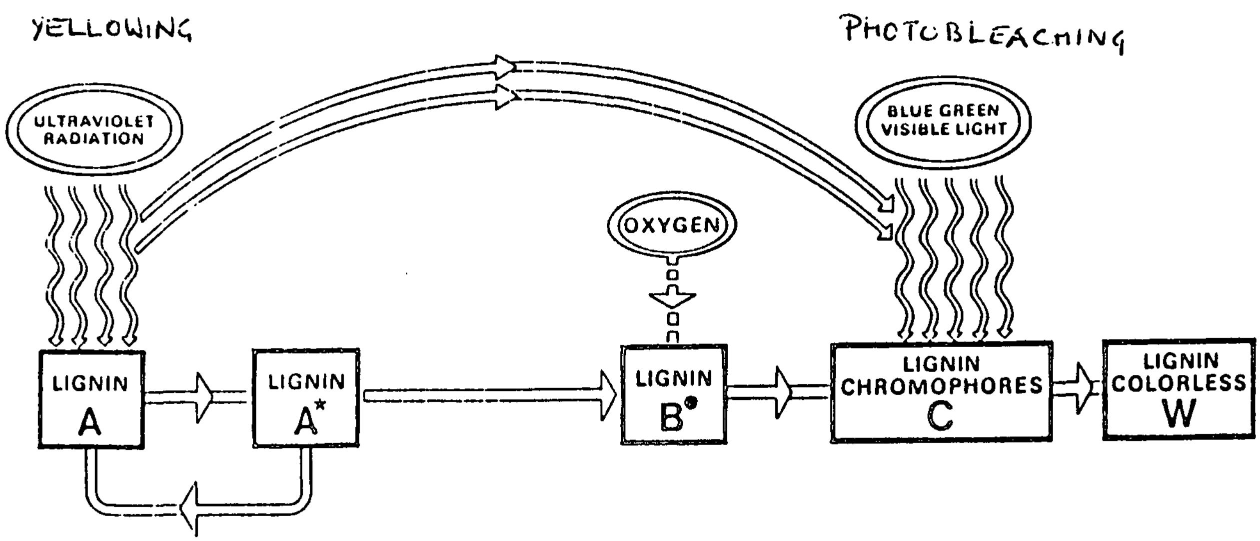
FUNDAMENTALS OF BRIGHTNESS STABILITY

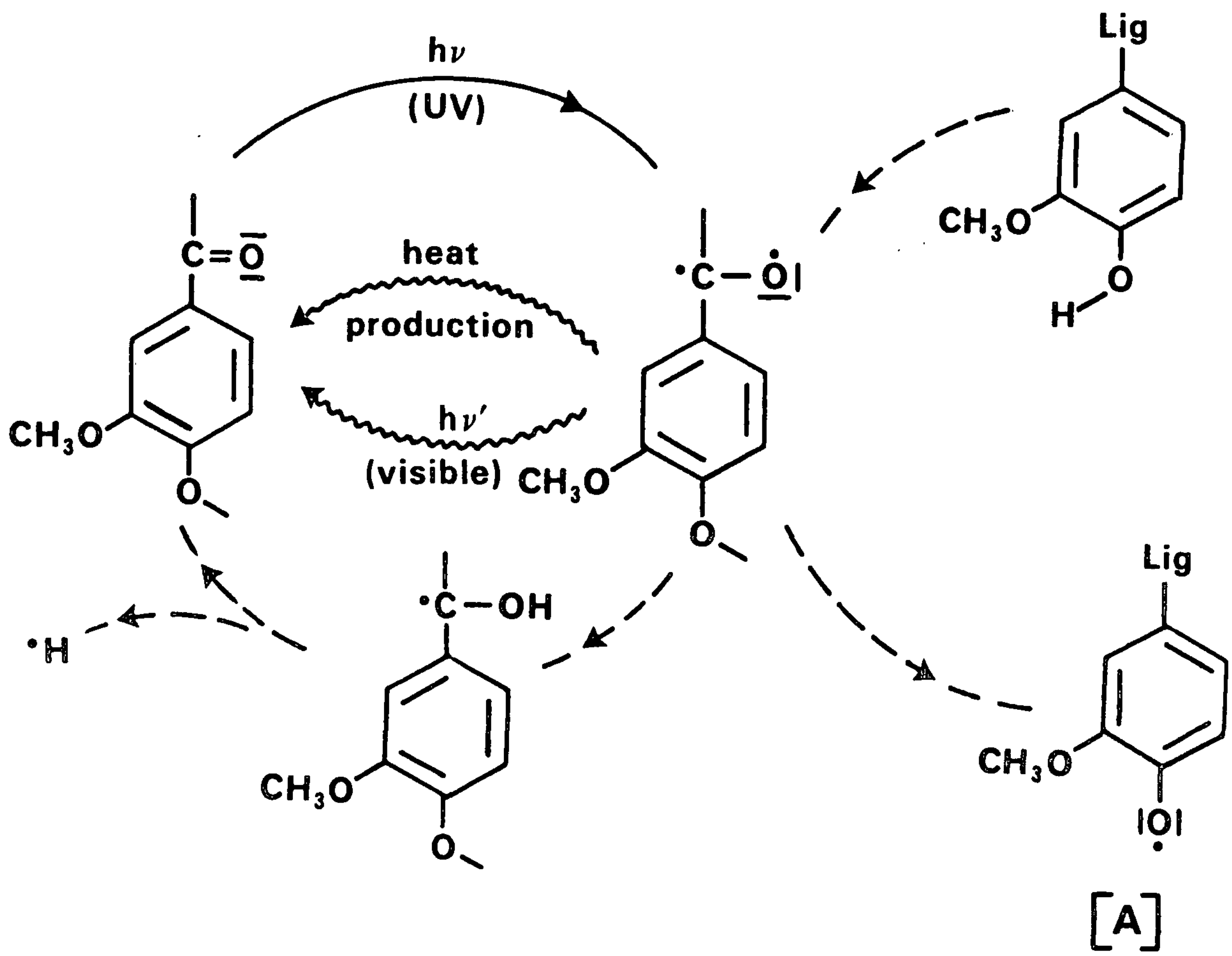
OBJECTIVE:

ESTABLISH MECHANISM FOR BRIGHTNESS LOSS IN HIGH YIELD PULPS

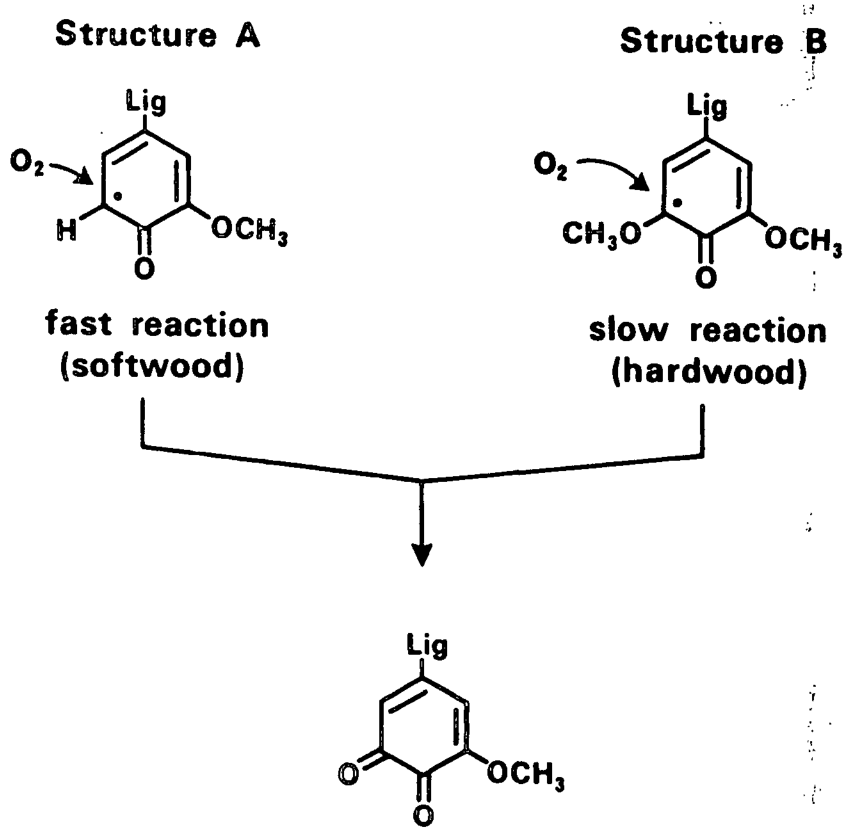
- OBSERVATIONS LEADING TO A PROPOSED MECHANISM
- ADDITIONAL EVIDENCE FOR THE MECHANISM
- STUDIES ON THE MECHANISM

CHEMISTRY OF COLOR REVERSION

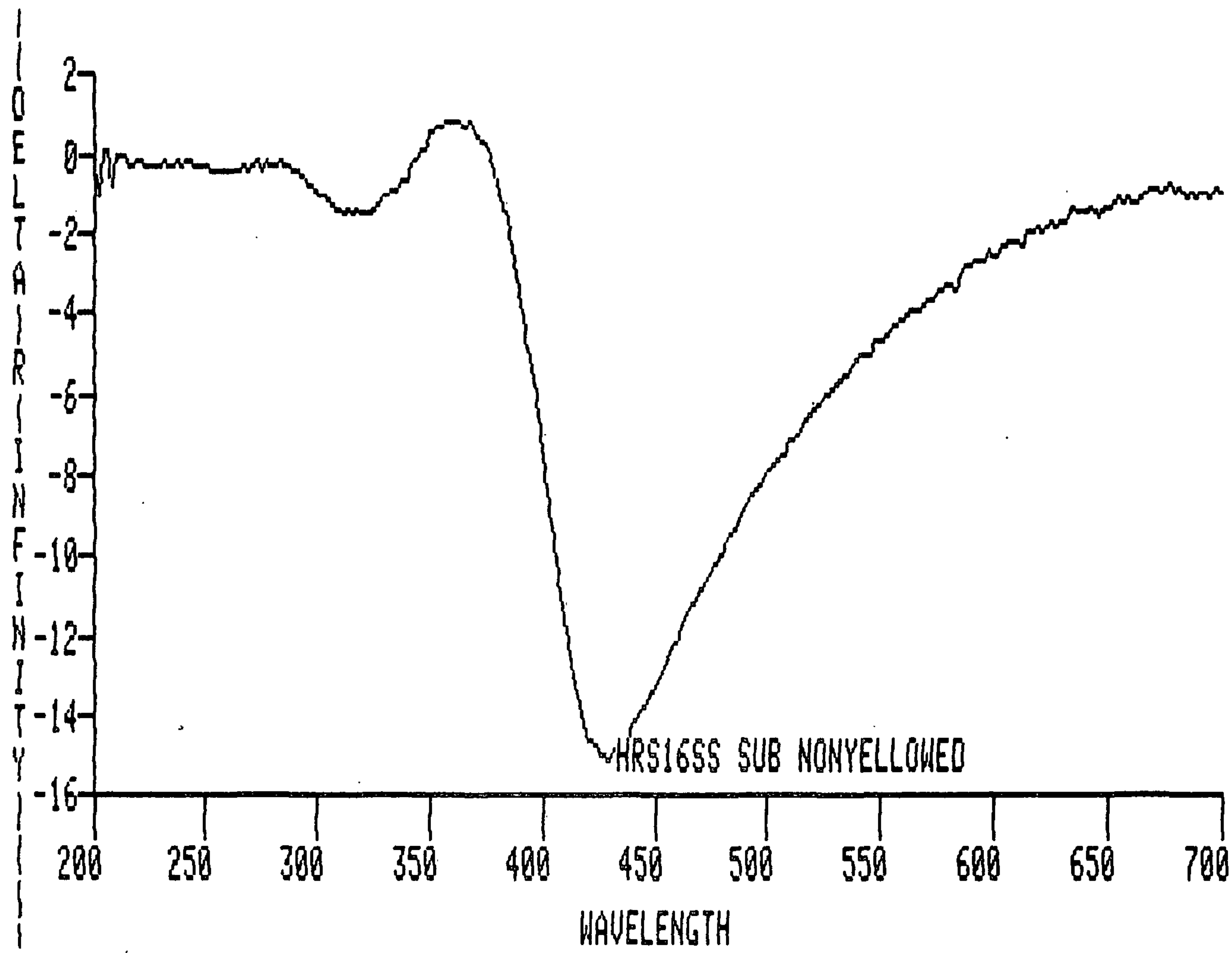




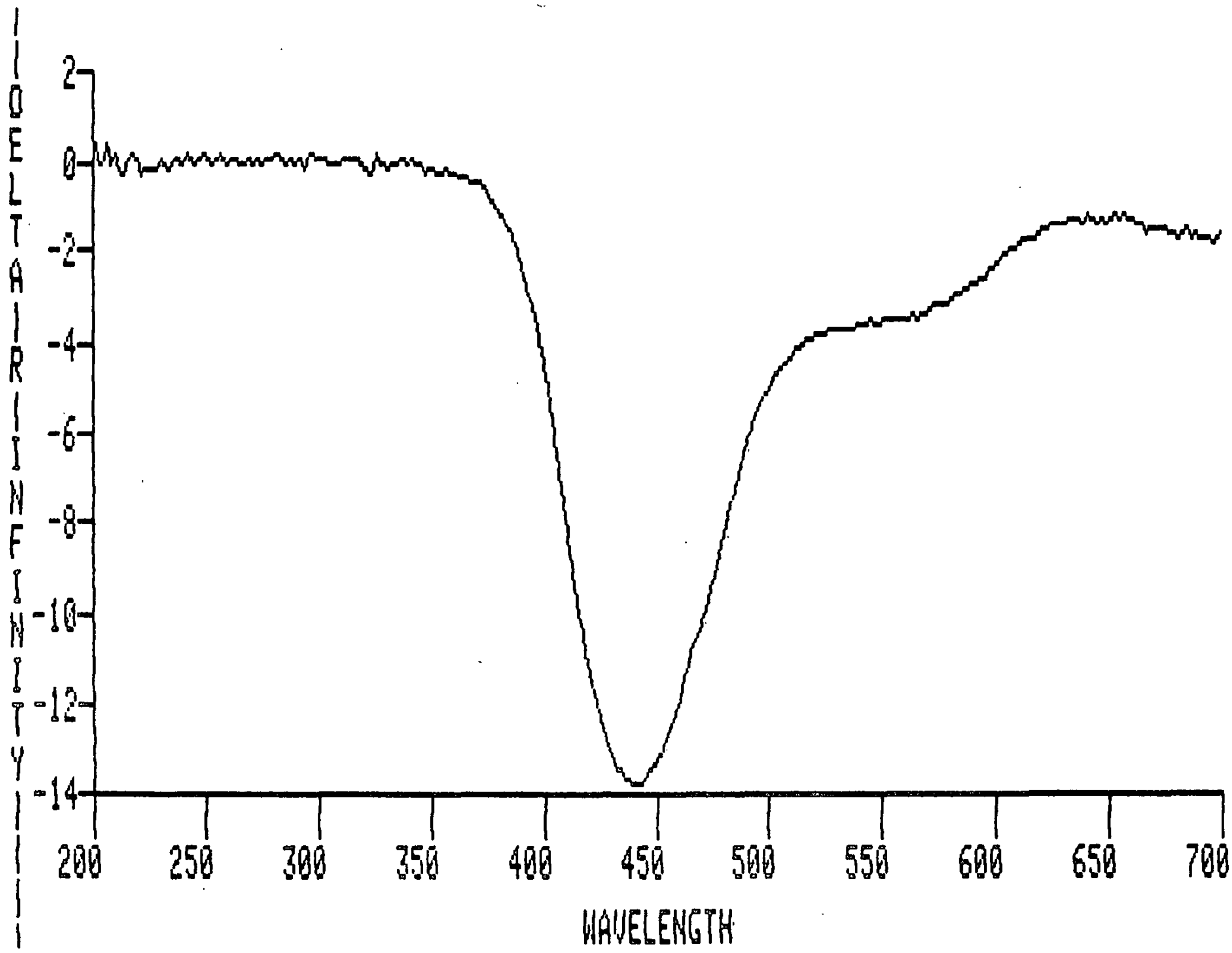
The Photochemical Induction Cycle



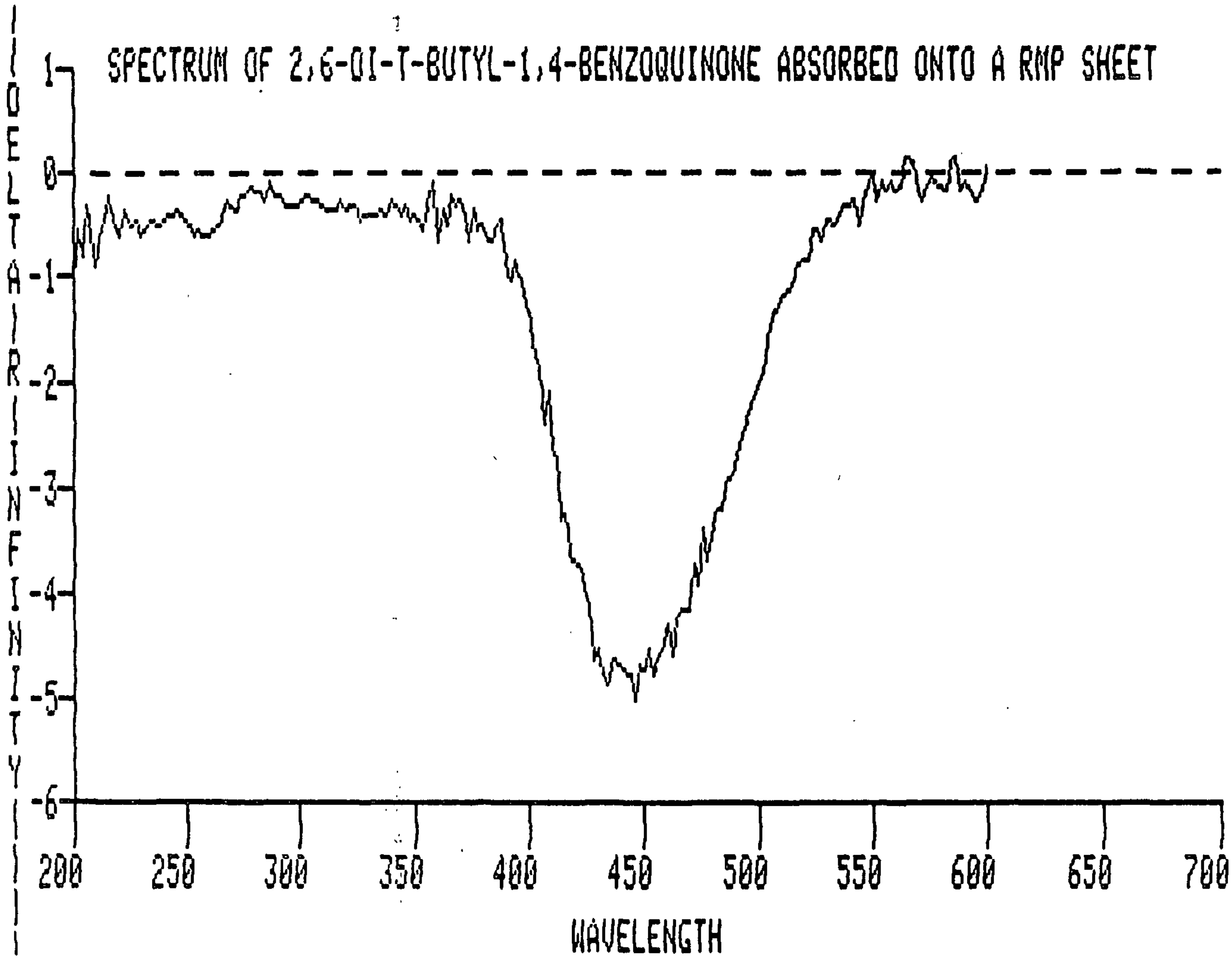
Softwoods and hardwoods generate
the very same chromophore



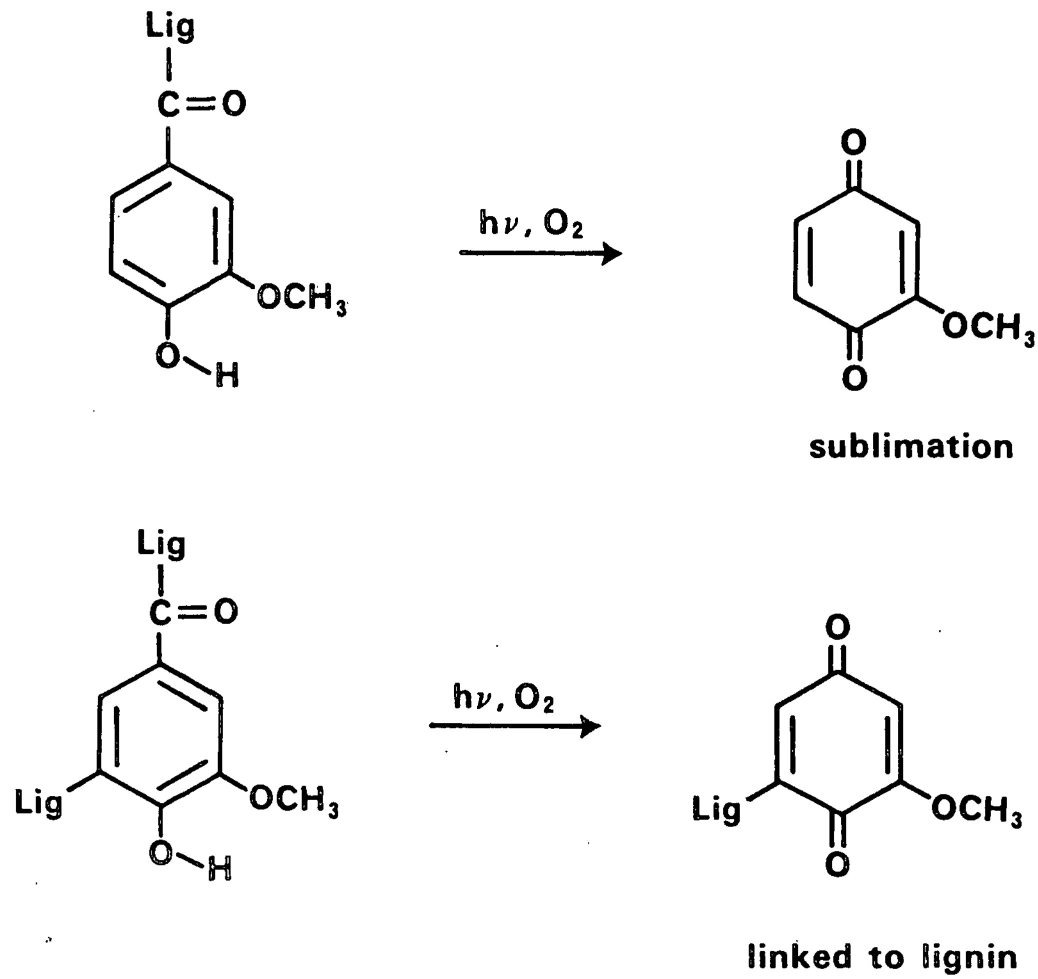
White spruce RMP sheet: The absorption band caused by yellowing with sunlight



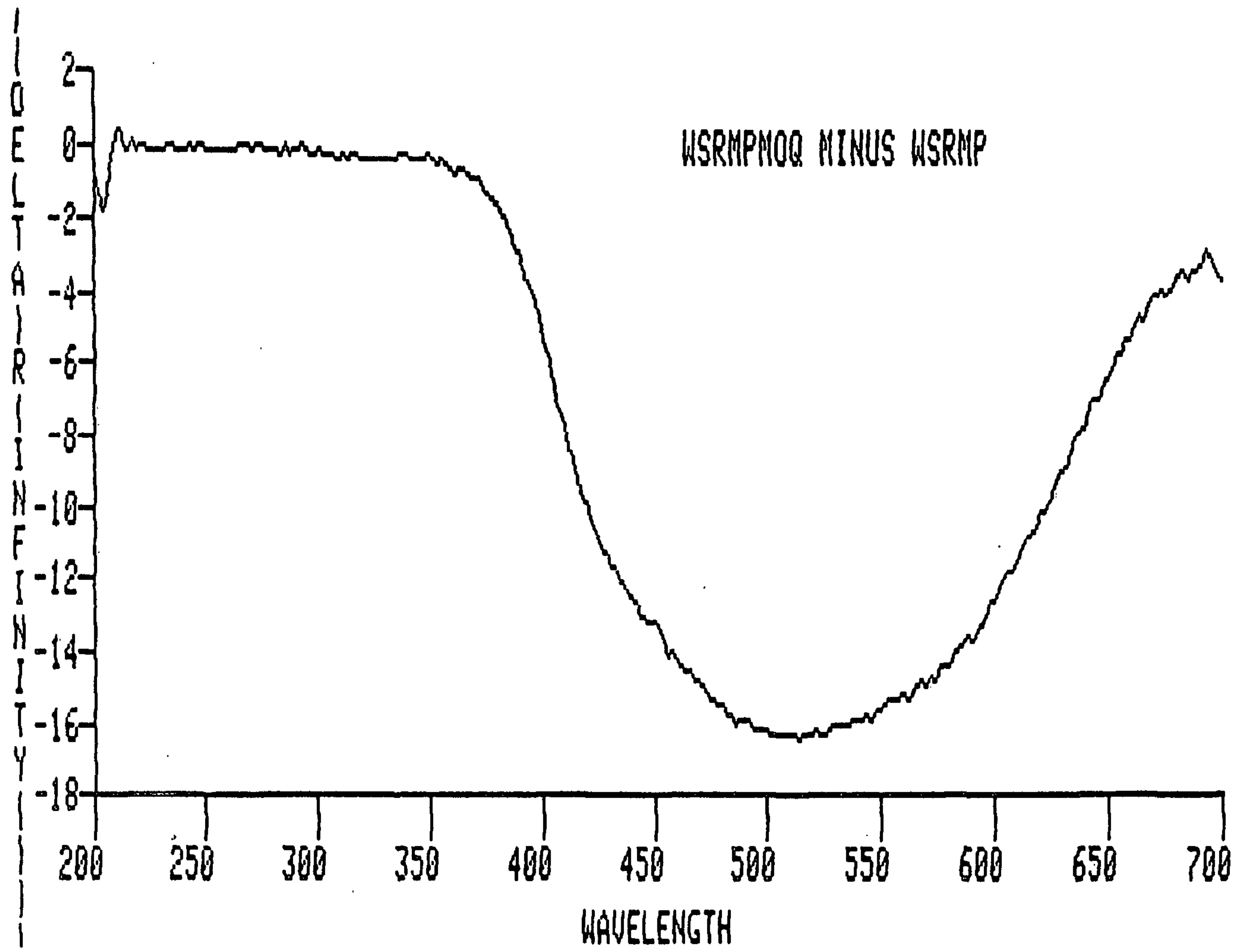
White spruce RMP sheet: The absorption band of 3,5-di-tert.butyl-o-benzoquinone



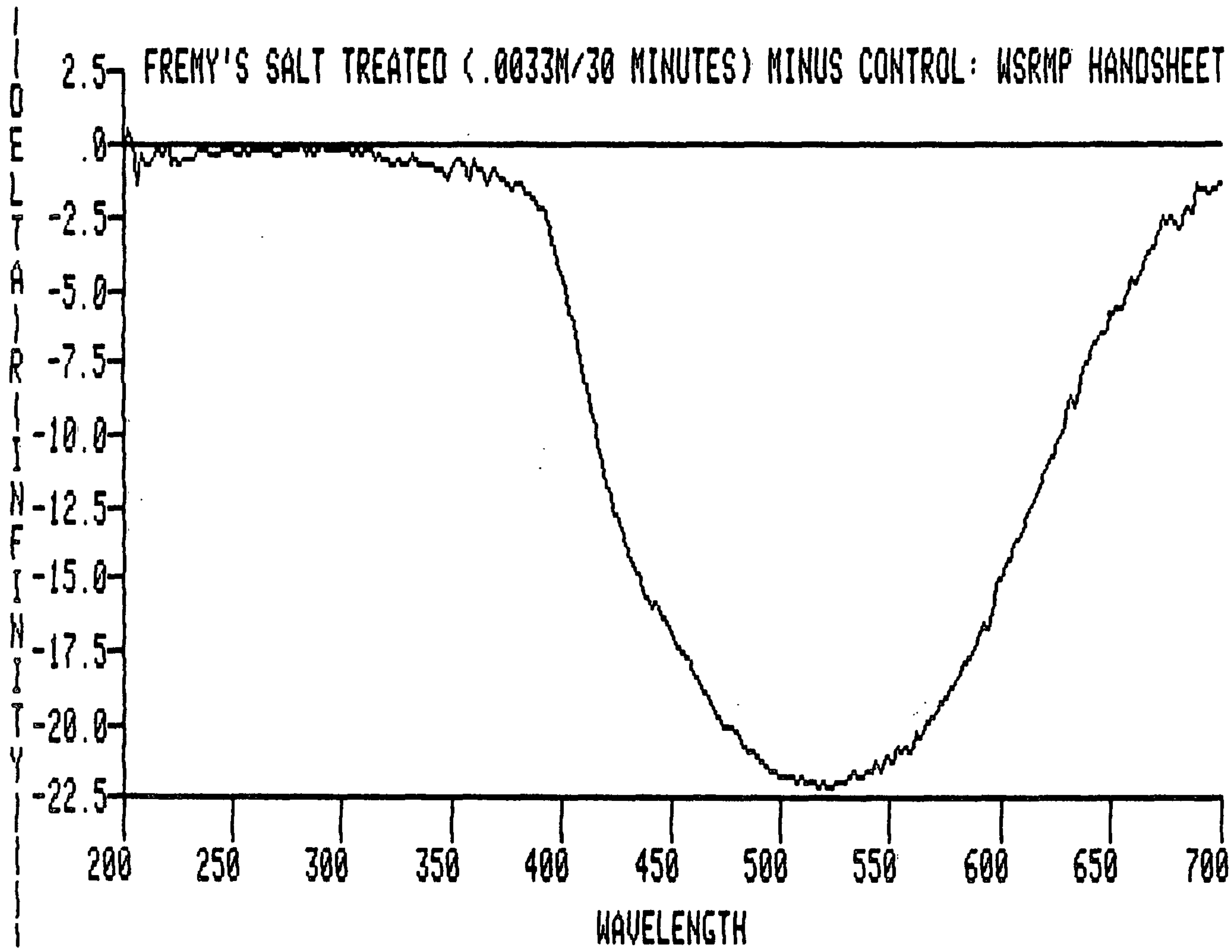
White spruce RMP sheet: The absorption band of 2,6-di-tert.butyl-p-benzoquinone



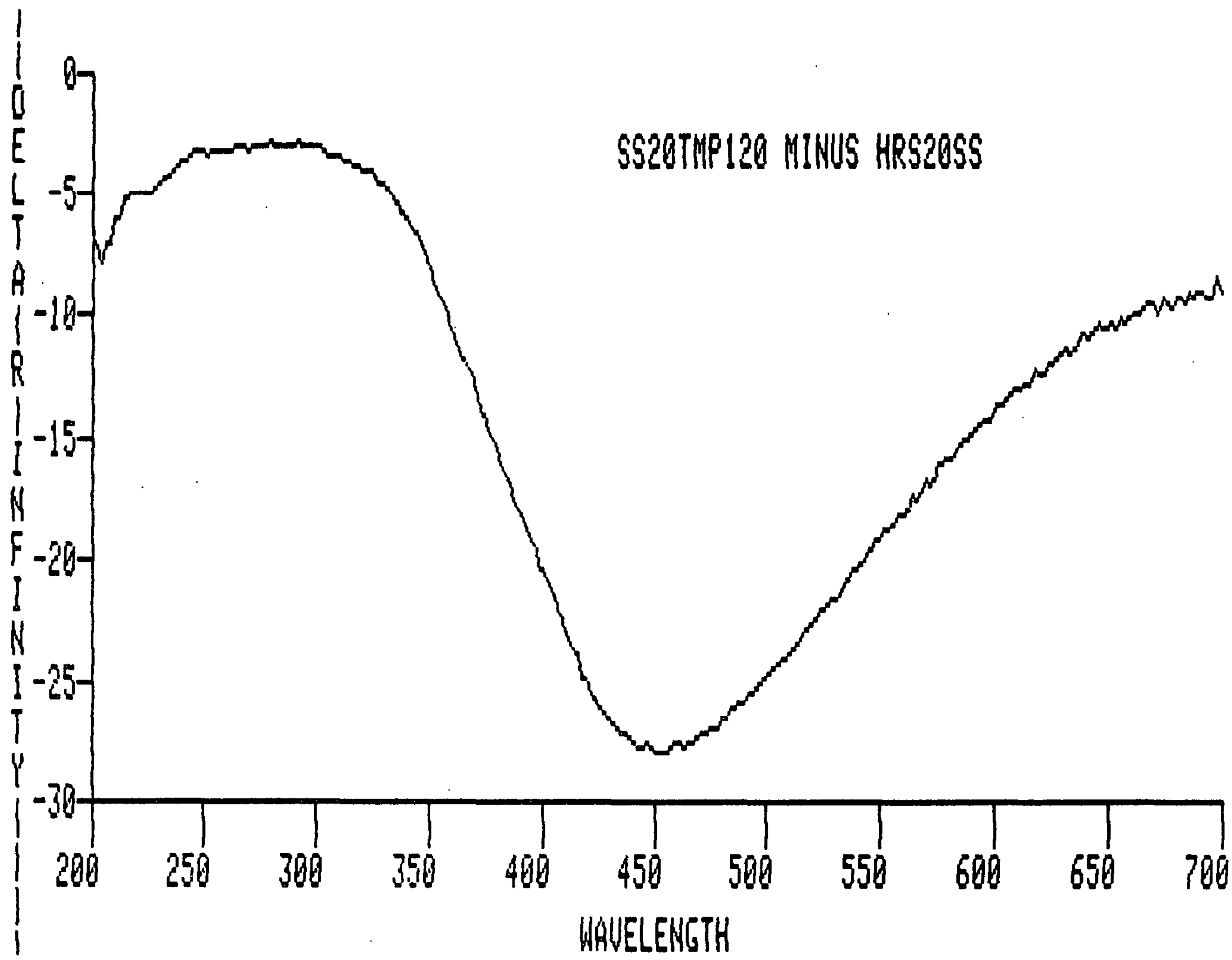
What is the likelihood for p-quinones to be major contributors to the color?



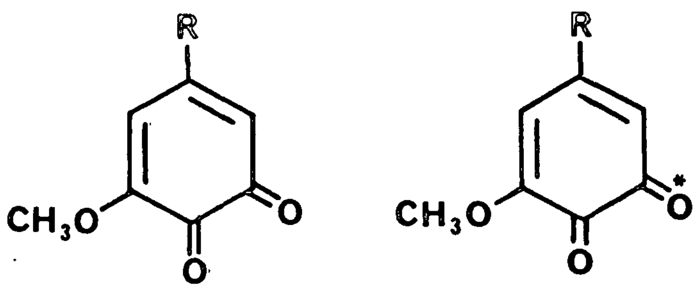
White spruce RMP sheet: The absorption band of 2-methoxy-o-benzoquinone



White spruce RMP sheet: The absorption band of o-benzoquinones formed from the lignin in the sheet by treatment with Fremy's salt. Theoretically, phenolic guaiacyl units should be converted to 3-methoxy-o-benzoquinonoid structures.

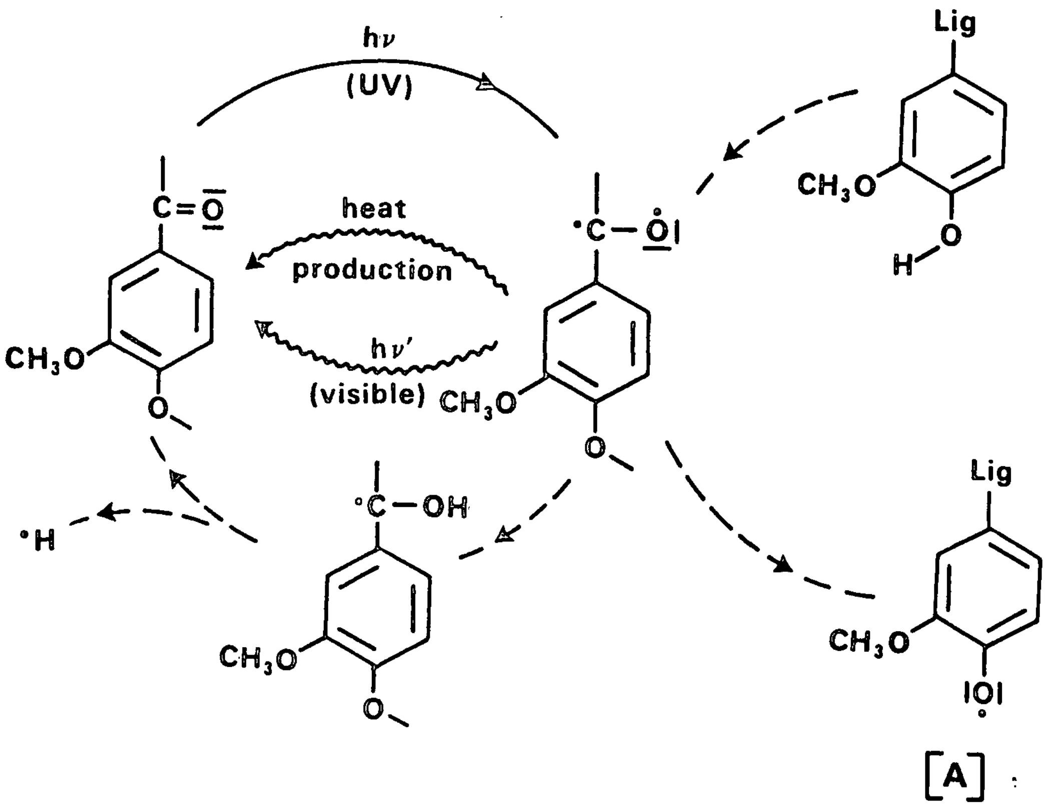


White spruce RMP sheet: The absorption band of o-quinones produced by sunlight (determined through treatment with trimethylphosphite)

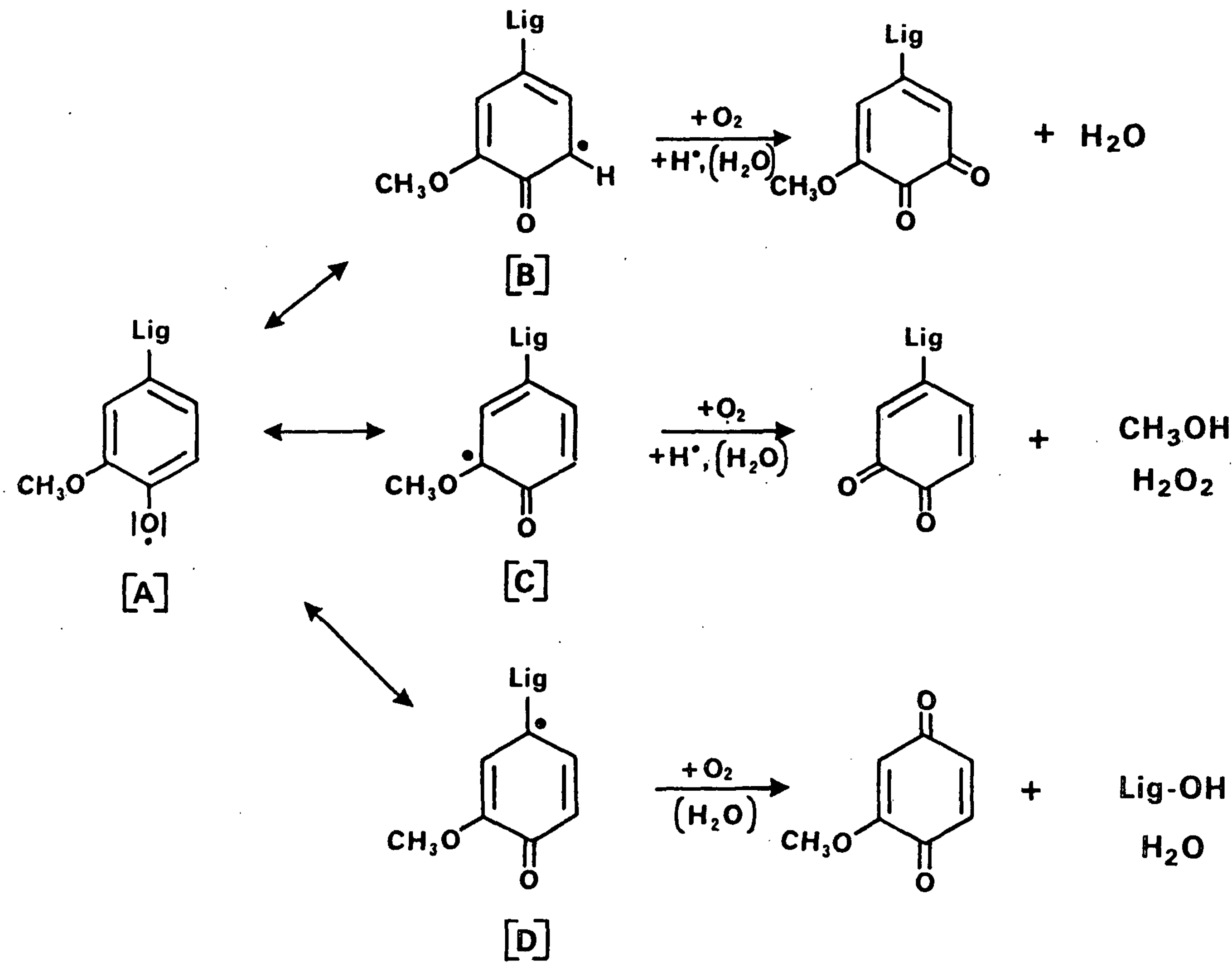


(Pat Medvecz; MS thesis)

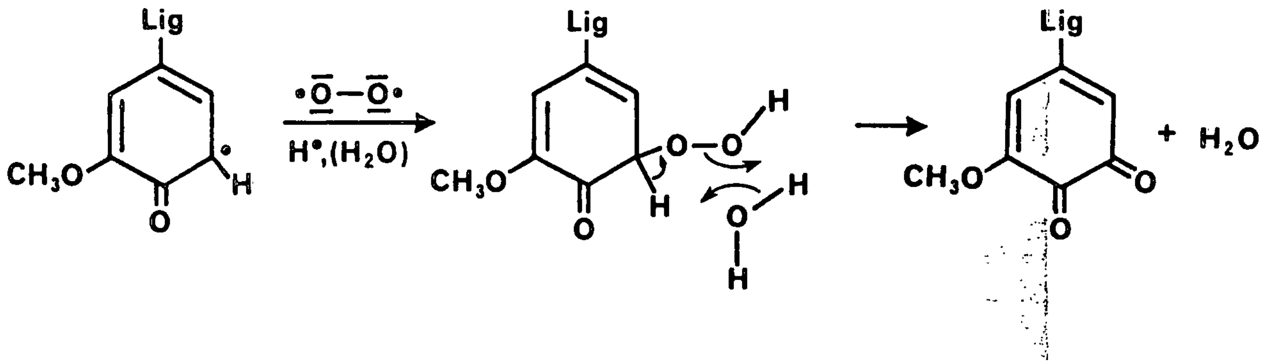
Supportive Model Studies



The Photochemical Induction Cycle



The various products formed in the "dark reaction"



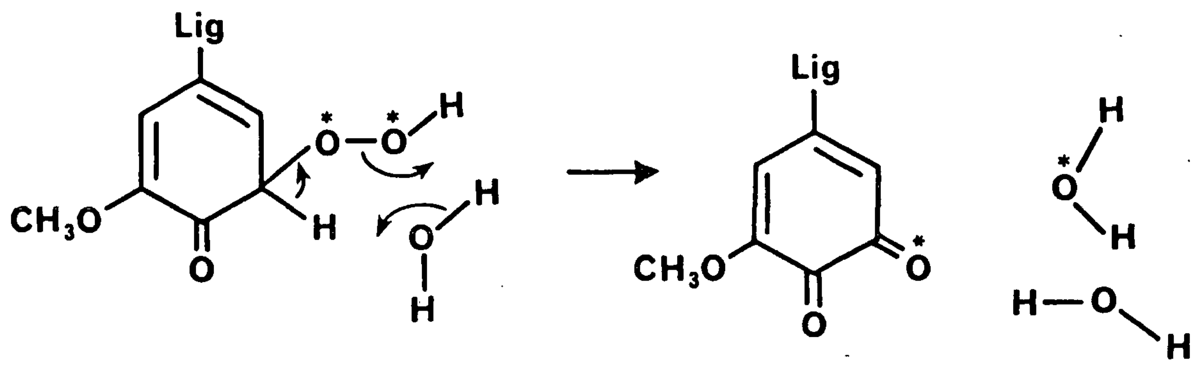
Humidity assisted rearrangement

FUTURE WORK

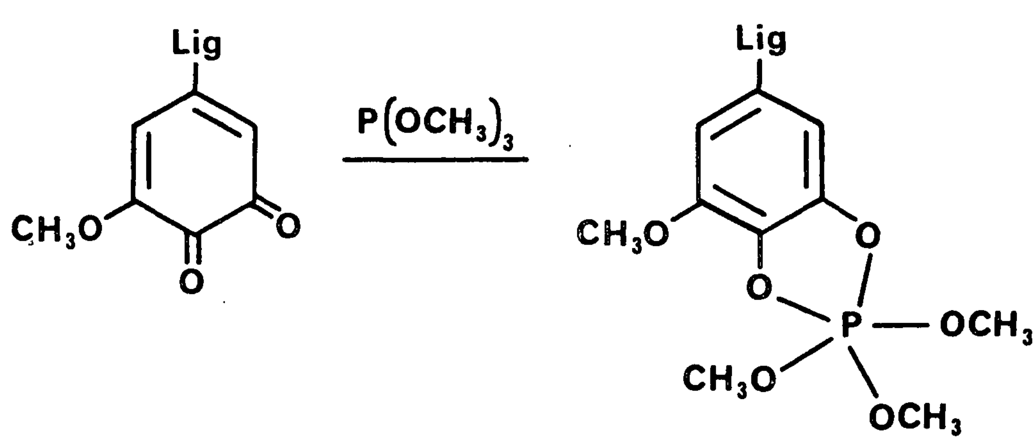
- EVIDENCE FOR PROPOSED YELLOWING MECHANISM
- BRIGHTNESS STABILIZATION

EVIDENCE FOR PROPOSED YELLOWING MECHANISM

- INCORPORATION OF 18-OXYGEN GAS (IR, MS)
- O-QUINONE SPECIFIC REACTIONS (P-31 NMR)
  - PHOSPHITE ESTERS
  - DIELS-ALDER REACTIONS
- QUINONE CONCENTRATION PROFILE ALONG CALIPER
  - PHOSPHITE ESTERS (STEM, P ANALYSIS)
    - VARIATION OF BASIS WEIGHT
    - VARIATION OF EXPOSURE TIME
- BY-PRODUCT ANALYSIS
  - METHANOL
  - 2-METHOXY-P-BENZOQUINONE

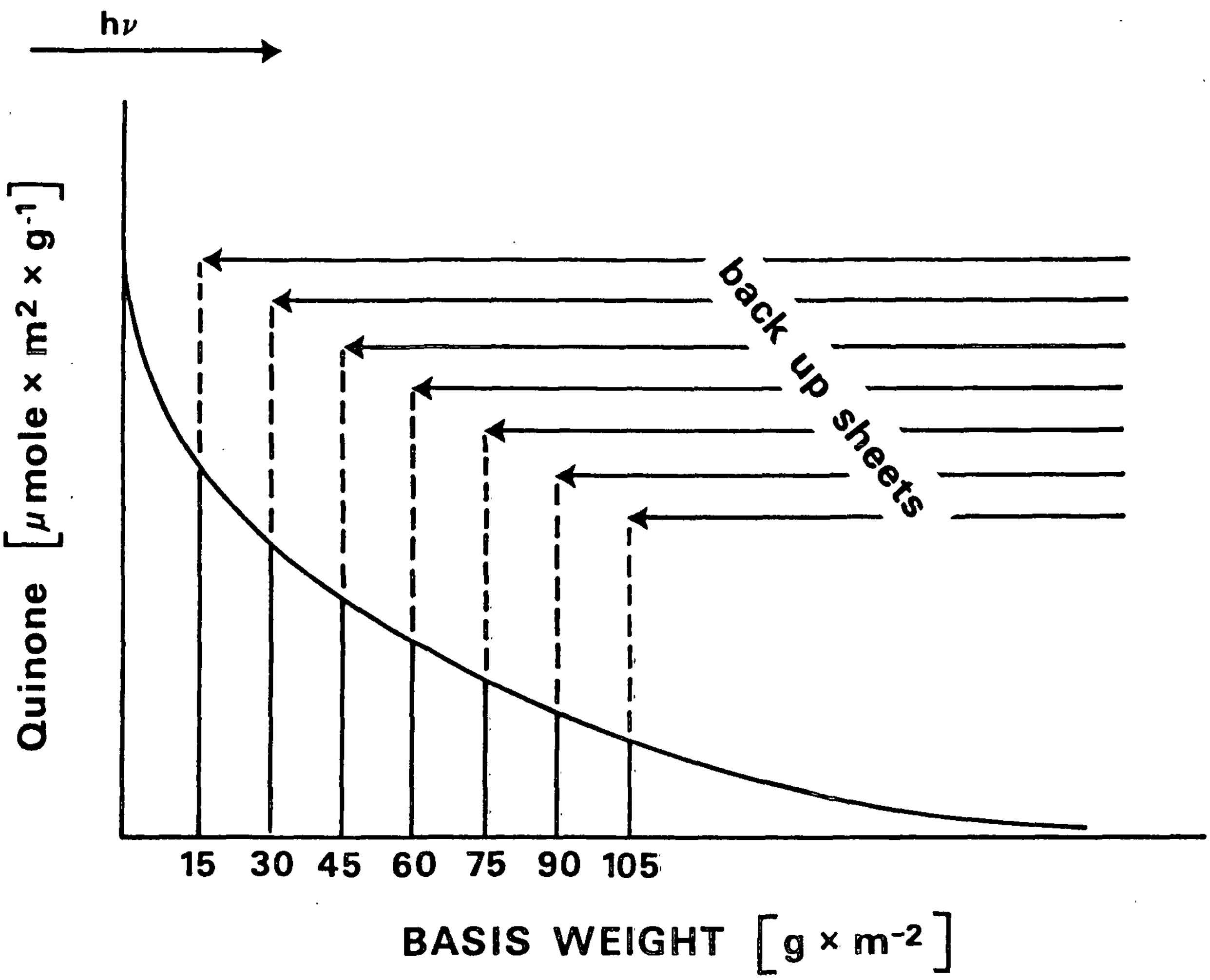


18-Oxygen Studies



(Stuart Lebo, PhD thesis)

An "ortho-quinone specific" reagent



Phosphor analysis of yellowed and trialkyl phosphite treated sheets should provide information on concentration and concentration gradient.

BRIGHTNESS STABILIZATION

- NEW BLEACHING METHODS
  - CONTROL PHENOLIC HYDROXYL INCREASE
  - PHENOL BLOCKING REACTIONS
- ANTIOXIDANTS
- FLUORESCENT DYES

$$NaBO_3 \cdot 4\ H_2O$$

$$NaBO_2 \cdot H_2O_2 \cdot 3\ H_2O$$

$$CH_3CO(OH) + [H_2O_2] \rightleftharpoons CH_3CO(OOH) + H_2O$$

Peracetic acid formed <u>in situ</u>

Project 3566

SEPARATION OF STRONG, INTACT FIBERS

T. J. McDonough

PROJECT 3566

STRONG, INTACT HIGH YIELD FIBERS

PROJECT 3566 STAFF

PROJECT LEADERS
TOM MCDONOUGH
SALMAN AZIZ

TECHNICAL STAFF
HARRY GRADY
AMY MALCOLM
KRISTIE RANKIN

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

PINE SINGLE FIBER PROPERTIES AND THEIR STANDARD ERRORS

PULP	LOAD,	AREA, MM^2	STRESS, KG/MM^2	MODULUS, KG/MM^2
RMP	32 ± 2	580 ± 35	59 ± 4	1100 ± 135
CMP	34 ± 2	590 ± 30	59 ± 2	1350 ± 80
BK*	15 ± 1	250 ± 20	62 ± 3	580 ± 30
UBK	22 ± 3	250 ± 20	86 ± 9	1040 ± 140

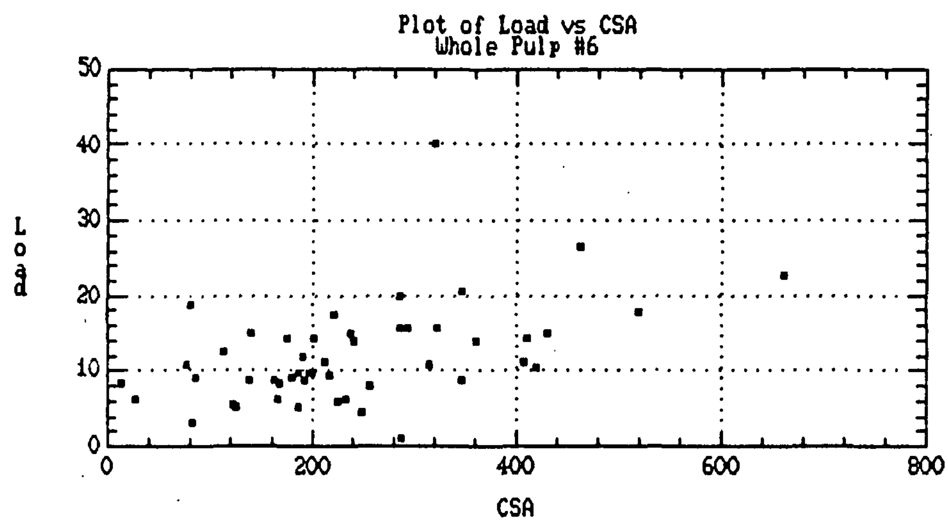
* COMMERCIAL BLEACHED KRAFT

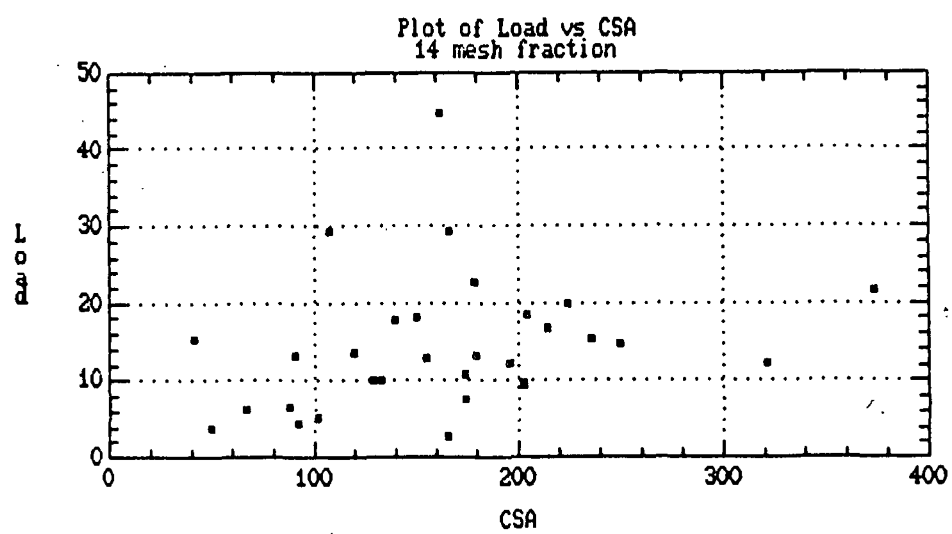
SPRUCE SINGLE FIBER PROPERTIES AND THEIR STANDARD ERRORS

PULP	MESH SIZE	LOAD, G	AREA, MM^2	STRESS, KG/MM^2	MODULUS, KG/MM^2
RMP	14	14 ± 2	165 ± 15	100 ± 15	1930 ± 340
	28	12 ± 1	170 ± 10	90 ± 15	1690 ± 230
	48	10 ± 1	150 ± 15	90 ± 20	2040 ± 425
CMP	14	12 ± 1	200 ± 10	60 ± 4	850 ± 60
	28	13 ± 2	195 ± 15	65 ± 5	640 ± 50
	48	9 ± 1	180 ± 10	55 ± 5	610 ± 50

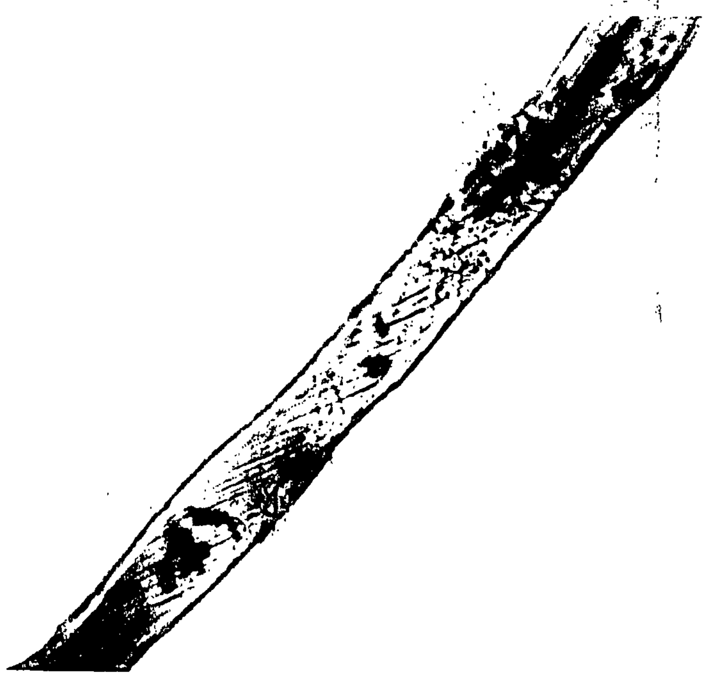
SPRUCE SINGLE FIBER PROPERTIES AND THEIR STANDARD ERRORS: ANOMALOUS FRACTIONATION EFFECTS

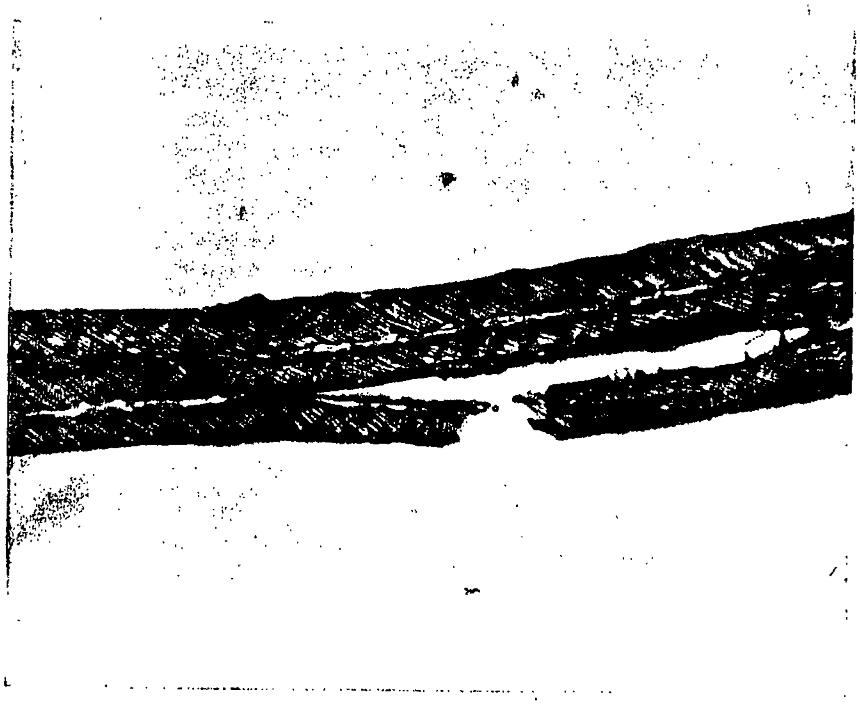
PULP	FRACTION	LOAD, G	AREA, μM^2	STRESS, KG/MM^2	MODULUS, KG/MM^2
RMP	WHOLE	12 ± 1	240 ± 20	72 ± 13	1410 ± 230
	14 MESH	14 ± 2	165 ± 15	100 ± 14	1930 ± 340
CMP	WHOLE	14 ± 1	155 ± 10	91 ± 6	1270 ± 130
	14 MESH	12 ± 1	200 ± 10	58 ± 4	850 ± 60

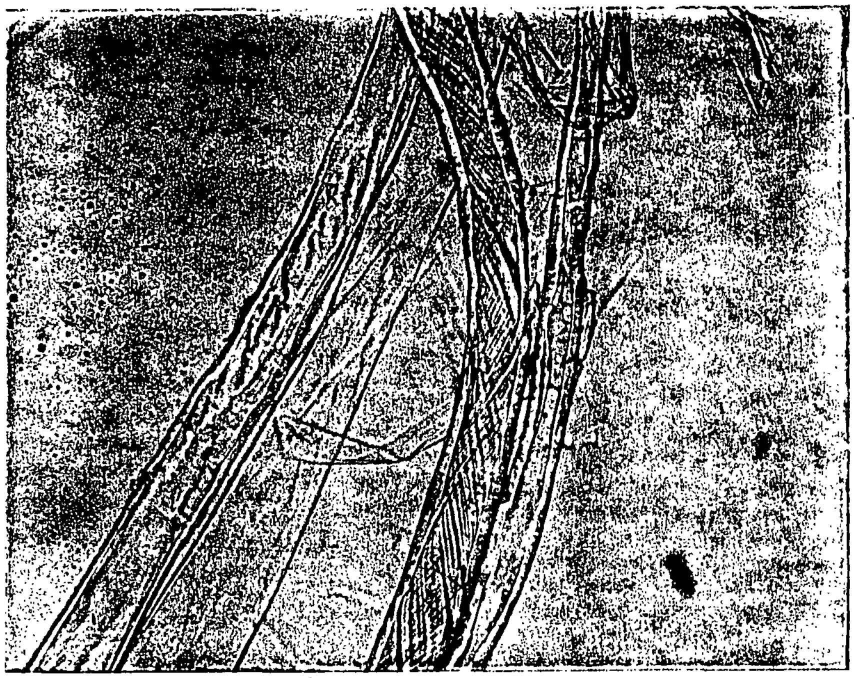




DETERMINATION OF
FIBRIL ANGLE





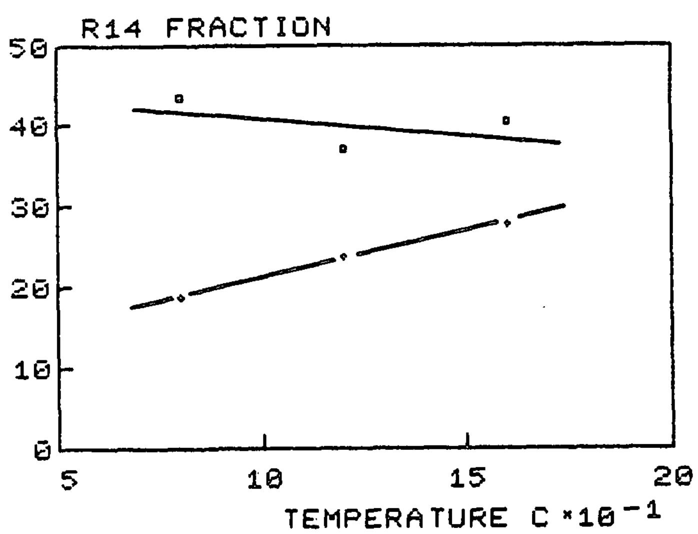


RELATING FIBER PROPERTIES
TO
FIBERIZATION VARIABLES

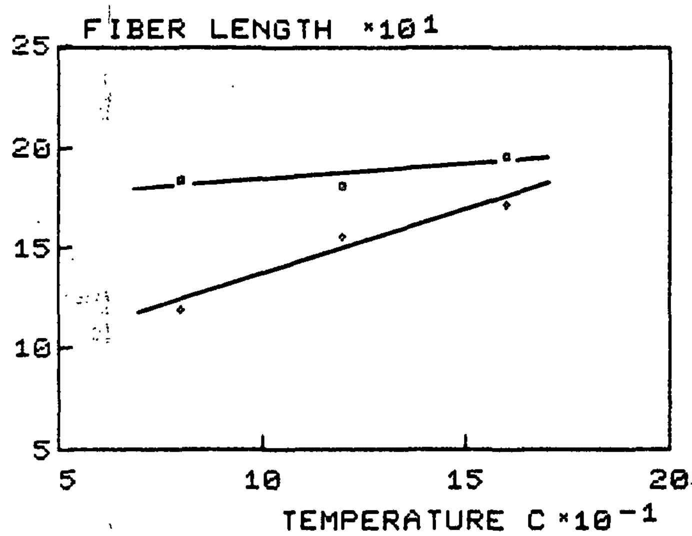
ASPLUND MILL FIBERIZATION EXPERIMENT
ACCEPTS AND LONG FIBER DATA

		UNSULFONATED		SULFONATED	
TEMP., °C	TIME, MIN	ACCEPTS, % WOOD	RI4, % PULP	ACCEPTS, % WOOD	RI4, % PULP
80	1	39	26	64	44
	2	59	15	79	46
	4	72	15	*	39
120	1	42	24	60	38
	2	55	22	75	38
	4	63	24	77	36
160	1	48	26	44	41
	2	52	29	55	40
	4	58	27	*	40

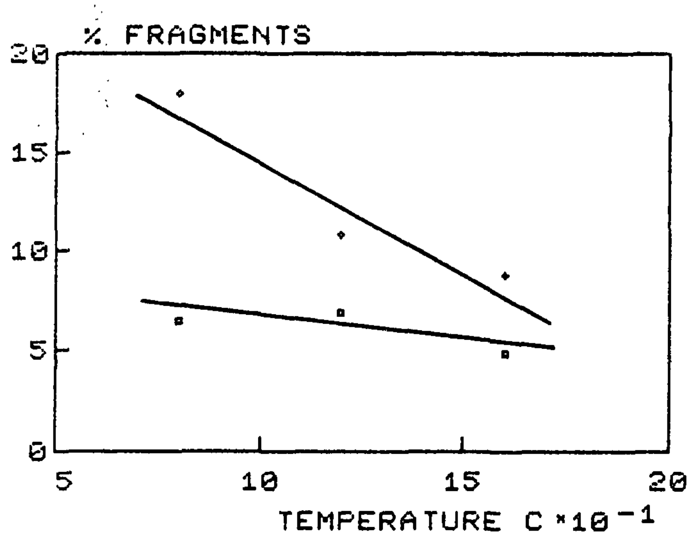
* SPURIOUS DATA DUE TO EQUIPMENT MALFUNCTION.



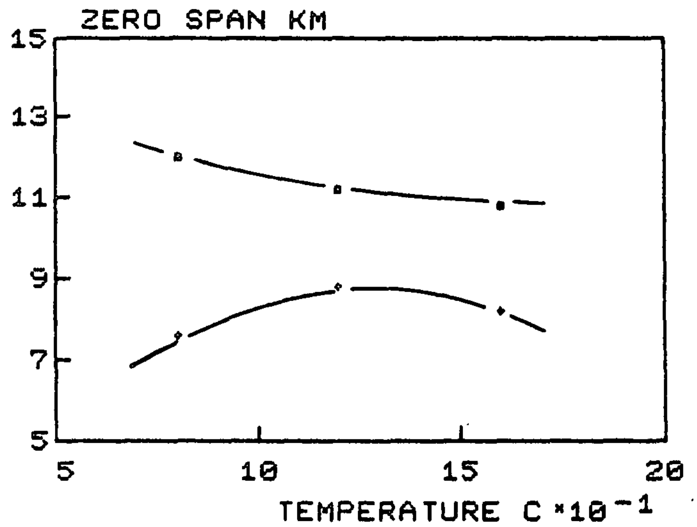
LONG FIBER FRACTION (% RETAINED ON 14 MESH SCREEN) VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (LOWER LINE) AND PRESULFONATED PULPS.



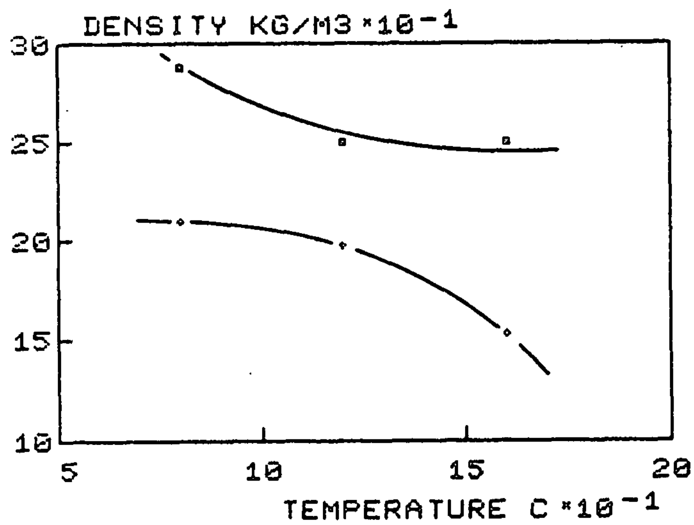
WEIGHTED AVERAGE FIBER LENGTH (MM) VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (LOWER LINE) AND PRESULFONATED PULPS.



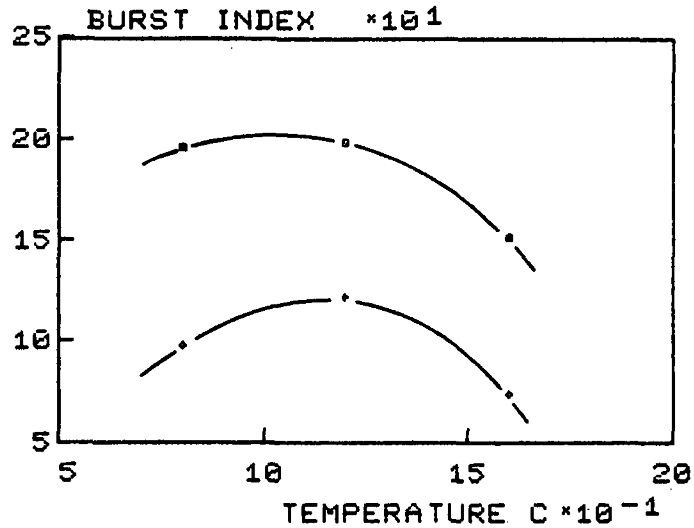
CONTENT OF FIBER FRAGMENTS (ARBITRARILY DEFINED AS % OF PULP HAVING FIBER LENGTH LESS THAN 0.4 MM) VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (UPPER LINE) AND PRESULFONATED PULPS.



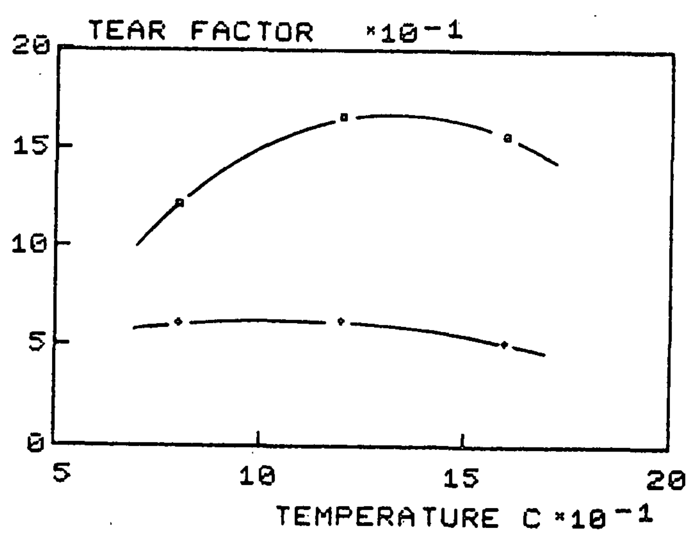
MAXIMUM ZERO-SPAN BREAKING LENGTH VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (LOWER LINE) AND PRESULFONATED PULPS.



MAXIMUM HANDSHEET DENSITY VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (LOWER LINE) AND PRESULFONATED PULPS.



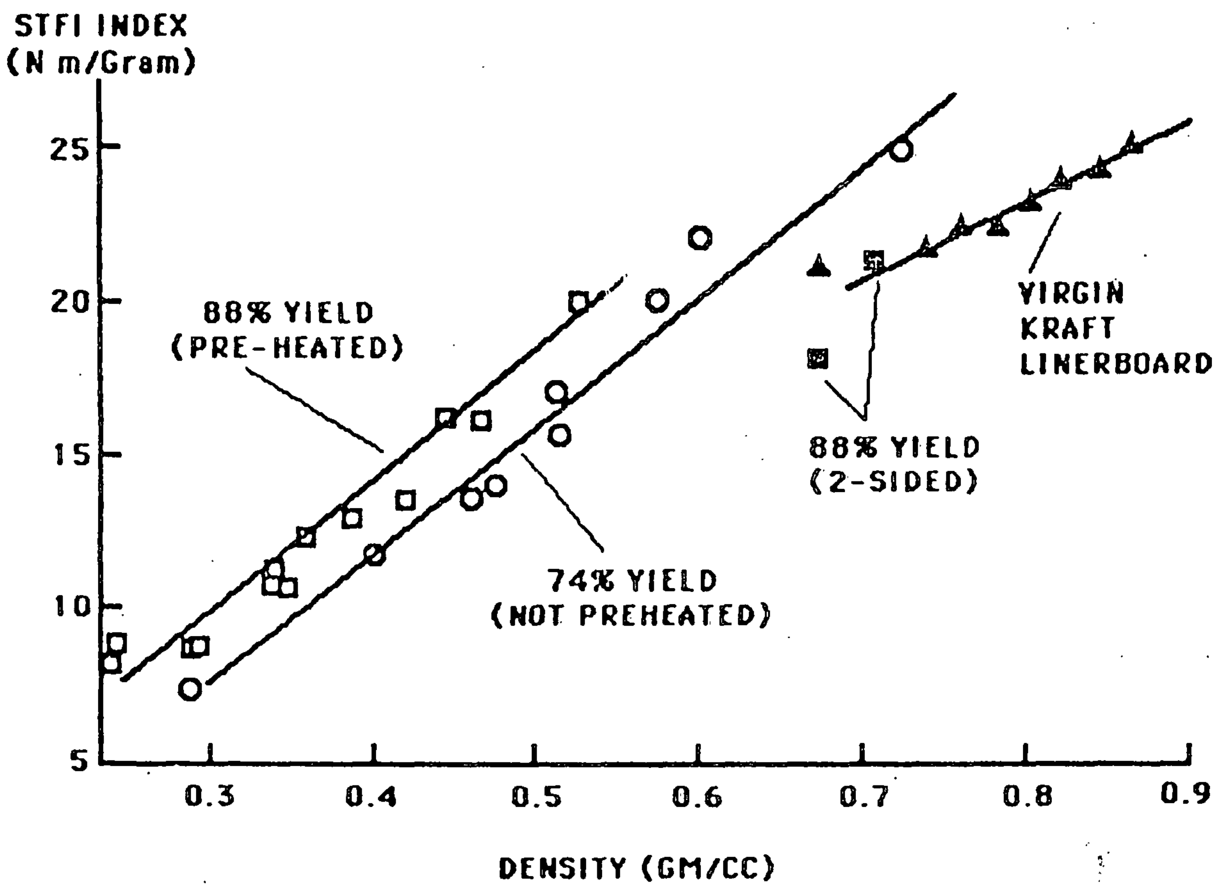
MAXIMUM BURST INDEX VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (LOWER LINE) AND PRESULFONATED PULPS.



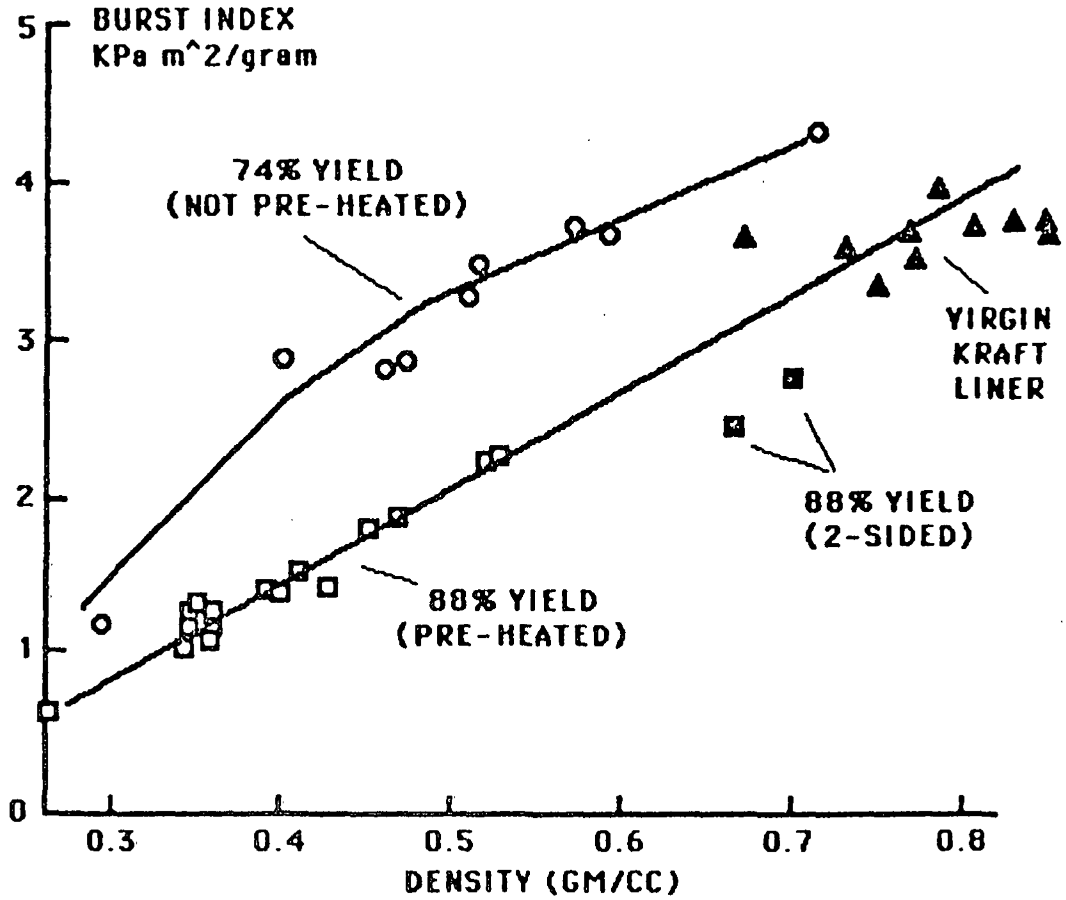
MAXIMUM TEAR FACTOR VS. FIBERIZATION TEMPERATURE FOR UNSULFONATED (LOWER LINE) AND PRESULFONATED PULPS.

INTEGRATED PROCESSING:

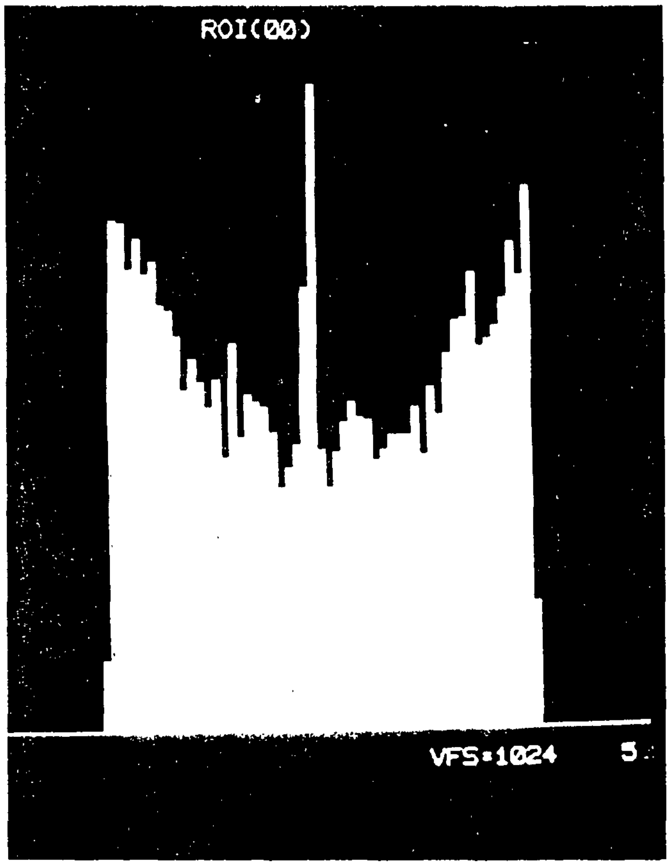
IMPULSE DRYING OF
HIGH YIELD FIBER



STFI - DENSITY RELATIONSHIP
HIGH-YIELD CMP SAMPLES



BURST INDEX - DENSITY RELATIONSHIP
HIGH-YIELD CMP SAMPLE



SULFUR CONCENTRATION (STEM-EDS SULFUR COUNTS) ALONG A LINE TRAVERSING A DOUBLE CELL WALL IN A RADIAL CROSS SECTION OF A SULFONATED SOUTHERN PINE CHIP.

RELATED ACTIVITIES

- PH.D. RESEARCH: T. HEAZEL (SULFUR DISTRIBUTION)
- M.S. RESEARCH: T. CORNBOWER (BIOCHEMIMECHANICAL PULPING)
- PROJECT 3470 (IMPULSE DRYING)
- PROJECT 3469 (ULTRASONIC CHARACTERIZATION OF PRETREATED WOOD)
- PROJECT 3526 (INTERFIBER BONDING AT HIGH YIELDS)
- USDA FOREST PRODUCTS LAB (ZERO SPAN TESTING OF PRETREATED WOOD)

PLANS

- SINGLE FIBER STUDIES
  - RESOLVE FRACTIONATION ANOMALY
  - EXAMINE FAILURE MECHANISMS, SITES
  - DETERMINE EFFECT OF SULFONATION ON AREA
  - DETERMINE EFFECT OF FIBERIZATION VARIABLES
  - RELATE TO FIBRIL ANGLE
  - RELATE TO FIBER SHORTENING

PLANS

- Complete spruce fiberization factorial experiment
- Artificial bonding experiments
- Effect of yield on impulse drying behavior
- Literature review: Factors affecting fiber strength
- Investigate mathematical cell wall models
- Reports: Preliminary Experiments
  Wood Section Zero Span Strength
  Fiberization Studies

PLANS

- Mount effort to obtain pilot refiner
- Identify site and prepare refiner pulps for fiber characterization studies