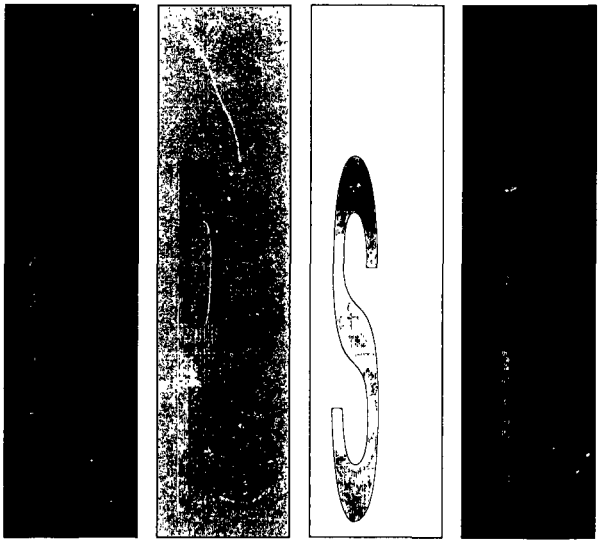
Institute of Paper Science and Technology

CHEMICAL PULPING AND BLEACHING

ANNUAL RESEARCH REVIEW

HANDOUT BOOK

April 2, 1991



Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

HANDOUT BOOK

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TABLE OF CONTENTS

WOOD CHEMISTRY GROUP OVERVIEW

WOOD CHEMISTRY GROUP

FACULTY: DONALD DIMMEL
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CRYSTAL TUCKER

VISITING SCIENTIST: KEN-ICHI KURODA

COOPERATING ORGANIZATIONS:
SERI
BATTELLE

WOOD CHEMISTRY

M.S. STUDENT RESEARCH

KAREN HODKIEWICZ (RAGAUSKAS)
CHARACTERIZATION OF SPENT BLEACH LIQUORS USING NMR SPECTROSCOPY

MICHAEL OSBORN (SONNENBERG)
THE EFFECTS OF MODIFYING BLEACHING PROCESSES ON ENVIRONMENTAL FACTORS

DAVID SAWYER (DIMMEL)
THE SYNTHESIS OF AN INSOLUBLE LIGNIN MODEL

ROSANN KAYLOR (DIMMEL)
SYNTHESIS AND DEGRADATION STUDIES OF A CELLULOSE MODEL COMPOUND

PULPING STUDIES

Project 3661 (DOE FUNDED)

SULFUR-FREE SELECTIVE PULPING PROCESS

Start: 9/1/88
End: Indefinite *Dimmel* *$207,700*

Project 3477

DEVELOPMENT OF NEW ANALYTICAL METHODS

Start: 7/1/90
End: 6/31/91 *Banerjee* *$15,000*

PRODUCT UTILIZATION STUDIES

Project 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

Start: 10/1/90
End: Indefinite *Ragauskas* *$150,000*

BLEACHING STUDIES

Project 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

Start: Fall, 1977
End: 6/91 *Dimmel* *$120,000*

Project 3684 (API/NCASI FUNDED)

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART I: PRECURSOR FORMATION AND REACTIVITY

Start: 9/89
End: 6/91 *Sonnenberg* *$89,000*

Project 3685 (CHLORINE INSTITUTE FUNDED)

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II: CHLORINATION AND DIOXIN REACTIONS

Start: 7/1/90
End: 6/31/91 *Dimmel* *$180,000*

NEW PROJECT

FUNDAMENTALS OF BLEACHING CHEMISTRY
Dimmel, Sonnenberg, Ragauskas

Start: **July, 1991**
End: **Indefinitely**

Project 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

Start: 1979
End: Indefinite *McDonough/Reed* *$250,000*

Project 3699

EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS

Start: 5/90
End: 12/91 *Courchene* *$55,000*

Project 3716 (CKPG)

ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMICHEMICAL PULPING

Start: 9/4/90
End: Indefinite *McDonough/Woitkovich* *$75,000*

Project 3661
(DOE FUNDED)

SULFUR-FREE SELECTIVE PULPING PROCESS

OIT Sulfur-Free Selective Pulping Process

A joint project between the Institute of Paper Science and Technology and the Solar Energy Research Institute

Funded by the Office of Industrial Technologies
Mr. Stanley Sobczynski
Project Manager

Under DOE contract No. DE-ACO2-83CH10093
and subcontract No. XX-8-18169-1

Advantages of Lignin as a Raw Material

Lignin is inexpensive ($0.03-$0.04/lb).

Lignin is readily available.

Lignin contains structural units necessary for anthraquinone preparation.

Lignin easily undergoes the reactions proposed for anthraquinone synthesis.

Lignin is an abundant, renewable resource.

Process for Anthraquinone Synthesis

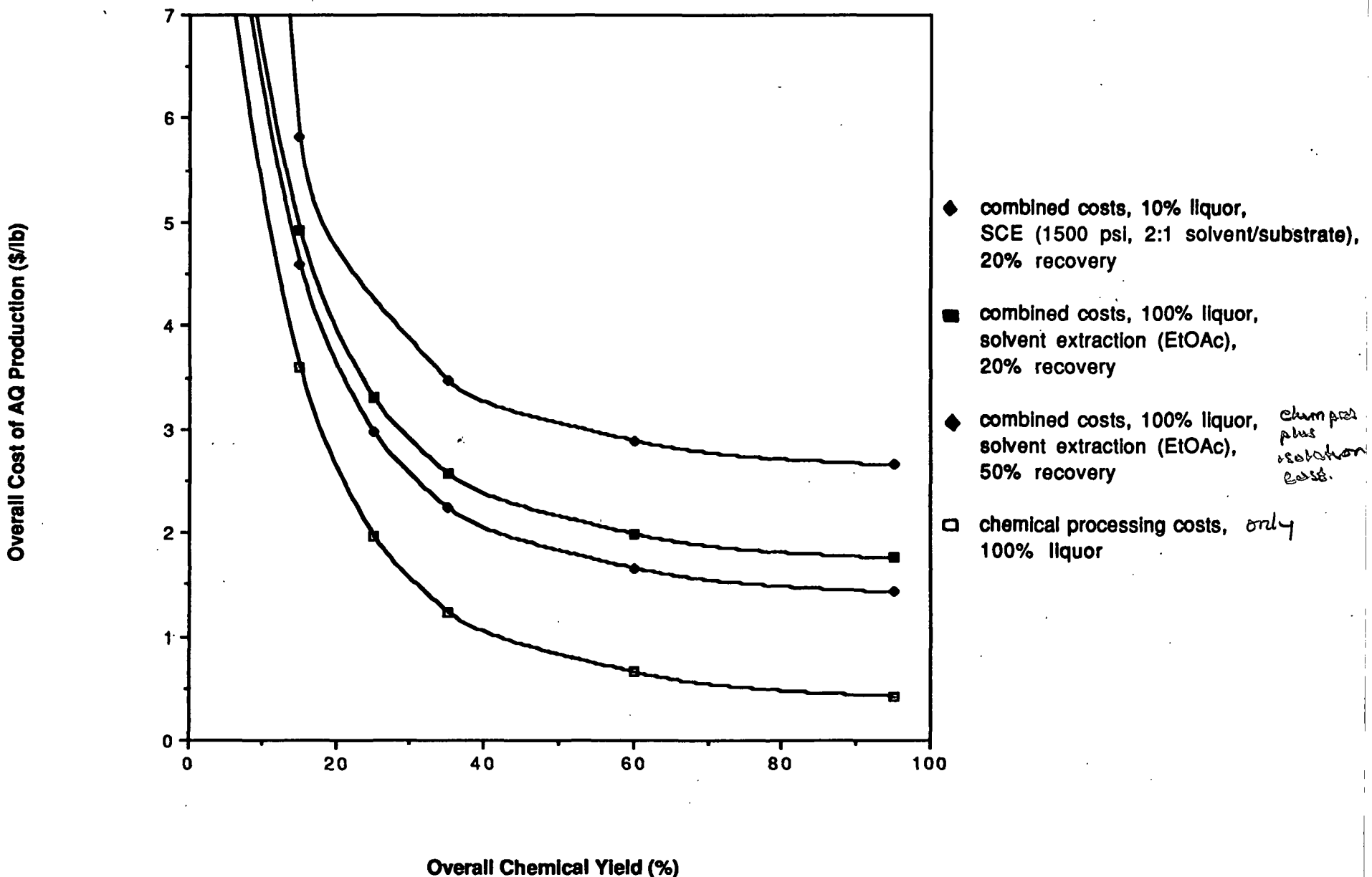
Stage 1: Lignin Processing

whole lignin —(separation)→ low molecular weight lignin

Stage 2: Chemical Processing

1. low molecular weight lignin —(oxidation)→ oxidation products (benzoquinones)
2. oxidation products (benzoquinones) —(diene)→ anthraquinone precursor
3. anthraquinone precursor —(hydrogen removal)→ anthraquinone

Projected AQ Amortized Production Costs



Economics of Competitive Routes

1. Anthracene oxidation

   "high costs"; no longer used in U. S.

2. Benzene/phthalic anhydride

   about $2.50-plus/lb; waste disposal problems

3. Phthalic anhydride

   about $2.50-plus/lb; new process, but operation appears expensive

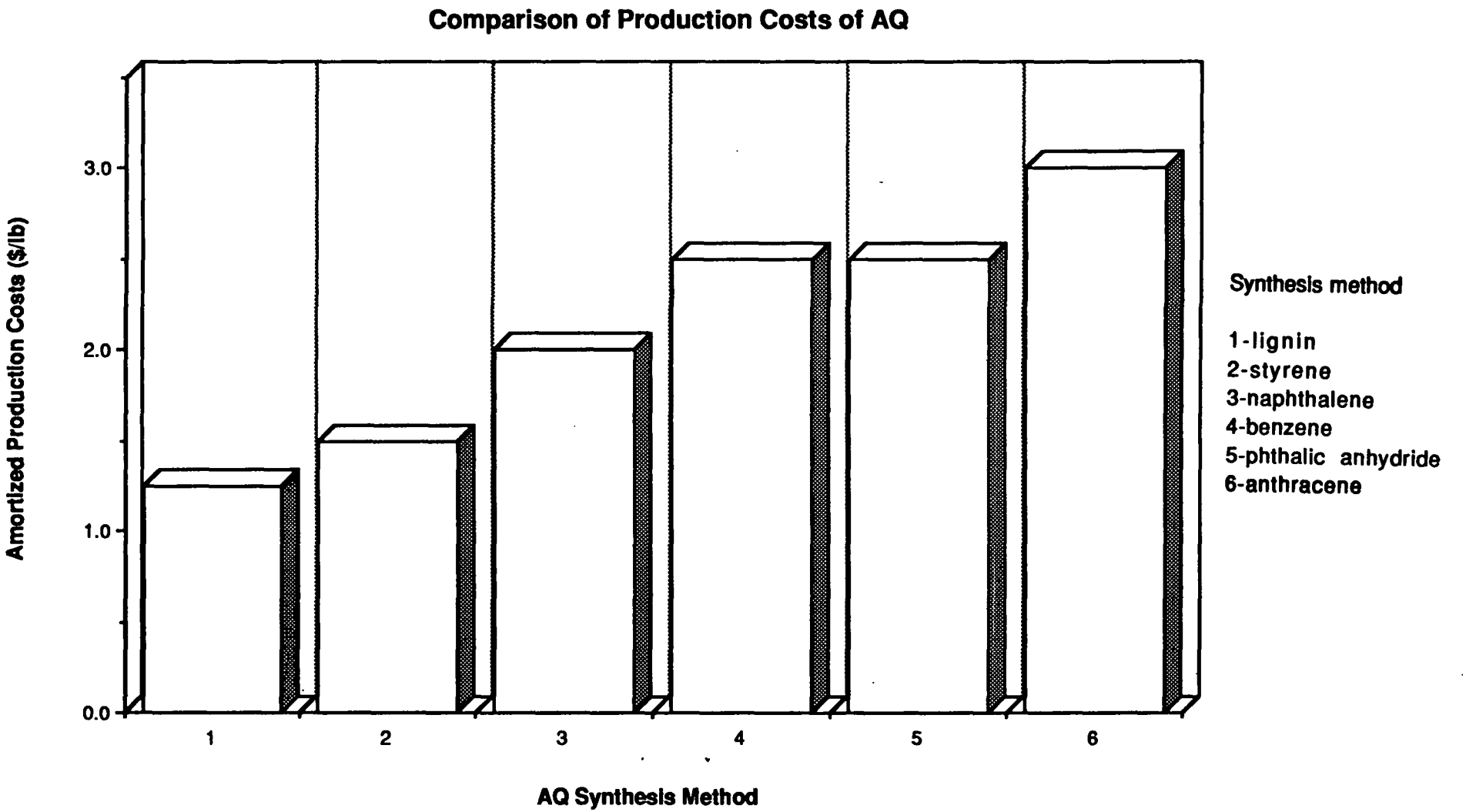
4. Naphthalene oxidation/butadiene addition

   $2.00/lb range; one attempted commercial application-abandoned due to technical difficulties. one Japanese installation

5. Styrene (BASF) route

   $1.50/lb on 100 M lb/yr. One attempt atcommercialization but later abandoned

Compare lignin based route at $1.25-$1.75/lb!



Amortized Production Costs of AQ Based on Starting Material

Process for Anthraquinone Synthesis

Stage 1: Lignin Processing

whole lignin —(separation)→ low molecular weight lignin

Stage 2: Chemical Processing

1. low molecular weight lignin —(oxidation)→ oxidation products (benzoquinones)
2. oxidation products (benzoquinones) —(diene)→ anthraquinone precursor
3. anthraquinone precursor —(hydrogen removal)→ anthraquinone

Lignin Processing: Results

Stage 1: Lignin Processing

whole lignin —separation→ **low molecular weight lignin (mw<1000)**

Methods:

1. Supercritical fluid extraction.

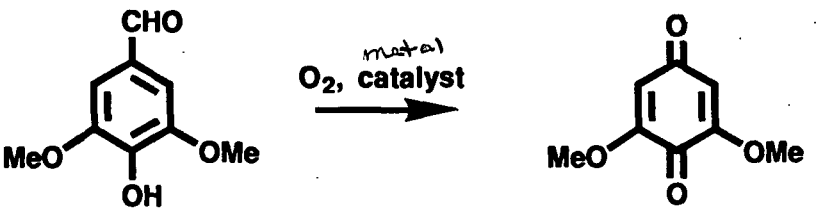
Results: Relatively low yield of lmw lignin, good yield of products after chemical processing.

2. Solvent extraction of organosolv lignins.

Results: Good yield of lmw lignin, lower yield of products after chemical processing. but sub reaction not as good as (1)

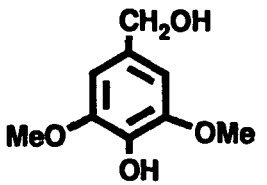
lmw ~ low mol. wt.

Metal Catalyzed Oxidation of Lignin Models

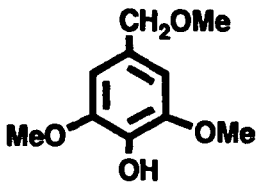


syringaldehyde

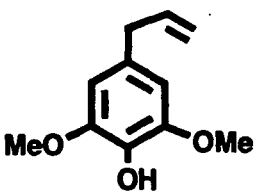
DMBQ, 97% selectivity at 84% conversion



45%, through syringaldehyde

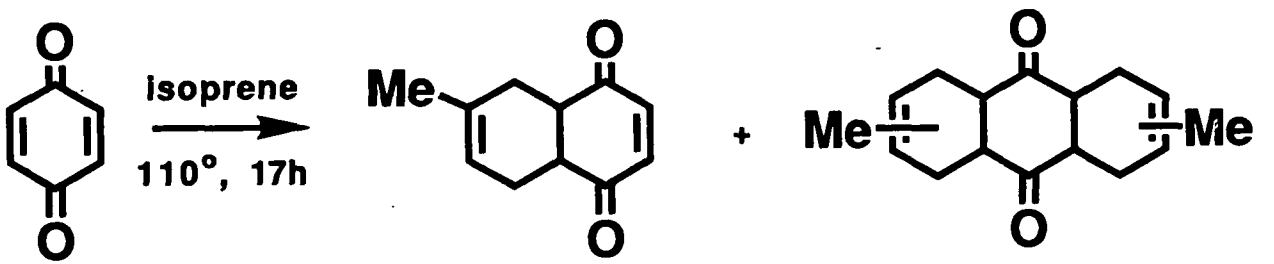


20%, through syringaldehyde

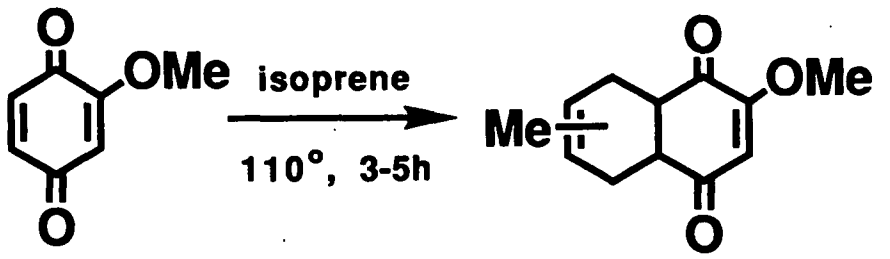


30-40%

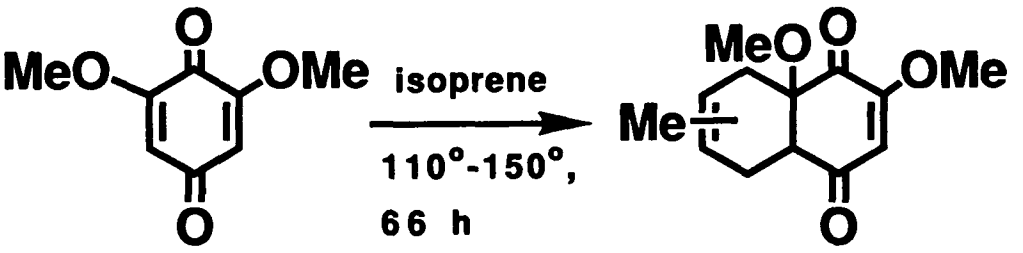
Diels-Alder Reaction of Benzoquinones



98% adduct,
68/30 mixture



75%

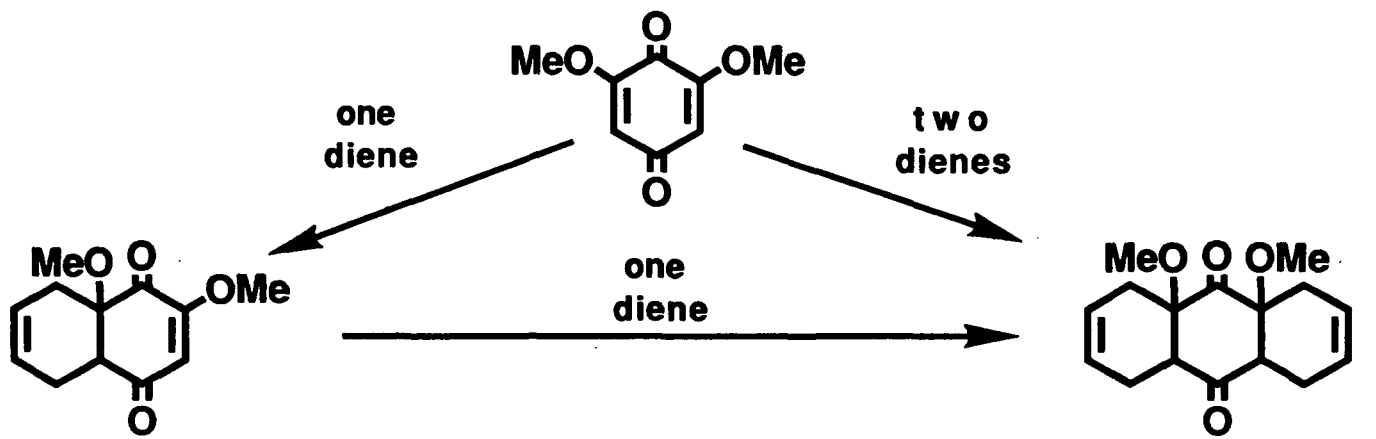


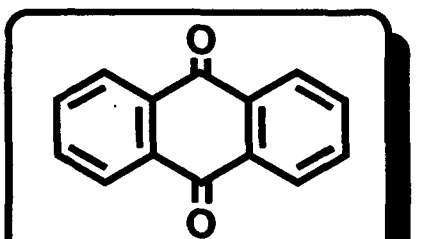
88%

Results of Chemical Processing

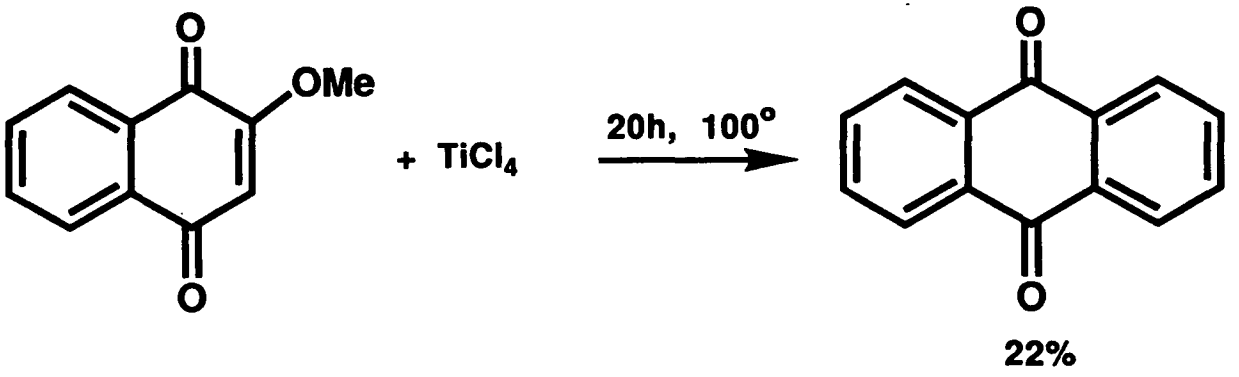
Stage 2: Chemical Processing

2. oxidation products (benzoquinones) —diene→ **anthraquinone precursor**

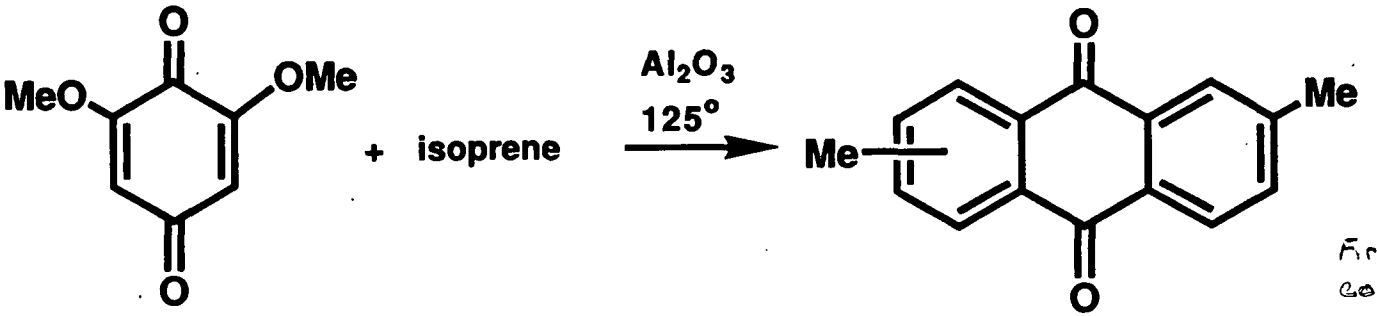




Other Approaches to Diels-Alder Adducts



22%



20-50%

First example of direct conversion to anthraquinone

Summary of Results

Process Economics

Lab research has given a factor of 10 drop in projected cost in only 18 months.

Stage 1: Lignin Processing

The amount of useable material extracted has been increased from 10% to 50%.

Stage 2: Chemical Processing

Significant progress has been made in each step of this stage:

Nitrogen dioxide allows oxidation of both types of lignin substructures.

Catalysis could allow use of inexpensive oxygen or air as an oxidant.

All oxidation products undergo reaction to form the anthraquinone skeleton.

Catalysis of the anthraquinone-forming step allows a direct, one-step conversion of benzoquinones to anthraquinones and streamlines the process.

PROJECT 3661 OBJECTIVE

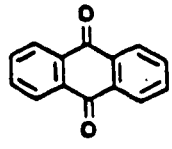
DEVELOP A SELECTIVE/ECONOMICAL PULPING SYSTEM BASED ON THE USE OF PULPING CATALYSTS GENERATED FROM LIGNIN

POTENTIAL BENEFITS

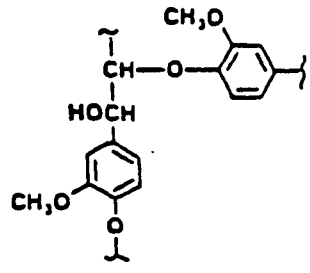
- GREATER PRODUCTIVITY
- LOWER ENERGY INPUTS
- LOWER BLEACHING COSTS/BY-PRODUCTS
- SIMPLIFIED RECOVERY SYSTEM
- CONSERVATION OF RAW MATERIALS

CATALYSTS FROM LIGNIN

JOHN WOZNIAK, Ph.D. THESIS

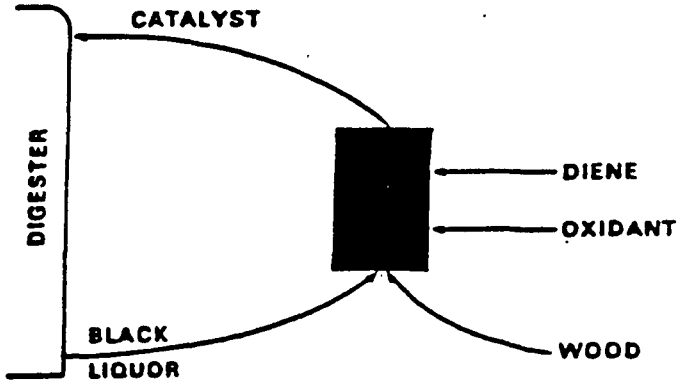


ANTHRAQUINONE



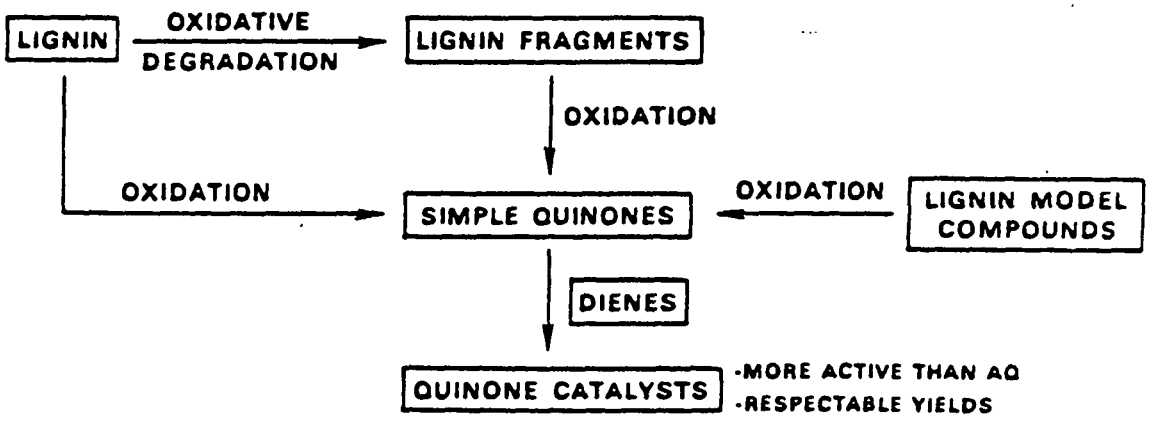
LIGNIN UNIT

CATALYSTS FROM LIGNIN APPROACHES



CATALYSTS FROM LIGNIN

RESULTS



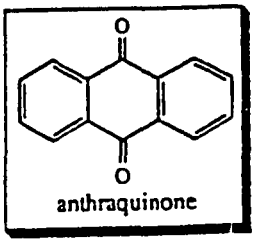
OIP Sulfur-Free Selective Pulping Process

A joint project between the Institute of Paper Science and Technolo
and the Solar Energy Research Institute

Funded by the Office of Industrial Programs
Mr. Stanley Sobczynski
Project Manager

Under DOE contract No. DE-ACO2-83CH10093
and subcontract No. XX-8-18169-1

Proposed Approach to Anthraquinone from Lignin

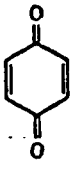


1) Lignin Processing

lignin $\xrightarrow{\text{separation}}$ low molecular weight fraction

2) Chemical Processing

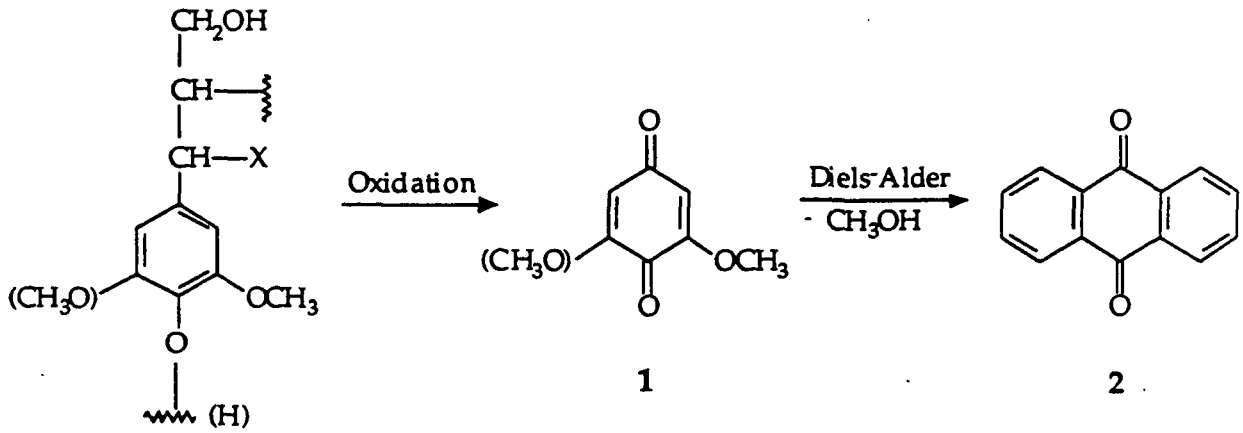
a) low molecular weight fraction $\xrightarrow{\text{oxidation}}$ benzoquinone mixture e. g.,



b) benzoquinone mixture $\xrightarrow{\text{diene}}$ anthraquinone precursor (The Diels-Alder reaction)

c) anthraquinone precursor $\xrightarrow[\text{catalyst}]{\text{dehydrogenation}}$ anthraquinone

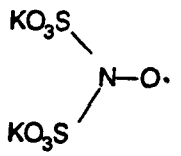
CHEMICAL STEPS IN THE CONVERSION OF LIGNIN TO ANTHRAQUINONE



LIGNIN

1

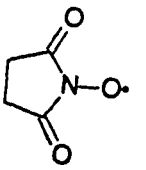
2



Fremy salt.

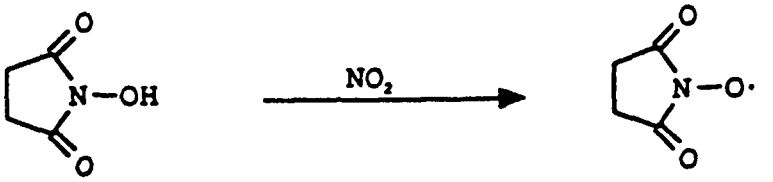
Expensive
Consumed
Requires >2 equivalents
Sometime explosive
Requires low reaction temperature
Reaction time is usually 2-5 hours

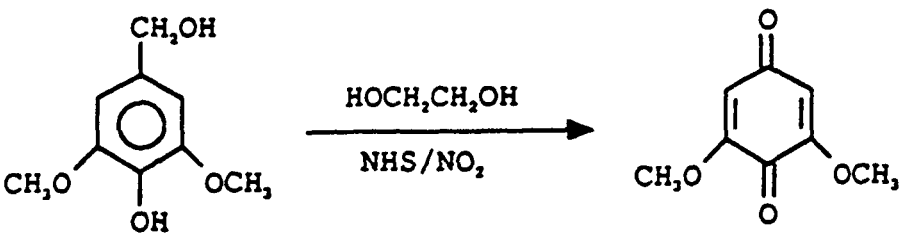
How About:



NHS
Not commercially available

N Hydroxy Succinimide





Good yield 90%

yield are lower when only one OH30 group present 3 < 20%

Table 12. Oxidation of SERI Lignin Samples by NO_2/NHS[a]

Lignin Source	% Yield DMBQ[b]	MBQ
Soluble white oak extract	6.5 (9.2)	Trace[c]
Soluble aspen extract	9.8 (9.8)	5.0
Soluble scarlet oak extract	7.7 (7.7)	1.07
White oak, insoluble	4.7 (5.1)	Trace[c]
Aspen, insoluble	4.7 (5.2)	0.75
Scarlet oak, insoluble	3.5 (3.5)	0.0

[a] 24 hours, 60 mg NO_2/50 mg lignin, NHS = 60 mg, 5 mL MeOH, rt.
[b] Numbers in parenthesis are yields calculated by HPLC.
[c] Trace = <0.5%.

Yields by ecol. are lower with H_2O_2 than with NHS.

Table 14. Oxidation of SERI lignin samples by hydrogen peroxide[a]

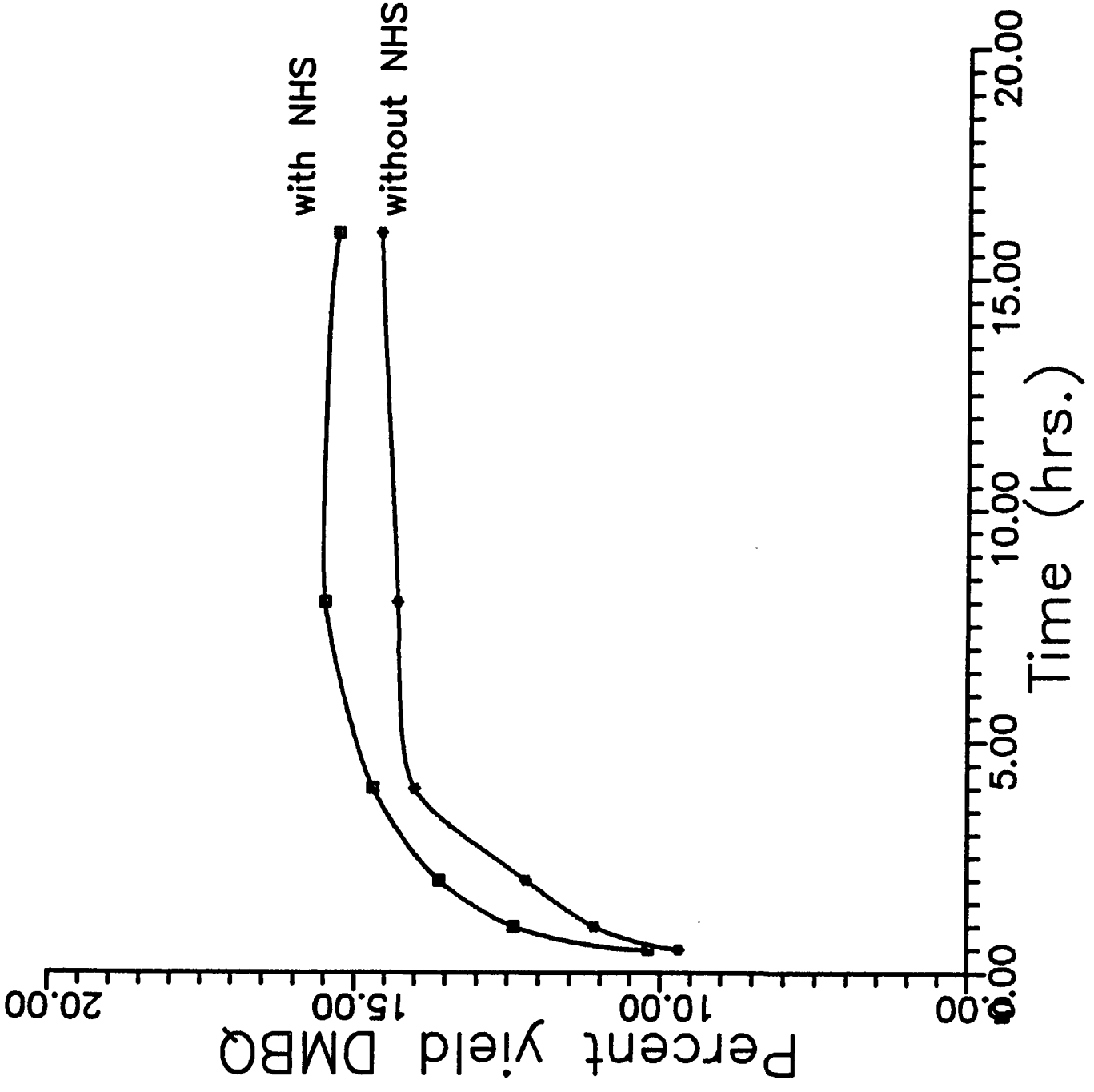
Lignin Source	Actual % Yield DMBQ[b]	% Syringaldehyde in extract[b,c]	% Vanillin in extract[b,c]
Soluble white oak extract	1.7	0.8	0.4
Soluble aspen extract[d]	2.1	9.3	3.0
Soluble scarlet oak extract	1.7	0.8	0.3

[a] 3.3 equiv. of H_2O_2/lignin monomer unit, starting pH 11, rt.
[b] Yields by HPLC.
[c] Sample analysis before reaction.
[d] MBQ was observed at a level corresponding to a 7% conversion of the available vanillin.

Table 13. A comparison of lignin oxidation results with NO_2/NHS.[a]

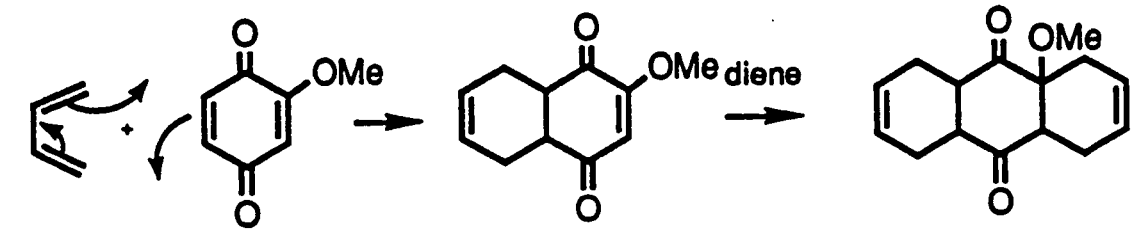
Lignin	DMBQ yield, %	MBQ yield, %
Hardwood kraft lignin 1[b]	5.0	Trace
Hardwood kraft lignin 2[c]	7.2	Trace
Hardwood ethanol lignin[d]	6.2	1.0
Organosolv aspen lignin[e]	7.9	2.1

[a] Ratio of NO_2/NHS/lignin monomer was 3/2/1.
[b] Experimental lignin from Westvaco.
[c] Experimental lignin from Westvaco different from above.
[d] Sample generated by SERI from an ethanol pulping process.
[e] Sample generated by SERI, but different from those in Table 12.

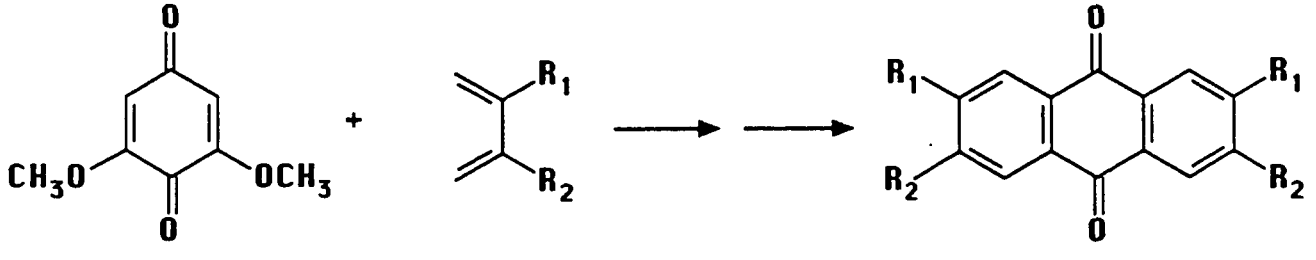

Percent yield DMBQ
0.00
5.00
10.00
15.00
20.00
Time (hrs.)
0.00
10.00
15.00
20.00
with NHS
without NHS

LIGNIN DEGRADATION PRIOR TO OXIDATION

(1) H_2O_2/NaOH oxidation
(2) Acidolysis ✓
(3) H_2O_2/NaOH oxidation after acidolysis
(4) CuO/NaOH oxidation
(5) $NaBH_4$ reduction ~
(6) CuO/NaOH oxidation and $NaBH_4$ reduction
(7) Kraft
(8) Sulfite
(9) Ozone



diene dienophile monoadduct typical bisadduct anthraquinone precursor



benzoquinone (DMBQ) diene AQ analog (R_1, R_2 = H, CH_3)

LONG-TERM RESEARCH AREAS 9/SERI

- Optimize oxidation yields for 2-3 reagents.
- Test best oxidants on low molecular weight lignin samples.
- Screen lignin samples for potential to generate quinone catalyst.
- Optimize Diels-Alder reaction yields.
- Continue economical evaluation updates.
- Select oxidation agent, starting lignin, diene, and quinone for commercial development.
- Scale up.

FUNDAMENTALS

OF

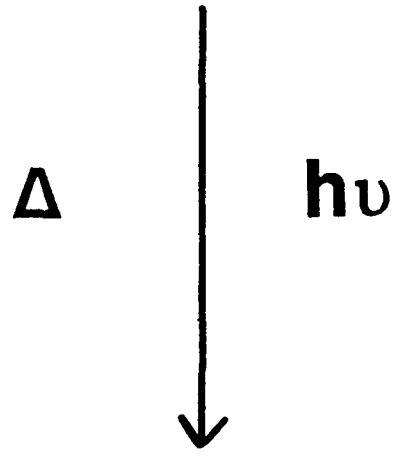
BRIGHTNESS STABILITY

PROJECT 3524

Dr. A.J. Ragauskas

INTRODUCTION

Bleached and/or Unbleached Mechanical Pulp



Yellowed Mechanical Pulp

Yellowing (catalyzed)
1) **Thermally**
2) **Photochemically**

Principal focus of this project is photo-yellowing

PHOTO-YELLOWING PARAMETERS

Important Experimental Parameters

1) λ = 300 - 400 nm

2) O_2 is required

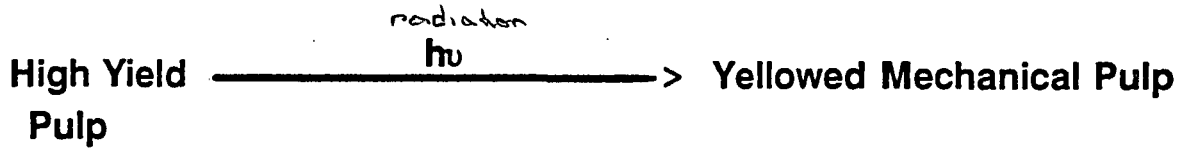
Yellowing Components

1) ortho quinones

2) para quinones

3) quinone derivatives

FUNDAMENTAL PARAMETERS OF BRIGHTNESS REVERSION



Reaction Parameters

- photo-yellowing process is initiated by the absorption of light by lignin

- cellulose and hemi-cellulose are not involved in the photo-initiate process but may contribute to secondary reactions

- extractives, moisture content, pH, and common inorganic salts have little impact on the rate of yellowing

Process Parameters

- variations in

1) mechanical pulping techniques

2) bleaching procedures

3) chemical additives

have not yielded a commericial viable means of controlling brightness reversion

PROJECT 3524 OBJECTIVES

Investigate the fundamental chemical reactions which are initiated when high yield pulps are photolyzed and to apply this knowledge to stop or significantly retard the yellowing process.

Research Directions

(i) the photo-formation of chromophoric structures employing model compounds and TMP

(ii) the photo-reactivity of chromophoric structures employing model compounds and TMP

(iii) the design of novel photostabilization techniques for mechanical pulp.

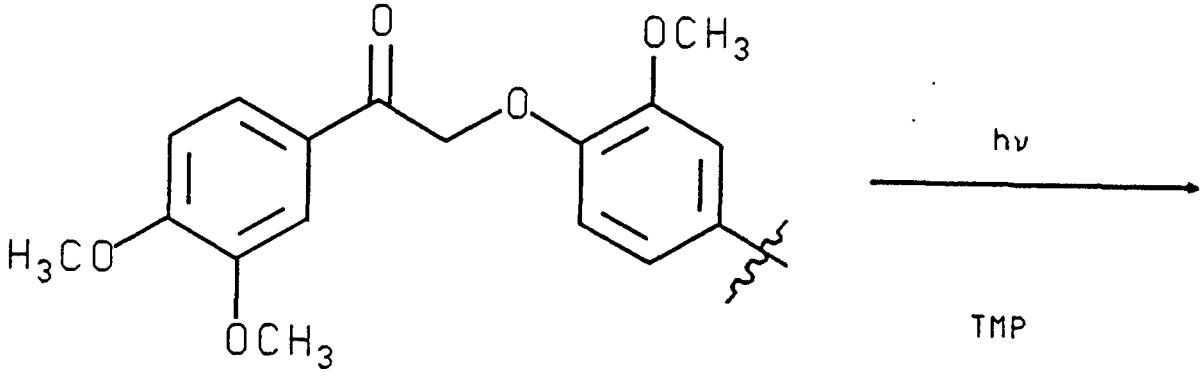
FUNDAMENTALS OF BRIGHTNESS REVERSION

High Yield Pulp $\xrightarrow{h\upsilon}$ Yellowed Mechanical Pulp

AIM OF CURRENT STUDIES

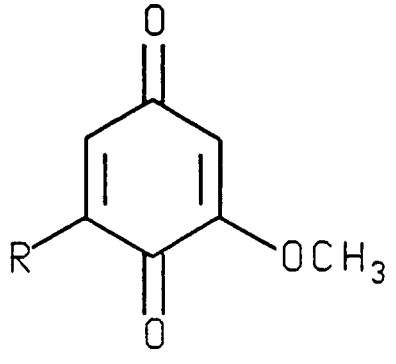
A/ **Investigate the fundamental photochemical initiation steps involved in the brightness reversion process**

i.e./



B/ Examine the photochemical behavior of quinones under the brightness reversion conditions

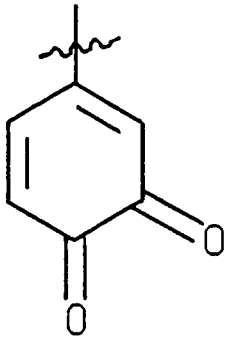
i.e./



R= H, OCH_3

$h\nu$ ⟶

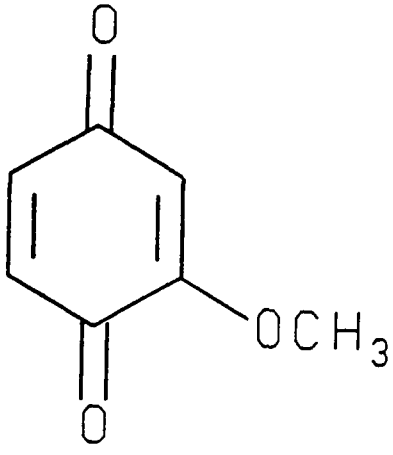
TMP



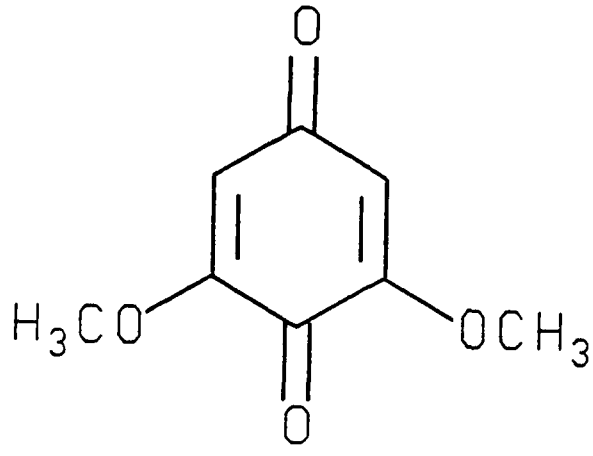
STUDIES DIRECTED AT INVESTIGATING THE PHOTO-REACTIVITY OF QUINONES UNDER THE BRIGHTNESS REVERSION CONDITIONS

Compounds of Interest

Para Quinones



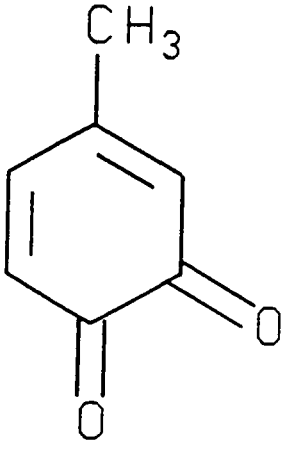
MMBQ

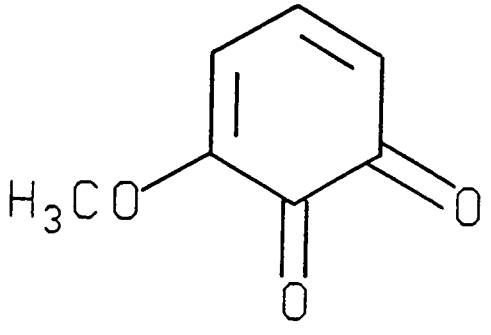


DMBQ

- frequently proposed as contributing to the yellowing of mechanical pulp, some UV/IR data supports the presence of these structures

Ortho Quinones





- detected in mechanical pulp by employing chemical derivatization and ^{31}P NMR

Photochemical behavior of these types of compounds in the solid state is currently poorly defined

PREPARATION OF QUINONES

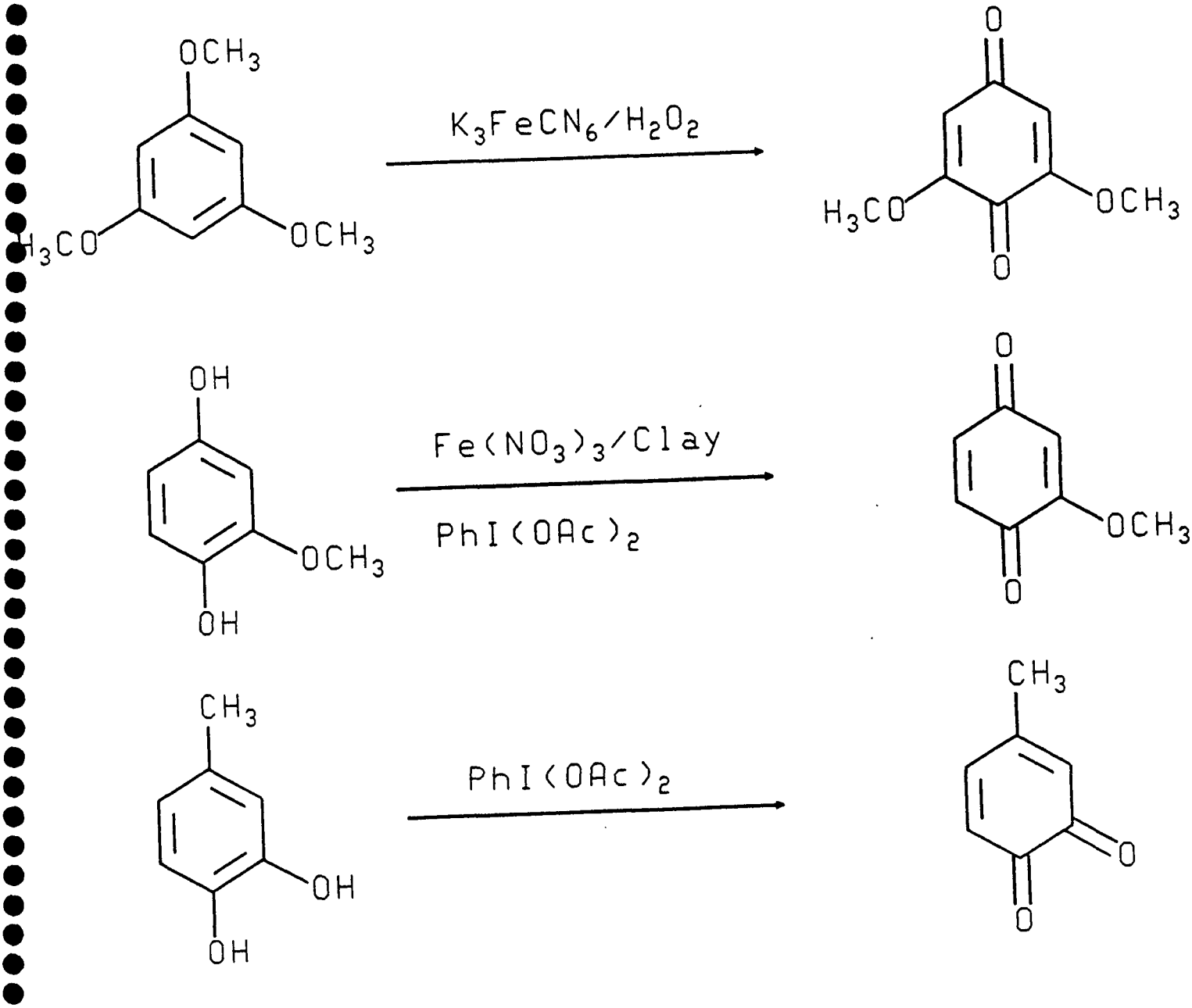
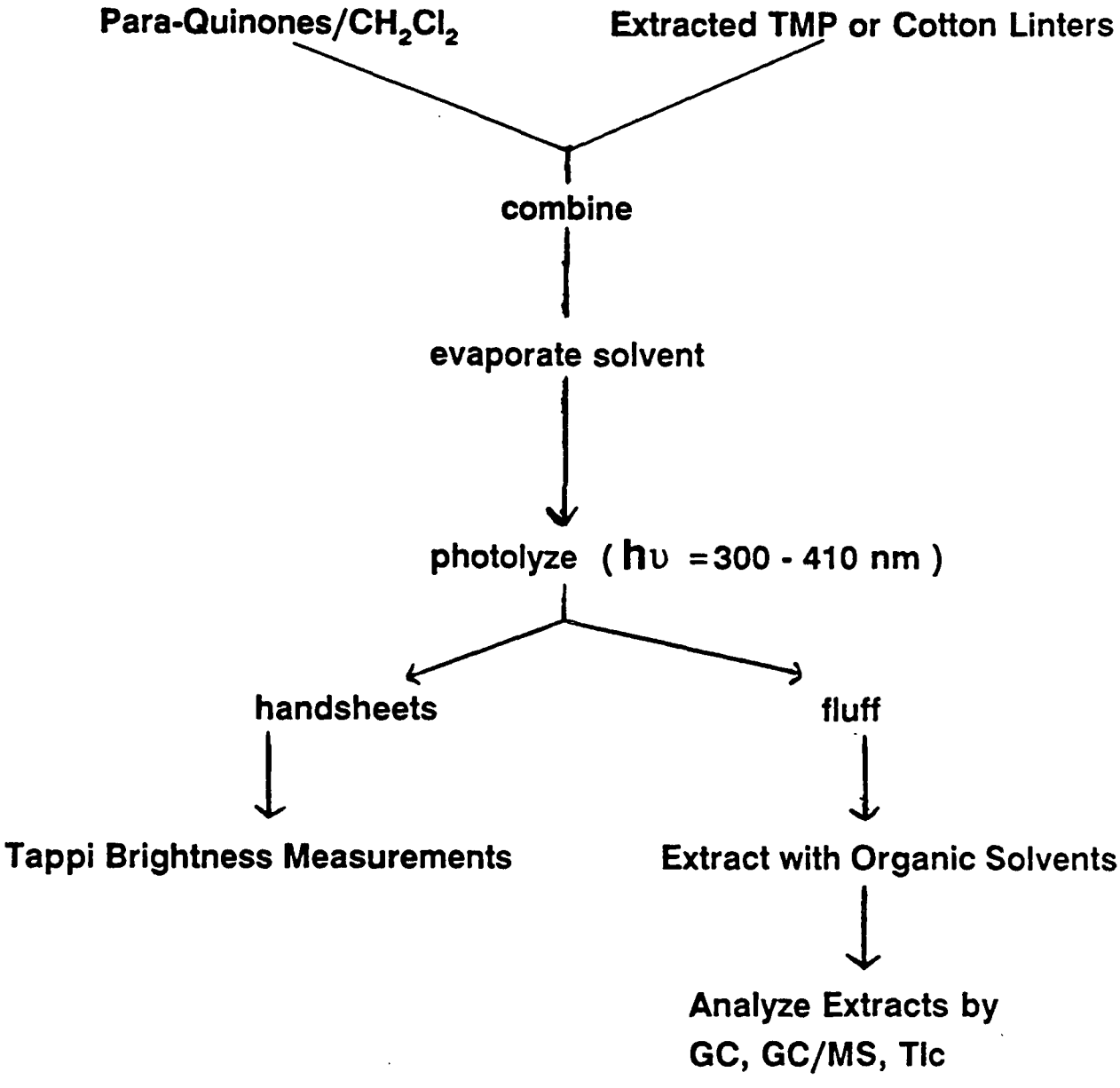


PHOTO-CHEMICAL STUDIES OF PARA-QUINONES

Experimental Procedures



-para quinones were selected as initial targets in this study due to ease in preparation and handling

PHOTOLYSIS OF DMBQ IN THE SOLID-STATE

DMBQ/Cotton Linter Fluff

Period of Irradiation (h)	% DMBQ Recovered[a]
0	93
1	81
2	73
4	69
8	76

a - GC yields, no other compounds were detected in the extracts

- prolonged irradiation for > 24 h did result in the formation of a variety of minor dimeric components (< 10% by GC/MS)

DMBQ/Cotton Linter Handsheet

Period of Irradiation (h)	Sample	Tappi Brightness	
		Trial 1	Trial 2
0	Cotton Linter	89	
0	Cotton Linter\DMBQ	38	42
1	Cotton Linter	88	
1	Cotton Linter\DMBQ	40	43
2	Cotton Linter	88	
2	Cotton Linter\DMBQ	44	42
4	Cotton Linter	89	
4	Cotton Linter\DMBQ	56	42

-brightness measurements demonstrate that the handsheets are not undergoing photo-bleaching

-DMBQ/cotton linter experiments suggest that DMBQ is stable to the brightness reversion conditions

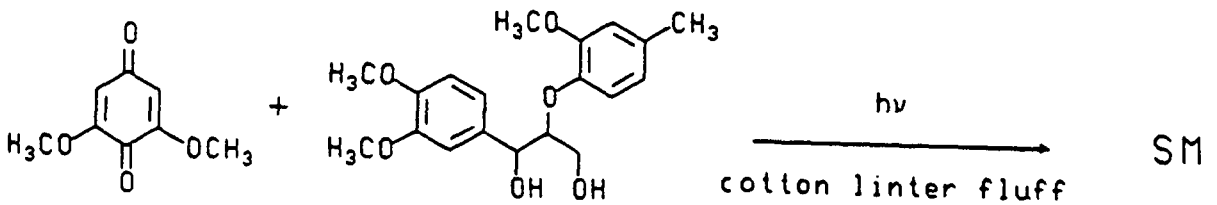
DMBQ/TMP Fluff

Period of Irradiation (h)	% DMBQ Recovered[a] (GC Yields)
1	83
2	100+[b]
4	76
8	100+[b]

a - no other major components were detected in the extracts

b - samples gave greater than 100% yields since the reaction mixture is not homogeneous

DMBQ/Lignin Model Compound/Cotton Linter Fluff



Conclusion: **DMBQ appears to be photo-stabile under the brightness reversion conditions and does not lead to the formation of singlet oxygen or other oxidative processes.**

PHOTOLYSIS OF MMBQ IN THE SOLID-STATE

MMBQ/Cotton Linter Fluff

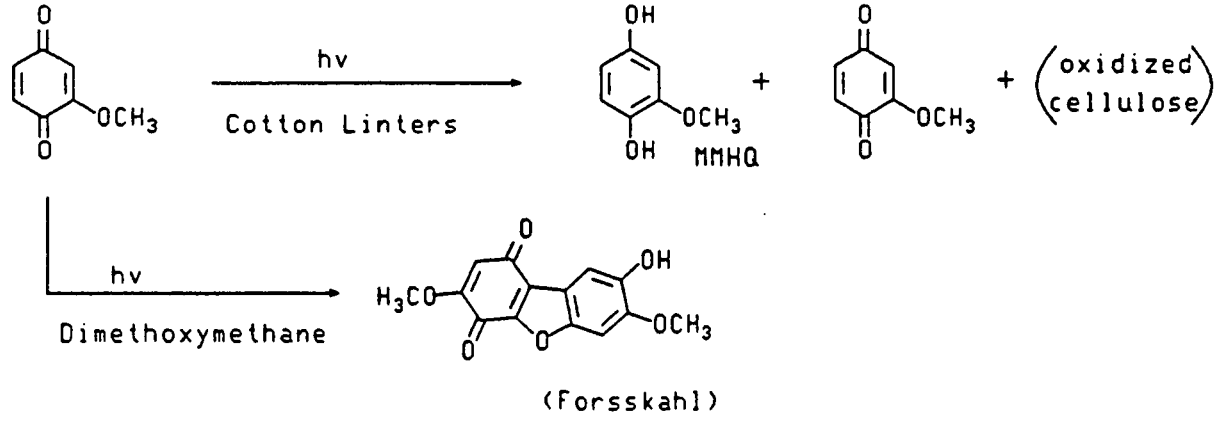
Period of Irradiation (h)	% MMBQ Recovered[a]	% MMHQ[a]
0	82	
1/2	65	6
1	58	5
2	65	5
4	70	8

a - GC yields, no other compounds were detected in the extracts

- MMHQ = monomethoxyhydroquinone

- GC analysis indicates that the mayor product from photolysis is the reduced MMBQ

MMBQ/Cotton Linter Fluff



(Forsskahl)

MMBQ/Cotton Linter Handsheets

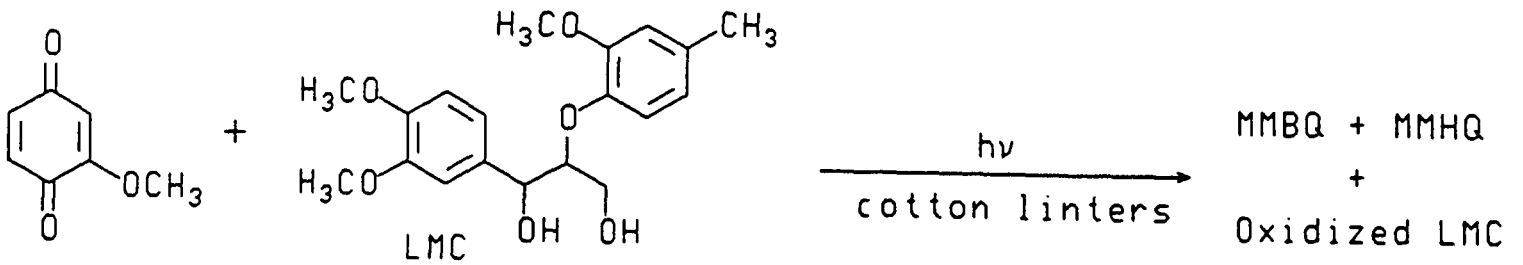
Period Irradiation (h)	TAPPI Brightness
0	44
1	35
2	32
4	33

-the cause of the brightness decrease has not been identified, but an attractive possibility is the formation of a charge complex between MMBQ and MMHQ

-the photo-reduction of MMBQ could provide a mechanism by which cellulose could be involved in the brightness reversion phenomena

-these results highlight the potential differences that can occur between solution and solid state photochemistry reactions

MMBQ/Lignin Model Compound/Cotton Linters



-experimental analysis suggests that lignin type structures are photoreactive to MMBQ

MMBQ/TMP Fluff

Period Irradiation (h)	% MMBQ Recovered[a]
0	100
1	18
2	28
4	24

a - GC yields

-fate of MMBQ on TMP currently remains uncertain but these results clearly suggest that MMBQ is not a final photochemical product in the brightness reversion phenomena

CONCLUSIONS

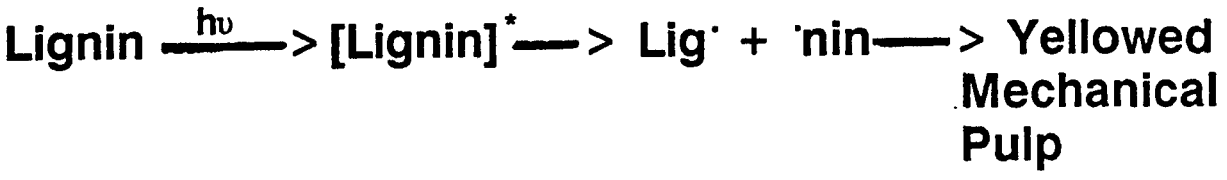
DMBQ appears to be relatively photo-stable under brightness reversion conditions.

MMBQ is photo-reactive under the brightness conditions and contributes to the "yellowing" of high yield pulp. Current studies clearly demonstrate differences in solution and solid phase photochemistry. Experimental results suggest that photolysis of MMBQ leads to the oxidation of lignin and cellulose.

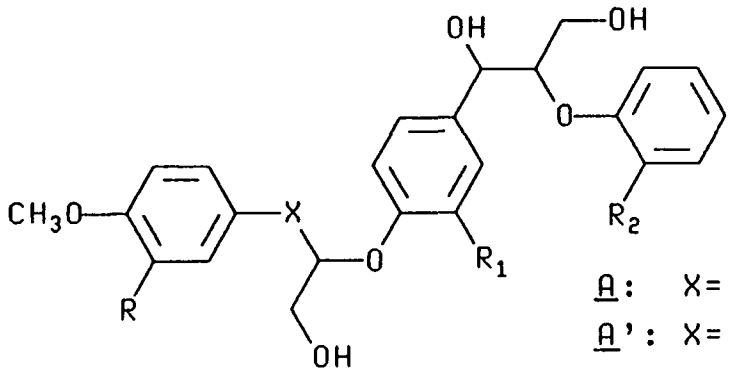
Research Efforts Directed At Studying

The Fundamental Photo-chemical Initiated

Oxidative Yellowing of High Yield Pulp

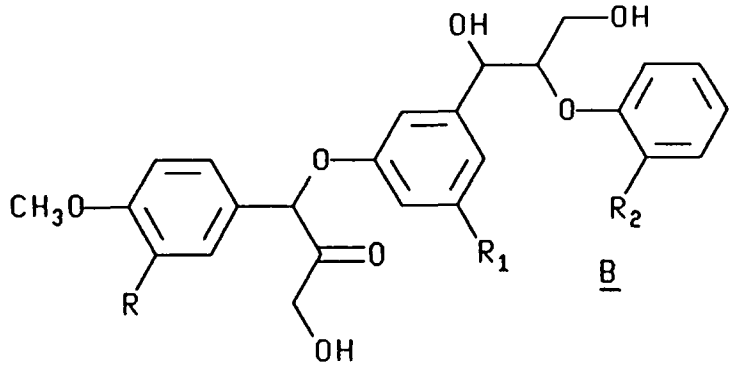


Lignin Model Compounds To Be Prepared

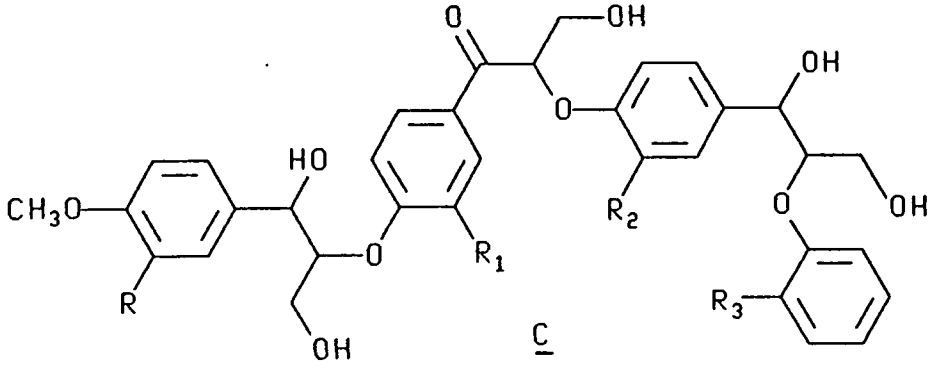


A: X= C=O

A': X= -CHOH-



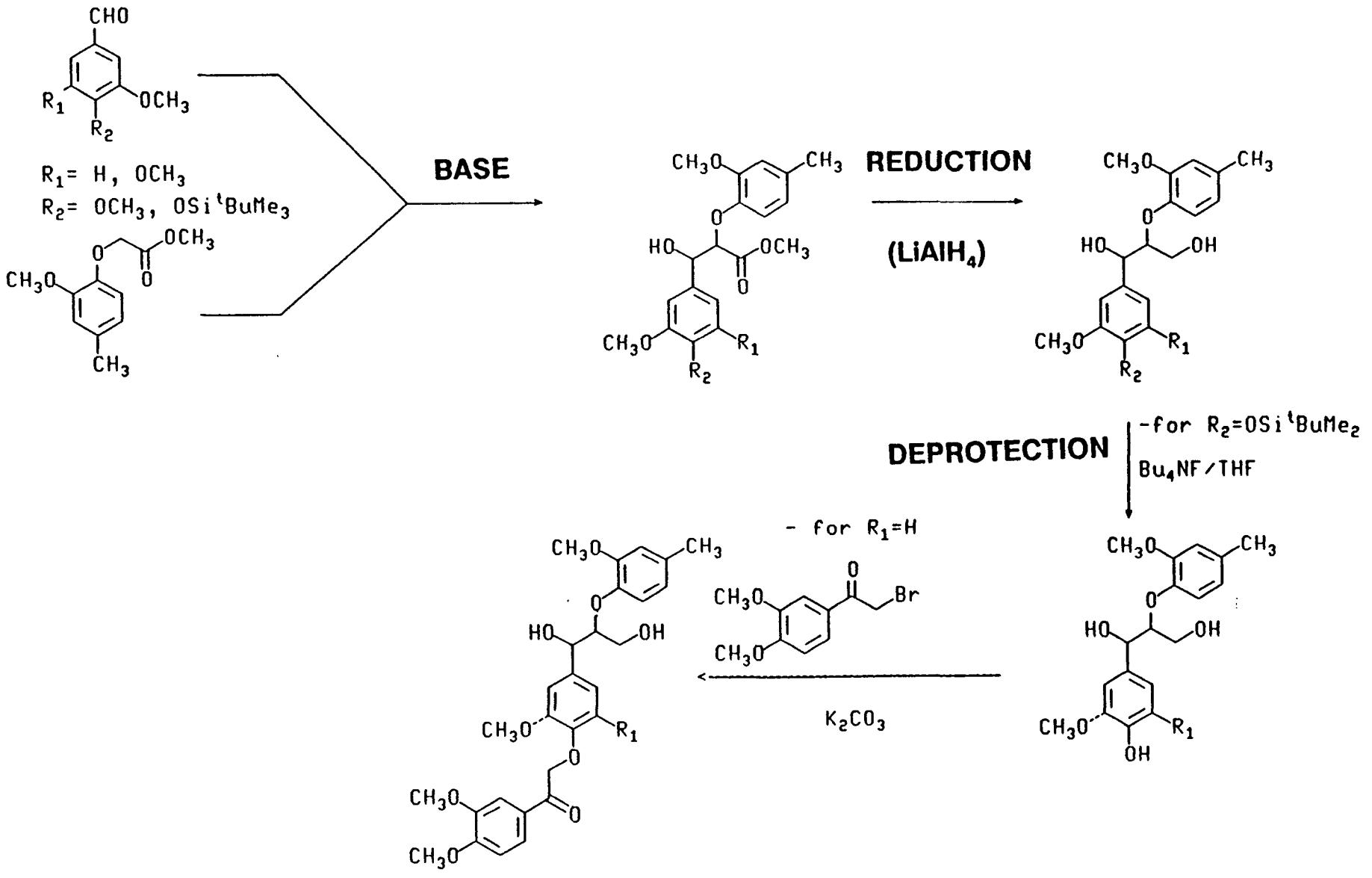
B



C

R, R_1, R_2, R_3= H, OCH_3

Synthesis of Lignin Oligomers

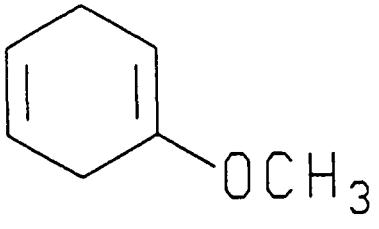


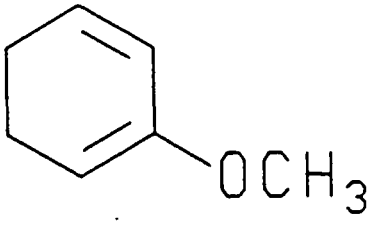
FUTURE GOALS

1/ Continue photochemical studies of MMBQ and ortho quinones adsorbed on TMP and cotton linters.

2/ Complete synthesis of lignin model compounds and start photolysis studies.

3/ Examine the use of Birch reduced aromatic systems as inhibitors for the brightness reversion process





PROJECT 3477

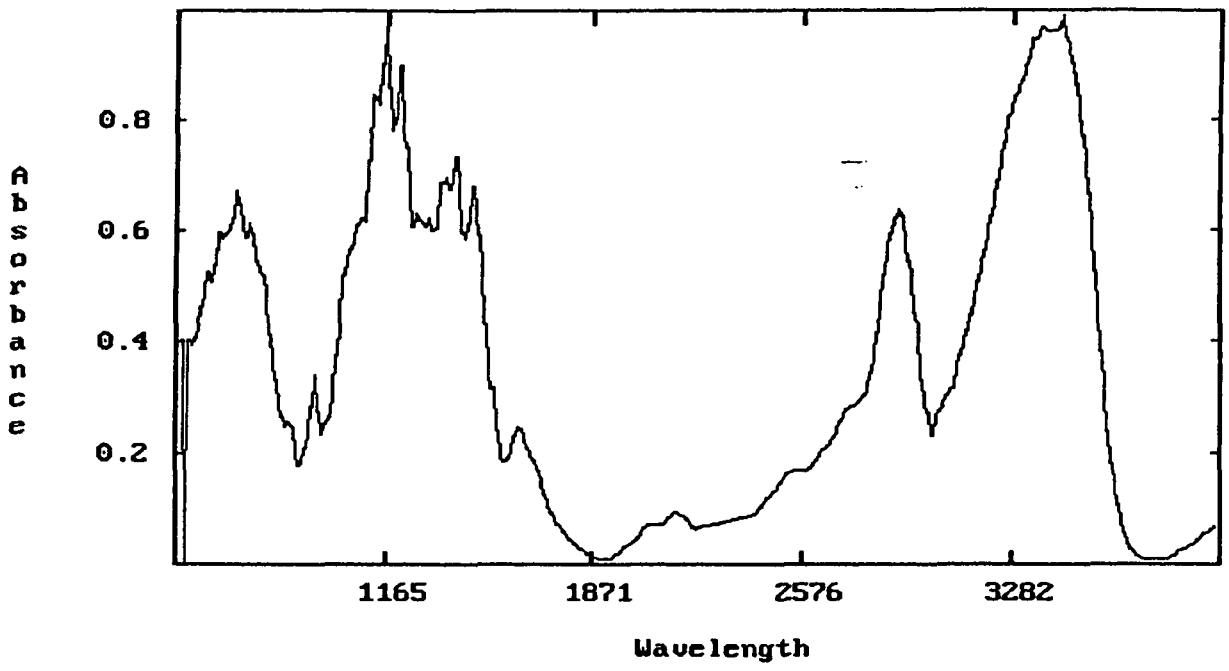
DEVELOPMENT OF NEW ANALYTICAL METHODS

April 2, 1991

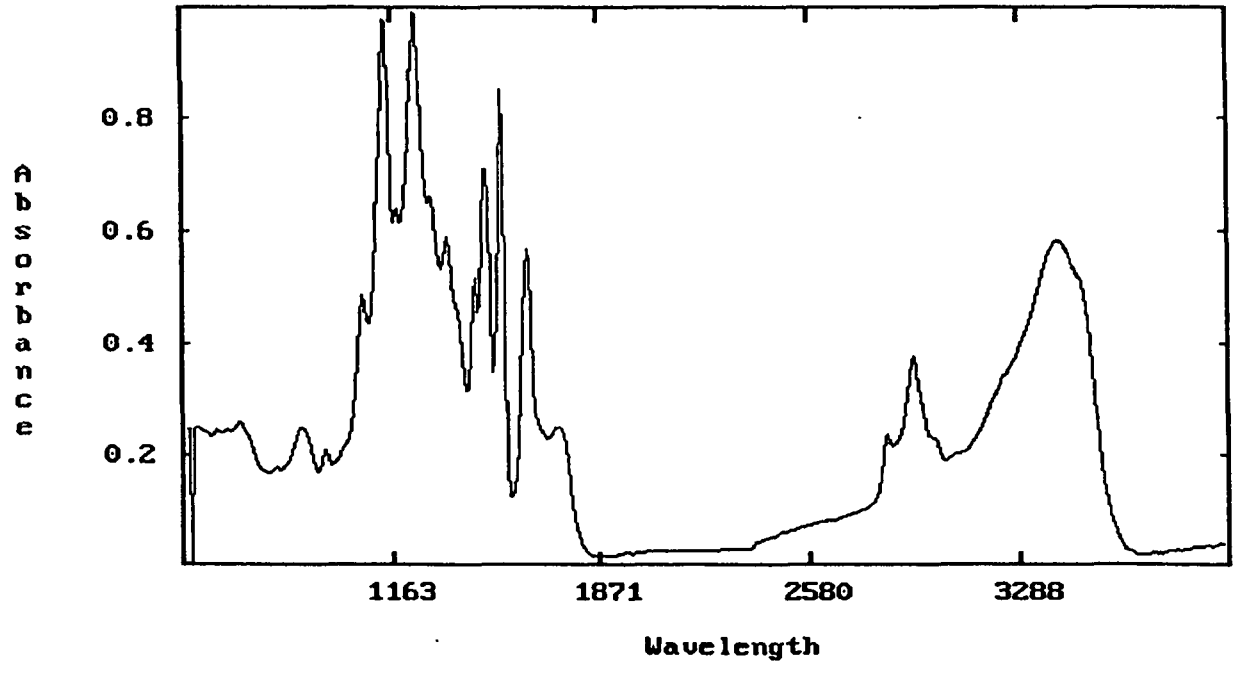
Sujit Banerjee

Purpose:

To develop an algorithm to automatically identify and quantify components in a mixture by IR spectroscopy.



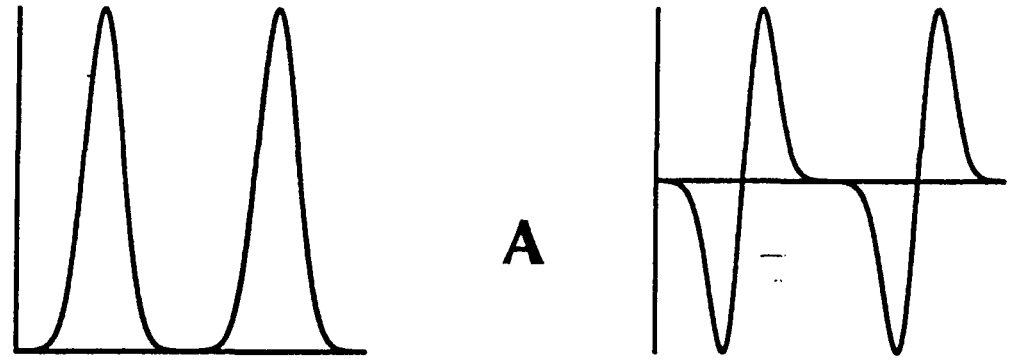
Unknown



Possible component?

Fitting a library spectrum to the target is difficult if the target is complex.

Multicomponent spectra have more lines than pure-component spectra. If a pure-component spectrum is exactly subtracted out, the number of lines should decrease.

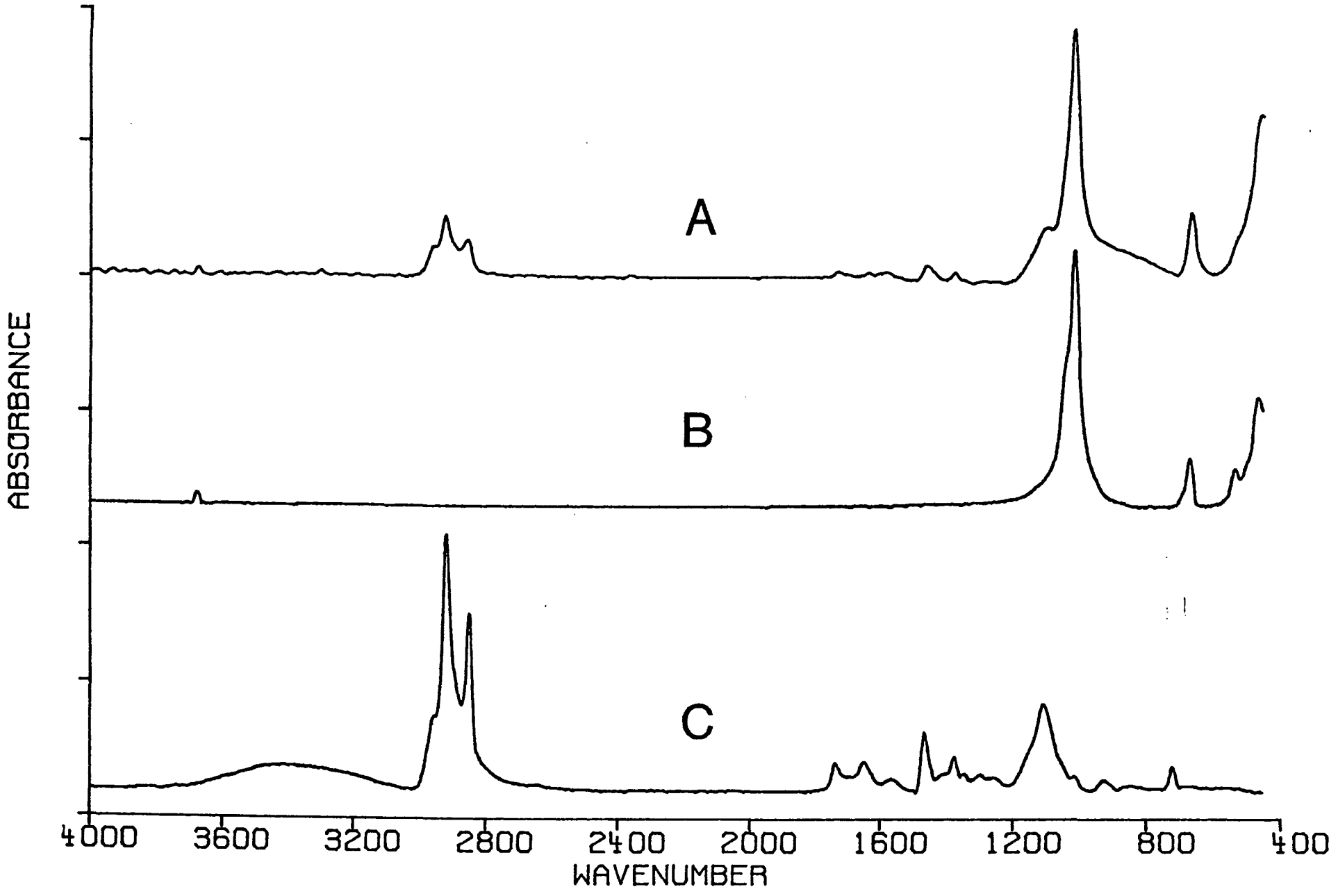


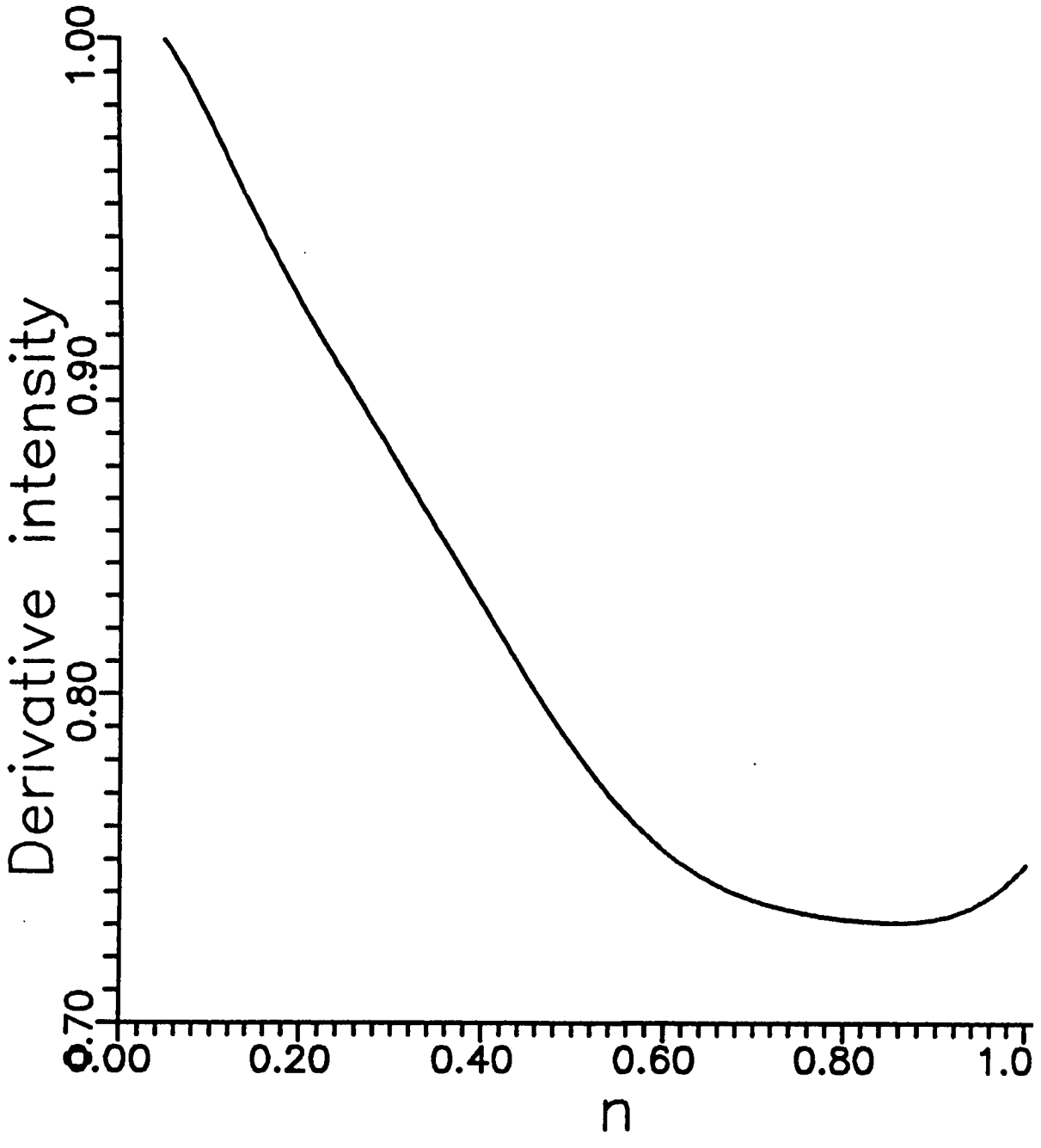
A

B

C

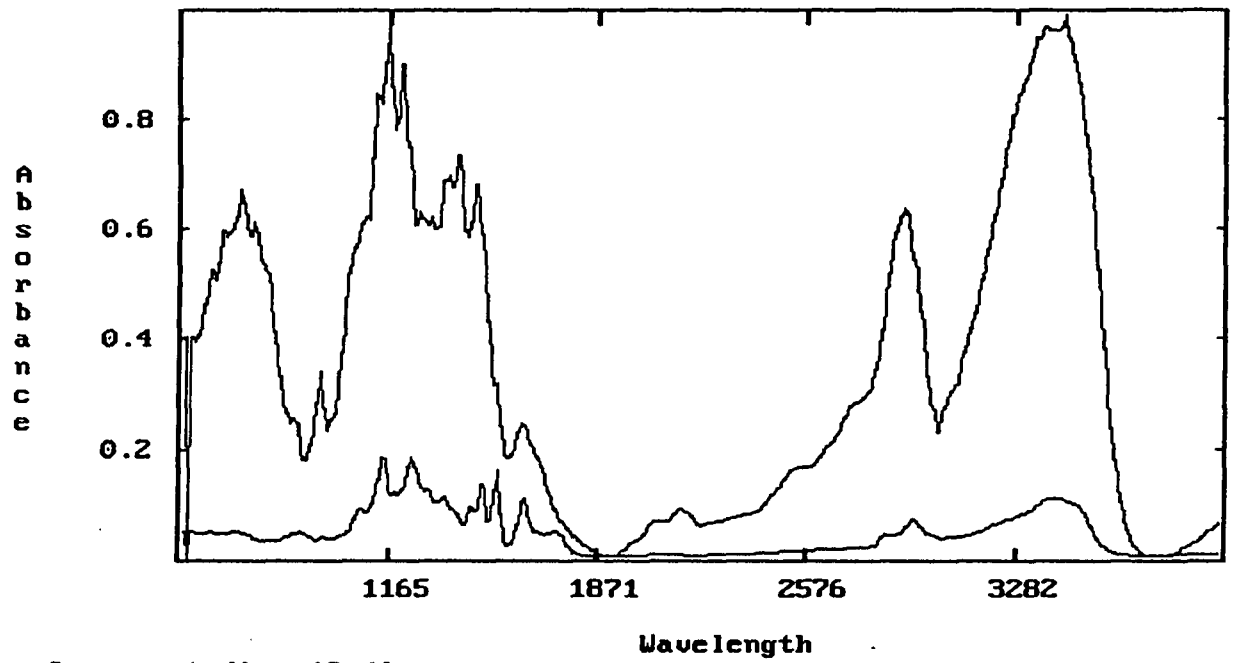
D


A
B
C
ABSORBANCE
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBER


Derivative intensity
1.00
0.90
0.80
0.70
0.00
0.20
0.40
0.60
0.80
1.0
n

Computer program (SPEC/ID)

- Accepts disk or hard-copy spectra
- Lines up & scales target with library spectrum
- Attempts to subtract out each spectrum in the IPST 310 spectrum library
- Run time: 9 min. on an IBM 386/16 PC



Component (): 18.40%

PROJECT 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

April 2, 1991

Donald R. Dimmel

PROJECT 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

OBJECTIVES PROJECT 3475

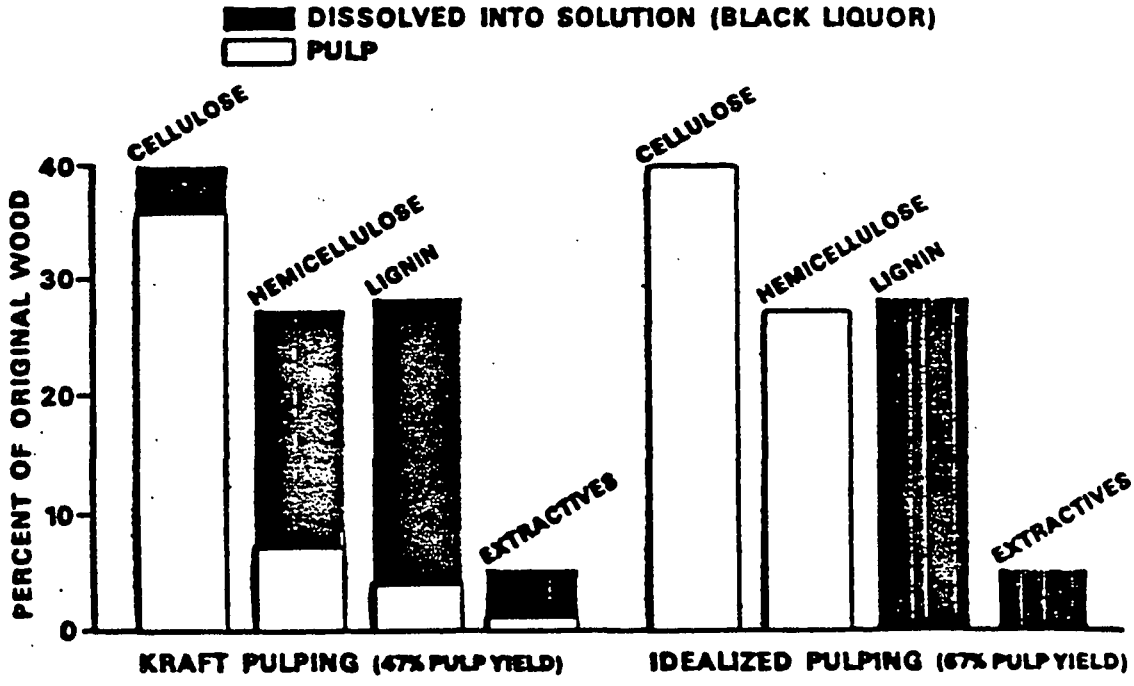
Develop a fundamental understanding of
the chemical and physical reactions
that control
degradation rates and structural changes of
lignin, cellulose, and hemicelluloses
during
pulping and bleaching

PROJECT 3475 CARBOHYDRATE STUDIES

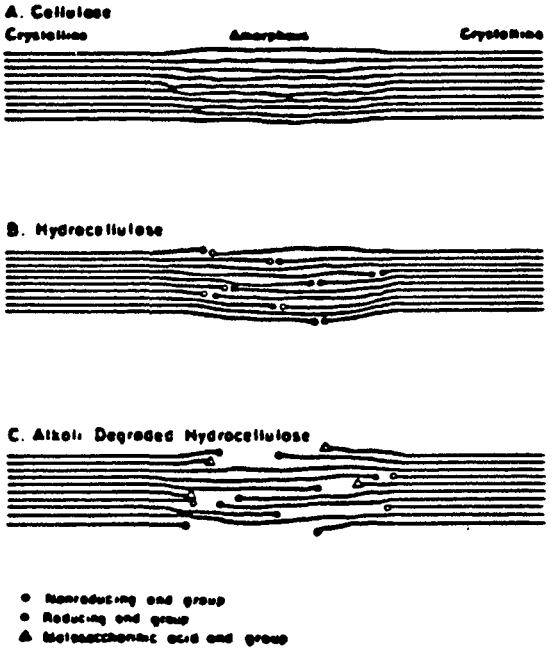
SIGNIFICANCE

A FUNDAMENTAL KNOWLEDGE OF CARBOHYDRATE CHAIN CLEAVAGE REACTIONS WILL LEAD TO BETTER PULPING AND BLEACHING STRATEGIES FOR PRODUCING HIGH QUALITY FIBERS

COMPONENT CHANGES WITH PULPING



PHYSICAL EFFECTS IN CARBOHYDRATE REACTIONS

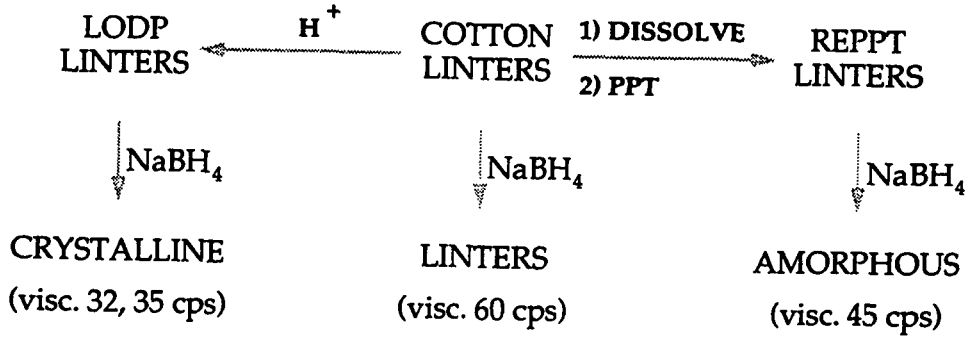


D. W. Haas, B. F. Hrutfiord, and K. V. Sarkanen,
J. Appl. Polymer Science, 1967, 11, 587

AQ CHAIN CLEAVAGE EFFECTS

- AMYLOSE IS EXTENSIVELY DEGRADED
- CELLULOSE IS STABLE (?)
- DIFFERENCES: WATER SOLUBILITY
  α - VS β - LINKED POLYMER
- DEGRADATIONS OF 1,5-ANHYDROCELLOBIITOL (α-LINKED DISACCHARIDE) AND 1,5-ANHYDROMALTITOL (β-LINKED DISACCHARIDE) SHOWED SIMILAR RESPONSES TO AQ

Cellulose Sample Preparations

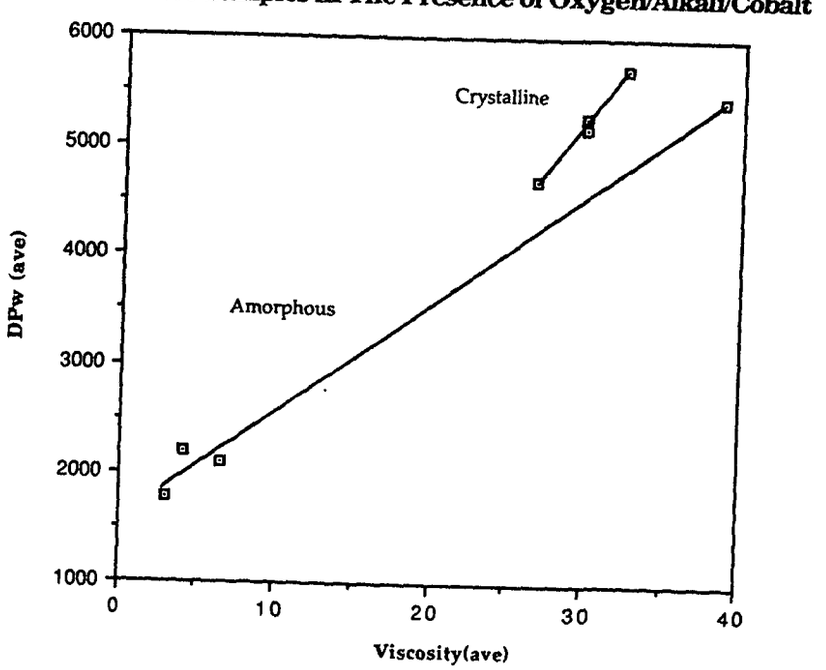


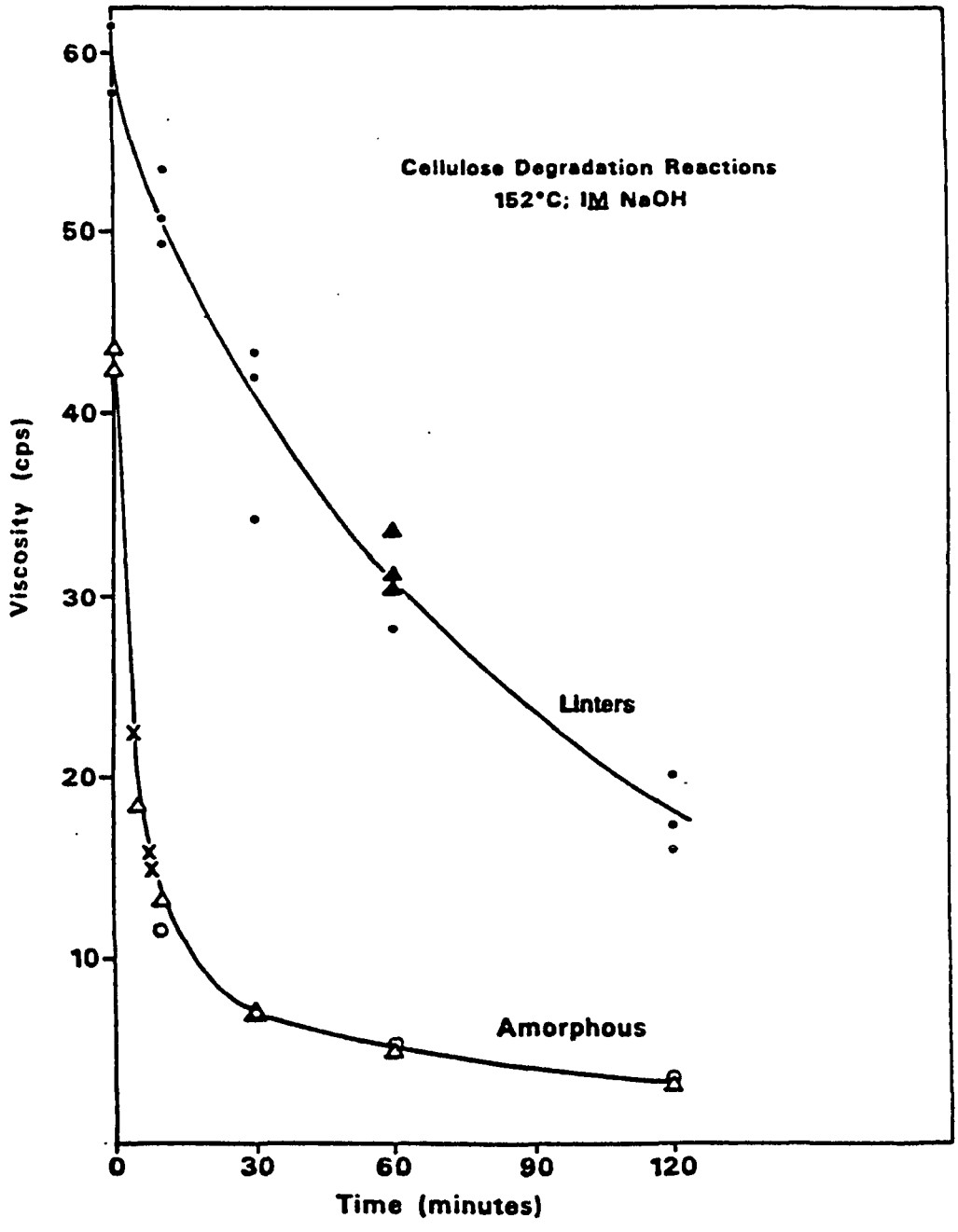
Estimating Chain Cleavage

- Degree of Polymerization from Carbonilation and Gel Phase Chromatography
- Viscosity Measurements

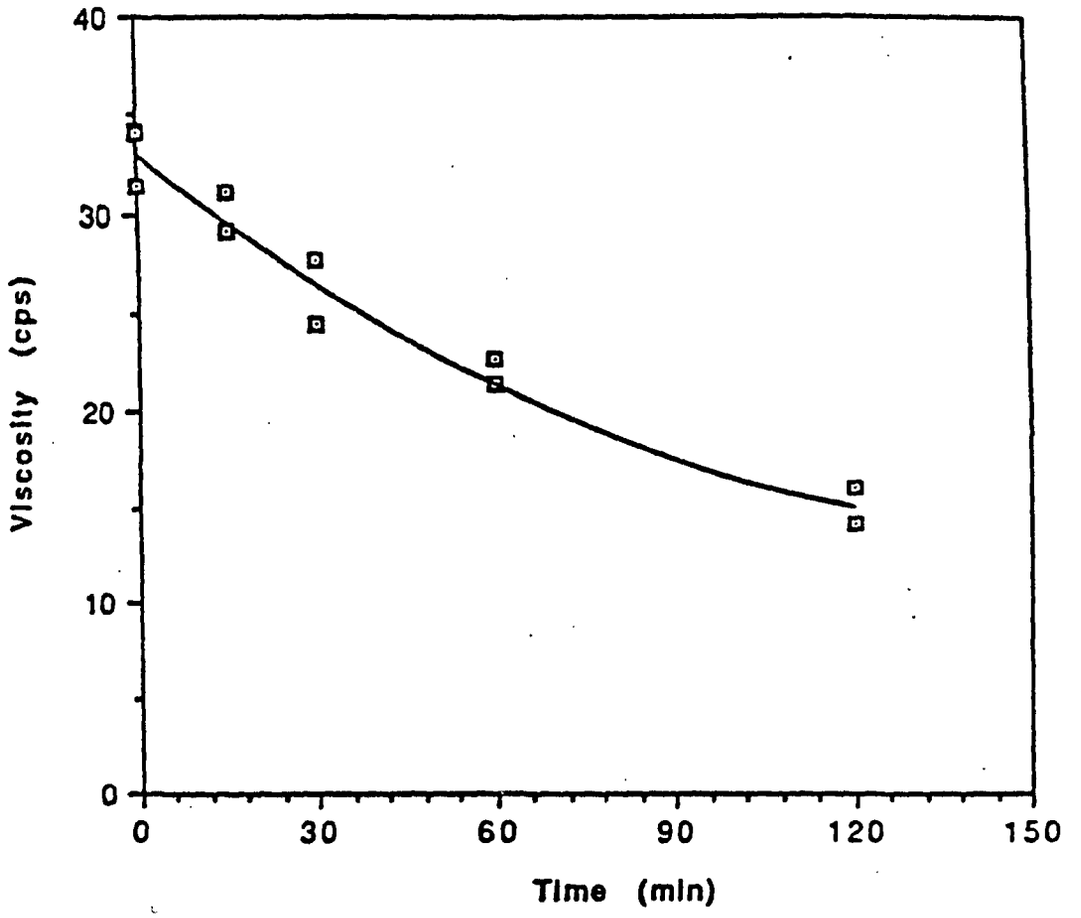
Correlation of DPw and Viscosity

Cellulose Samples in The Presence of Oxygen/Alkali/Cobalt




Cellulose Degradation Reactions
152°C; 1M NaOH
Viscosity (cps)
60
50
40
30
20
10
0
30
60
90
120
Time (minutes)
Linters
Amorphous

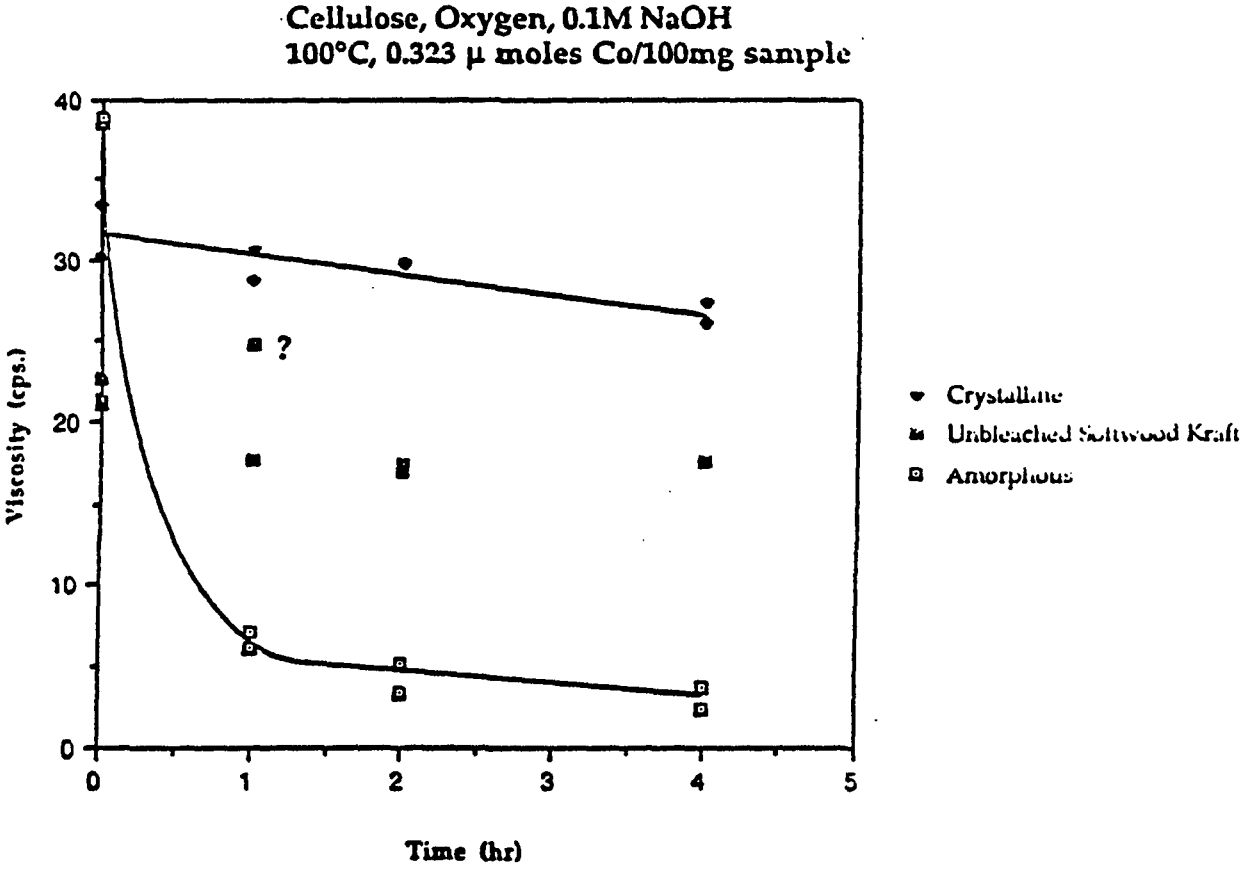
Crystalline (LODP-NaBH4) Cellulose Degradation Reactions
150°C; IM NaOH

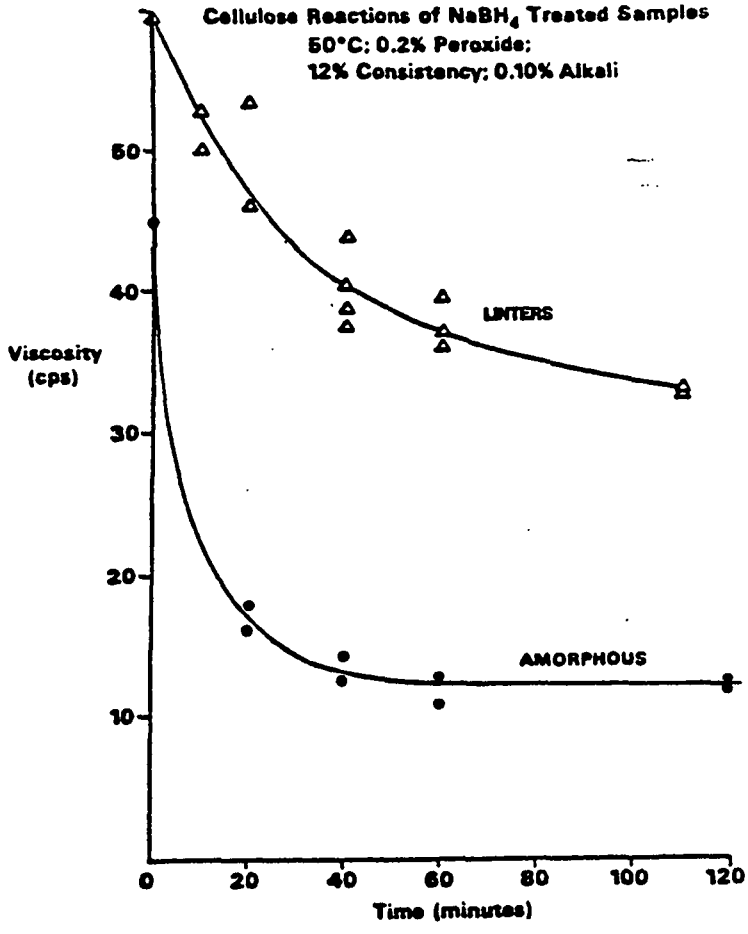


AQ Chain Cleavage Effects

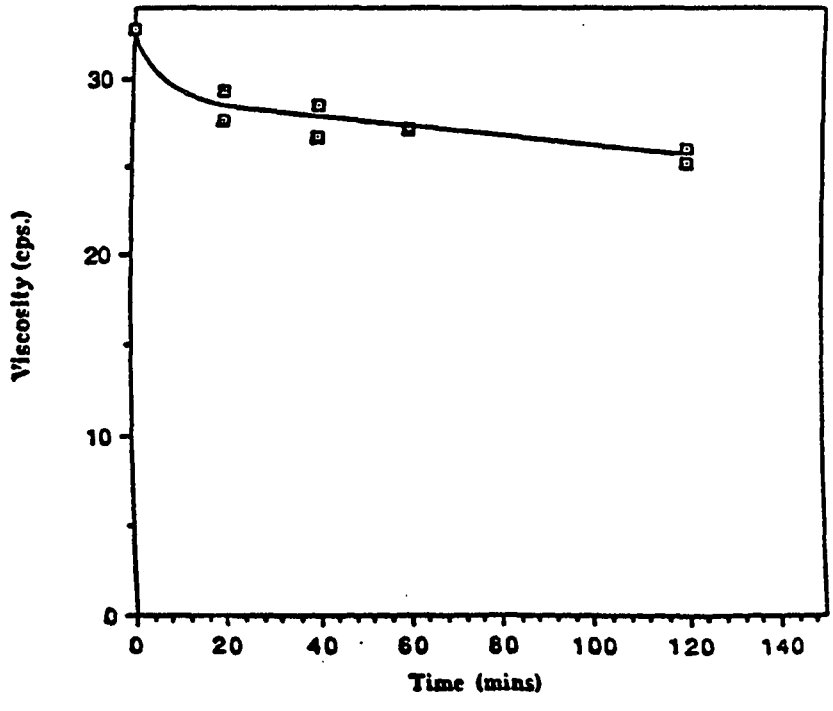
- Very Pronounced with Soluble Carbohydrates
- Minor with Either Crystalline or Amorphous Cellulose

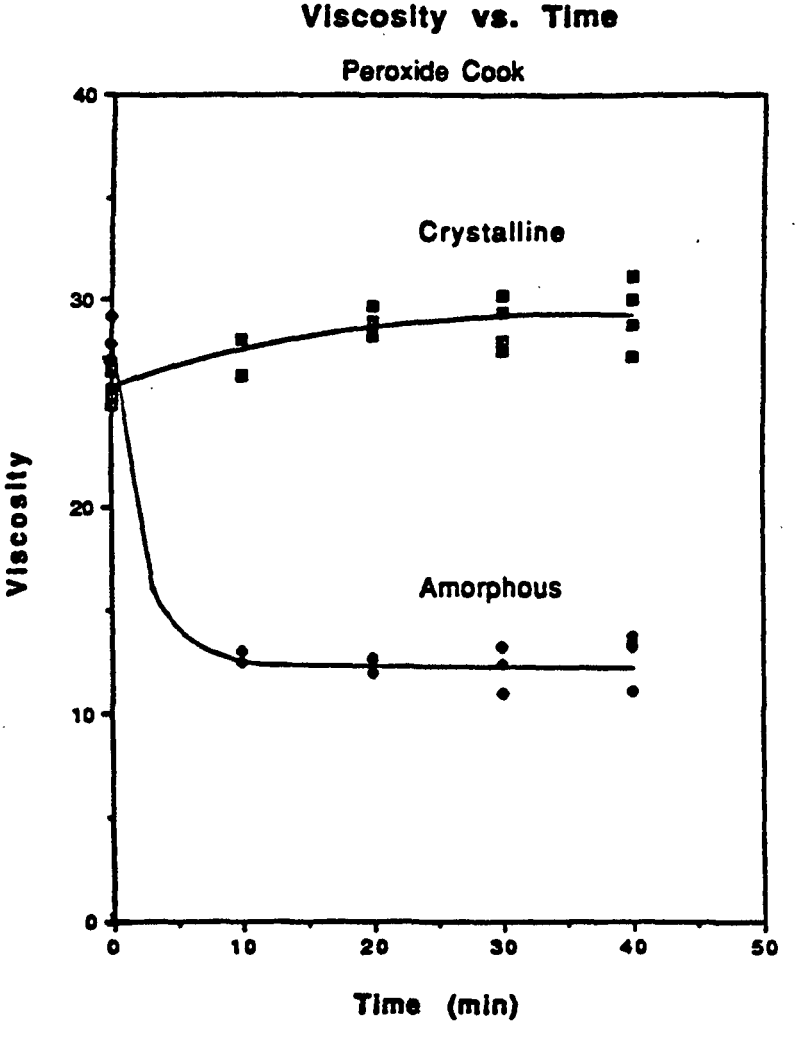
Low tear strength of AQ pulps probably reflects greater Hemicellulose content more than shorter Cellulose fiber length.

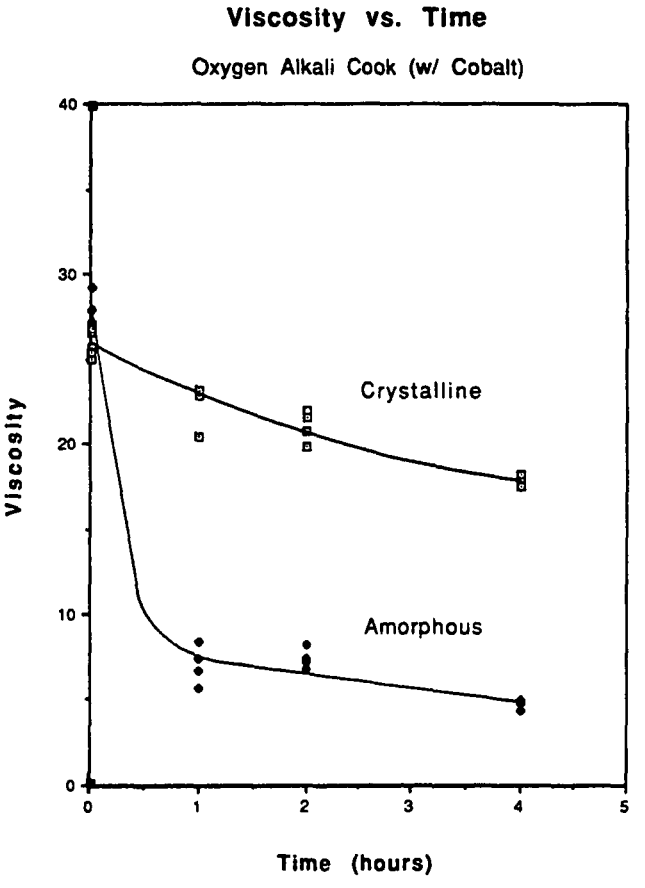

Cellulose, Oxygen, 0.1M NaOH
100°C, 0.323 μ moles Co/100mg sample
Viscosity (cps.)
Time (hr)
0
10
20
30
40
0
1
2
3
4
5
?
Crystalline
Unbleached Softwood Kraft
Amorphous



Crystalline (LODP-NaBH4) Cellulose
50°C; 0.2% Peroxide;
12% Consistency; 0.10% Alkali




Viscosity vs. Time
Peroxide Cook
Crystalline
Amorphous
Viscosity
Time (min)
0
10
20
30
40
50


Viscosity vs. Time
Oxygen Alkali Cook (w/ Cobalt)
Viscosity
Time (hours)
Crystalline
Amorphous
0
10
20
30
40
0
1
2
3
4
5

Summary

- Physical Effects Have Pronounced Effects on Reactivity:

  Soluble > Amorphous > Crystalline

- Amorphous Cellulose Reactions Are Sensitive Indicators of Pulp Degradation Reactions

PROJECT 3684

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTIVITY. PART I: PRECURSOR FORMATION AND REACTIVITY (API/NCASI FUNDED)

April 2, 1991

Lucinda B. Sonnenberg

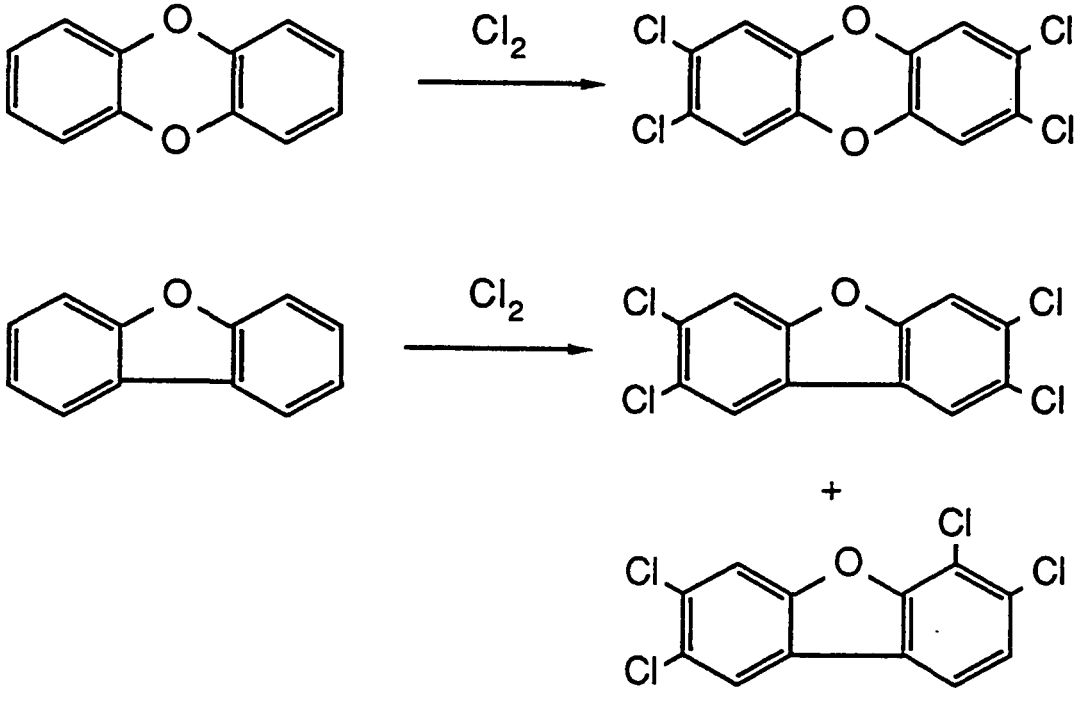
Project 3684

Mechanisms of Dioxin Formation in Pulp Production
Part 1: Precursor Formation and Reactivity

Lucinda B. Sonnenberg

Sponsored by API / NCASI

Chlorinated Dioxin and Furan Formation



PROJECT 3684

PART I

OBJECTIVES

1. Determine the reagent(s) that are the most reactive with the precursors. (to act as inhibitors)

2. Determine the relative reactivity of the reagent(s) for the precursors and for pulp components.

Reagents

1. Nitrogen dioxide
2. Nitric acid
3. Sulfuric acid
4. Ozone
5. Peroxide
6. Oxygen / UV

Methods

- DBD/F Reactions with Electrophilic Reagents
  - spiked cotton linters
  - ppm levels of DBD/F
  - excess reagent
- Sample Preparation
  - soxhlet extract linters
  - liquid-liquid extract aqueous solutions
  - rotoevaporate extracts
- Analyses
  - GC/FID quantitation
  - GC/MS identification of major products

Reactions of DBD/F on Linters with Nitrogen Dioxide[1,2]

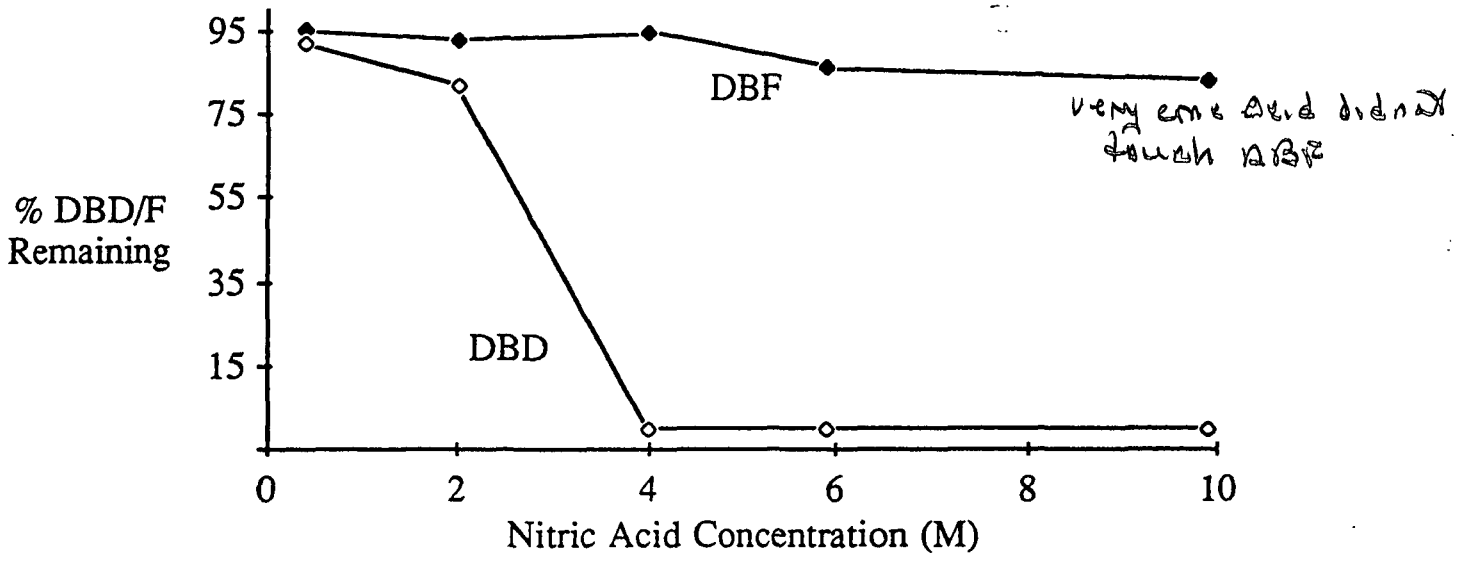
		ppm before NO_2	ppm after NO_2	% reacted
10 min.				
	DBF	37	24	33
	DBD	58	≤ 1	≥ 99
40 min.				
	DBF	37	32	13 - 47
	DBD	58	≤ 1	≥ 99

[1] Conditions: 2% NO_2 charge to air dried linters; (1000:1 molar ratio of NO_2 to total DBD/F)

[2] Mononitrated and dinitrated DBD detected; mononitrated DBF detected.

The precursors were undergoing oxidation reactions - chains were broken so that it could not form

Reactions of DBD and DBF in Solution with Nitric Acid



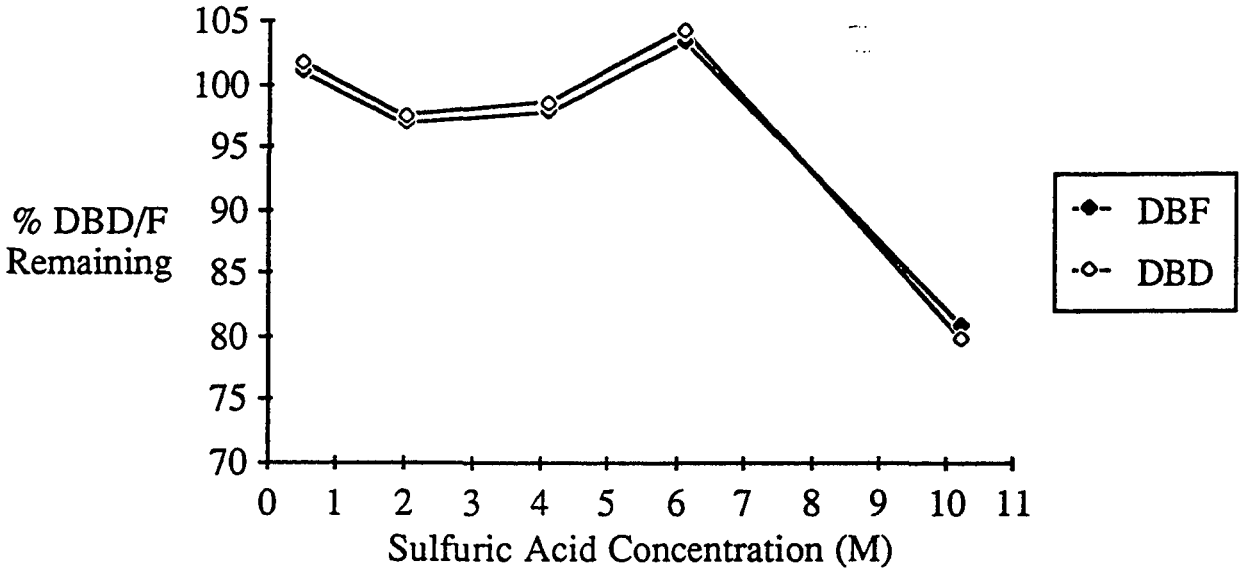
Reactions of DBD/F on Linters with Nitric Acid[1,2]

		ppm before nitric acid	ppm after nitric acid	% reacted
Exp. 1				
	DBF	26	29	0
	DBD	28	ND	100
Exp. 2				
	DBF	26	27	0
	DBD	28	<1	> 99
Exp. 3				
	DBF	26	33	0
	DBD	28	ND	100

1 Conditions: 9 % consistency; 1 hr. reaction time; 4 M HNO_3 (130,000 to 1 HNO_3 to DBD/F molar ratio)

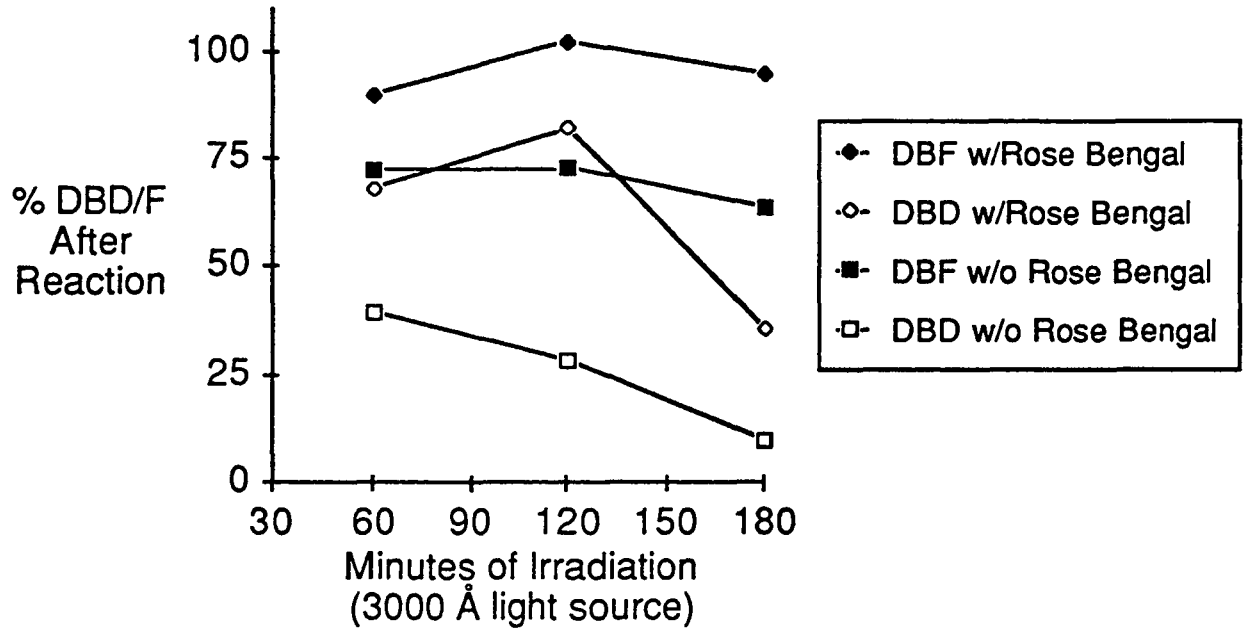
2 Mononitrated DBD detected.

Reactions of DBD and DBF in Solution with Sulfuric Acid



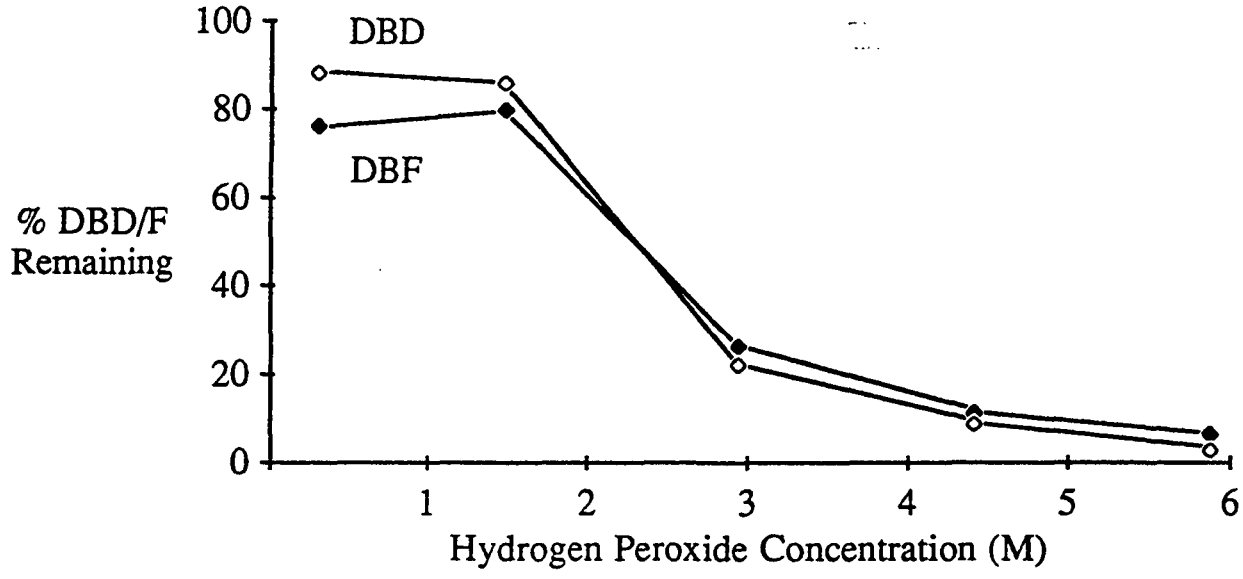
similar reaction with DBE & DBF but not efficient

Reactions of DBD and DBF in Solution Under O_2/UV



Degradation seemed inhibited with Rose B. which is a sensitizer? — confusing

Reactions of DBD and DBF in Solution with Peroxide



DBD/F reacts in solution, without pulp present, with H_2O_2

Reactions of DBD and DBF on Linters with Hydrogen Peroxide[1]

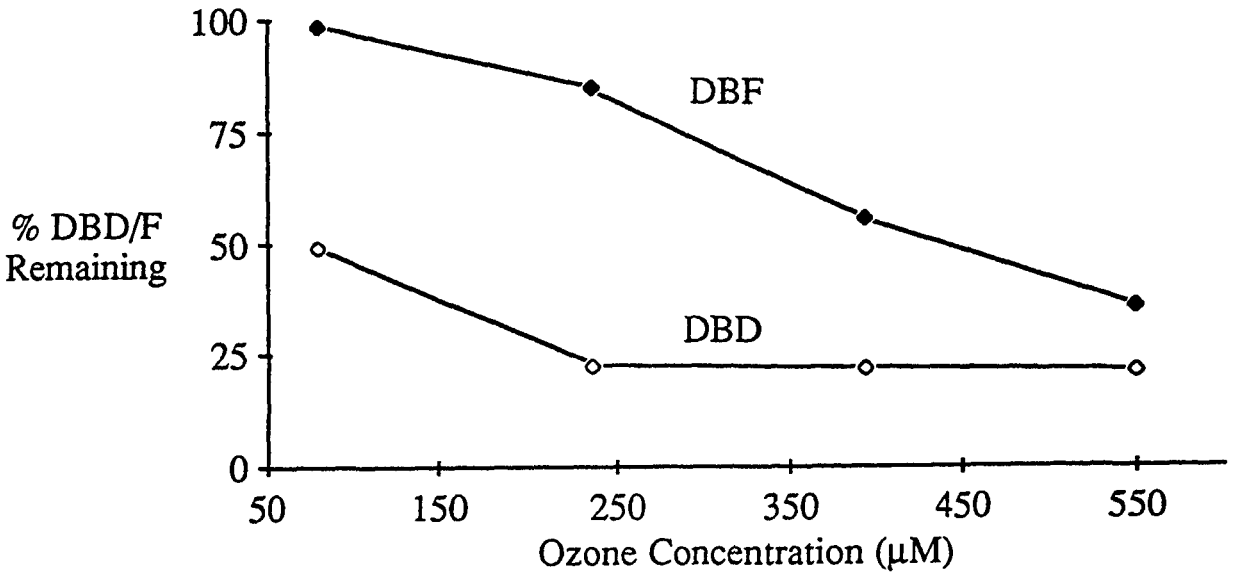
	ppm before peroxide	ppm after peroxide	% DBD/F reacted
Exp. 1			
DBF	18	18	0
DBD	19	19	0
Exp. 2			
DBF	18	20	0
DBD	19	19	0

[1] Conditions: 17% consistency; 5.9 M H_2O_2; 1 hour reaction time; unbuffered solution.

Reactivity is reduced in absorbed phase

H2O2 does not attack DBD/F in presence of pulp.

Reactions of DBD/F in Solution with Ozone



Even with low conc of ozone reduced both

pH was not measured
done in ionized water - near neutral pH

Later work showed increasing degradation with lower pH -

Reactions of DBD/F on Linters with Ozone[1]

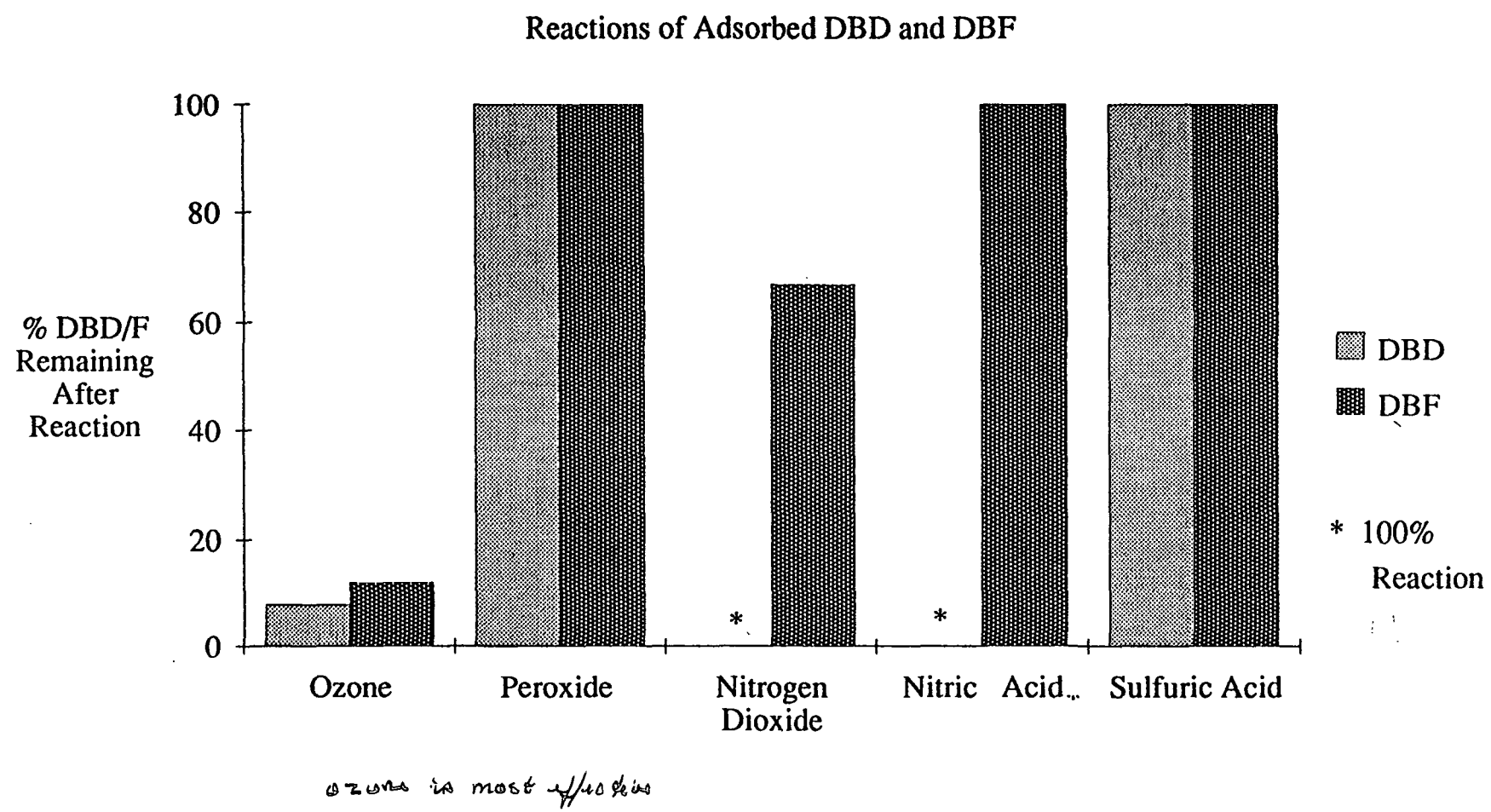
		ppm before ozonation	ppm after ozonation	% reacted
Blank				
	DBF	-	0.7 [2]	-
	DBD	-	0.8	-
Exp. 1				
	DBF	8.2	1.0	≥ 88
	DBD	10.3	0.9	≥ 92
Exp. 2				
	DBF	8.2	1.0	≥ 88
	DBD	10.3	0.9	≥ 92

1 Conditions: 2 % consistency; 500µM O3; 15 min. reaction time.

2 GC Retention time slightly different - maximum possible concentration; near detection limits.

nearly all of both were lightly degraded.

DBD/E in absorbed phase is more reactive than solution phase.



ozone is most reactive

CONCLUSIONS

* Lower concentrations of ozone were required to degrade DBD and DBF in solution and on linters than were required for other reagents.

* Peroxide degraded DBD and DBF in solution, but did not react with the precursors in the presence of linters.

* Dissolved precursors were degraded by O_2/UV after long reaction times, probably via direct photolysis.

* Nitrogen dioxide reacted with adsorbed DBD and DBF more than nitric acid, sulfuric acid and hyrogen peroxide.

* Oxidation reactions occurred more than substitution reactions when DBD and DBF were reacted with nitrogen dioxide and nitric acid.

CURRENT AND FUTURE WORK

* Application of ozone to unbleached pulp spiked with DBD and DBF. ie in presence in lignin

* Optimization of ozone reaction conditions and analytical procedures.

* ✓Clarification of the role of peroxide in precursor degradation.

Sulfitidation of DBF
effect on AOX
overall decay

PROJECT 3685

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II: CHLORINATION AND DIOXIN REACTIONS (CHLORINE INSTITUTE FUNDED)

April 2, 1991

Donald R. Dimmel

PROJECT 3685

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II: CHLORINATION AND DIOXIN REACTIONS

[FUNDED BY THE CHLORINE INSTITUTE]

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION
PART II: CHLORINATION AND DIOXIN REACTIONS

OBJECTIVES

The proposed research will develop a fundamental understanding of chemistry which leads to dioxins in bleached pulp, the reactions of dioxins with selected bleaching reagents, and ways to chlorinate pulps without dioxin production.

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION
PART II: CHLORINATION AND DIOXIN REACTIONS

AREAS OF STUDY

- **define the relative importance of DBD/F dioxin precursors**
- **determine reaction rates for chlorination of DBD/F and lignin**
- **determine the reactivity of chlorine with functionalized precursors**
- **define conditions to selectively chlorinate lignin and not DBD/F**
- **destroy dioxins in partially bleached pulps**

work was interrupted by work on Hurricane Sturm
Began work in last 6 weeks

PROJECT 3685
SUMMARY OF WORK

Chlorination conditions selected

Initial chlorination of controls and spiked linters

Poor recovery of labeled internal standards due to complex work up due to yellow residue formed

Modification of sample work up to avoid the "yellow residue"

Need to analyze liquid and solid phases

Second chlorination of controls and spiked, extracted linters

Good recovery of labeled internal standards with Al_2O_3 work up

Found **Conditions are appropiate for mono-, di-, tri-, and tetrachlorodioxins**

Spike levels need to be higher

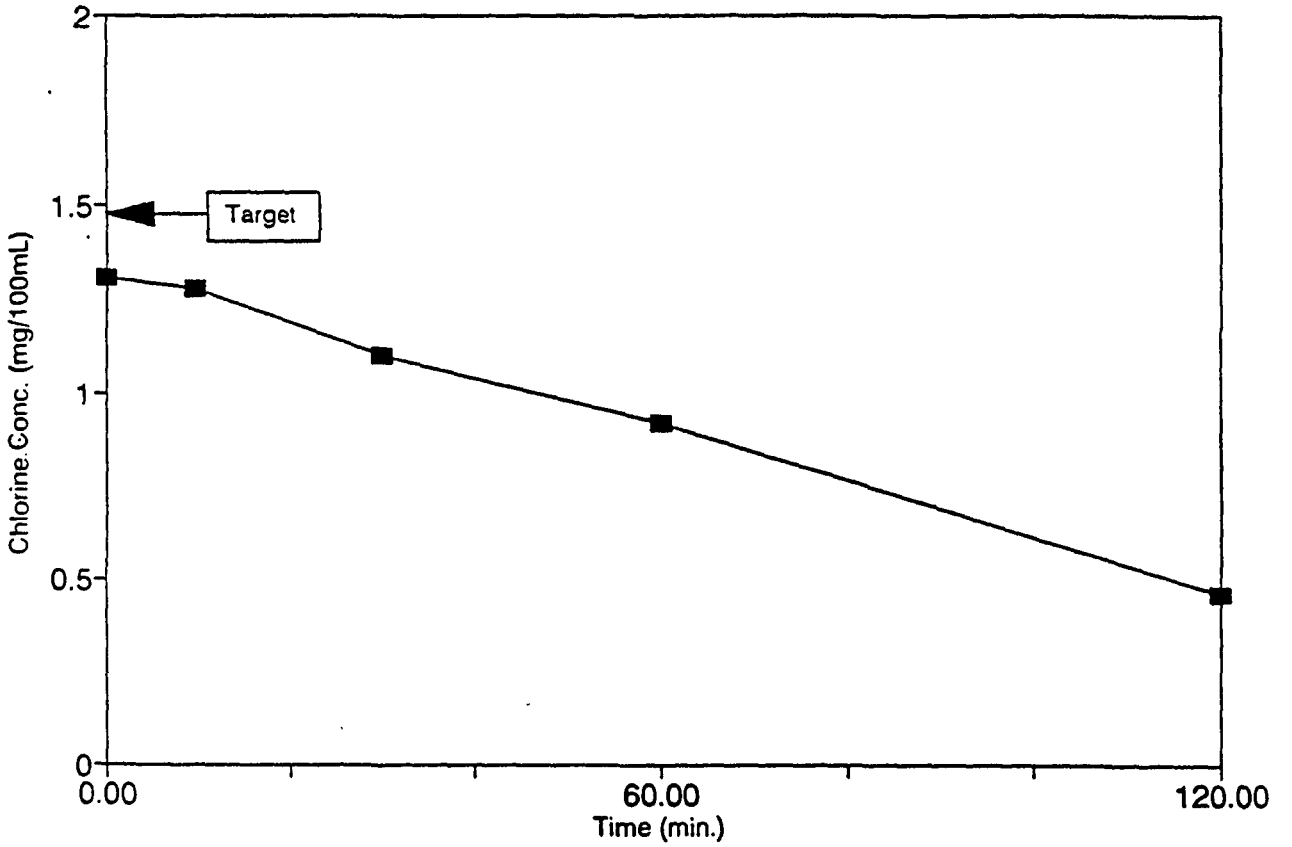


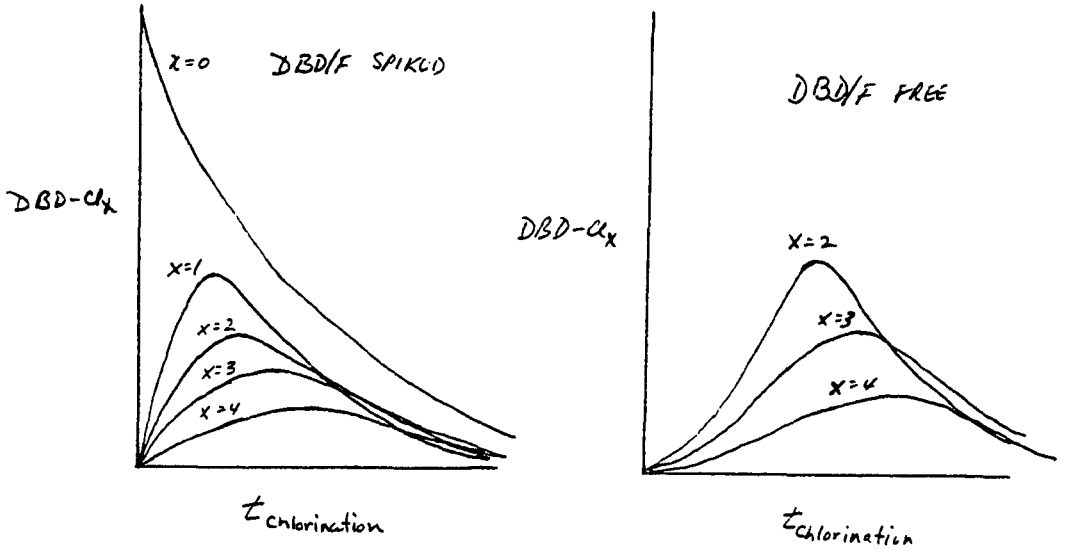
Figure 2. Chlorine Consumption
(1% Linter @ pH 1.0)

TABLE 5. TOTAL RESULTS FOR ADDITIONAL CHLORINATION SAMPLES

	Concentration (ng/g linter)		
Analyte	2 Hour DBD/DBF Spike	2 Hour Unspiked	Process Blank
DBF	10	10	17
DBD	0.009	0.0025	0.84
Mono-CDF	0.63	0.24	--
Mono-CDD	--	--	--
Di-CDF	2.7	1.3	--
Di-CDD	--	--	--
Tri-CDF	3.6	1.3	--
Tri-CDD	0.15	--	--
Tetra-CDF	0.16	0.024	--
Tetra-CDD	0.080	--	--

TABLE 1. EXPERIMENTAL PLAN

Experiment Number	Substrate	Reaction	Observation	Information	Experimental Variables (Number to be Tested)	Number of Samples Generated	Number of Samples for Analys DBD/DBF	Mono-through tetra-CDD/F	Lign Mode Compo
0	(A)DBD/DBF spiked linters	Cl_2	DBD/F-Cl_x yield with time TCDD/F isomer distribution	Spike level Experimental precision	Spike level (4)	13	13	13	-
1	(A)DBD/F spiked linters	Cl_2	Reaction rate DBD/F-Cl_x yield with time TCDD/F isomer distribution	Rate law, Ea Reaction course Cl_2-ation pattern	Time(5) Temp.(3)	32	25	25	-
2	(B)DBD/F-free or bleached pulp	Cl_2	DBD/F-Cl_x yield TCDD/F isomer distribution	Reaction course Dioxin source Cl_2-ation pattern dioxin source	Time(5)	12	9	9	-


DBD-Cl_x
x=0
DBDF SPIKED
x=1
x=2
x=3
x=4
t chlorination
DBD-Cl_x
DBDF FREE
x=2
x=3
x=4
t chlorination

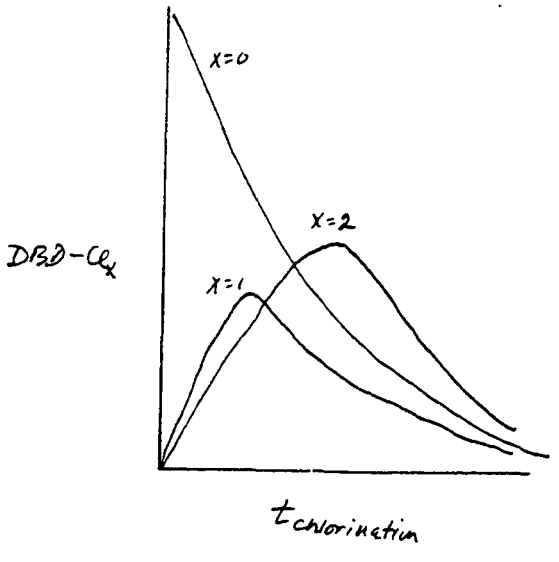

DBD-Cl_x
x=0
x=2
x=1
t chlorination

TABLE 1. EXPERIMENTAL PLAN (cont'd)

Experiment Number	Substrate	Reaction	Observation	Information	Experimental Variables (Number to be Tested)	Number of Samples Generated	Number of Samples for Analysis: DBD/DBF	Mono-through tetra-CDD/F	Lignin Model Compo
3	(C)Lignin model spiked linters	Cl_2	Reaction rate	Rate law, Ea	Time(5)	12	9	9	
4	(A) + (C)	Cl_2	Relative rates	Selectivity	--	3	3	3	
5	(A) + (C)	Cl_2/ClO_2	Relative rates	Selectivity	--	3	3	3	
6	(A)	NO_2	Reaction rate	Precursor reactivity	Experiments 6 and 7 to be conducted by Institute of Science and Technology				
	(A)	O_2	Reaction rate	Precursor reactivity					

TABLE 1. EXPERIMENTAL PLAN (cont'd)

Experiment Number	Substrate	Reaction	Observation	Information	Experimental Variables (Number to be Tested)	Number of Samples Generated	Number of Samples for Analy: DBD/DBF	Mono- through tetra- CDD/F	Ligr Mod Compc
8	(A)-NO_2 product	Cl_2	TCDD/F production	Modified precursor activity	--	3	--	3	-
9	(A)-O_2 product	Cl_2	TCDD/F production	Modified precursor activity	--	3	--	3	-
10	Unbleached pulp	NO_2 + Cl_2	TCDD/F production	Possible control measure	--	3	--	3	-
11	Unbleached pulp	O_2 and Cl_2	TCDD/F production	Possible control measure	--	3	--	3	-
12	Bleached pulp	O_3	Dioxin decrease	Possible control measure	--	2	--	2	-
		H_2O_2	Dioxin decrease	Possible control measure	--	2	--	2	-
		O_2	Dioxin decrease	Possible control measure	--	3	--	3	-

IMMEDIATE FUTURE ACTIVIES

(Dioxin Precursors)

Time profile run for the chlorination of DBD/F spiked linters giving mono-, di-, tri-, and tetrachlorodioxins

Time profile run for the chlorination of DBD/F-free pulp giving mono-, di-, tri-, and tetrachlorodioxins

PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

PART 1: FACTORS AFFECTING FORMATION OF PCDD/F IN KRAFT PULP BLEACHING

April 2, 1991

Thomas J. McDonough

CURRENT RESEARCH OF

THE IPST

PULPING AND BLEACHING GROUP

FUNDING SOURCES

* *IPST Member Dues*

* *API/CKPG/MTC/NCASI*

* *Private*

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PROJECTS BY

RESEARCH AREA

CHEMICAL PULP BLEACHING

3474: ***Environmentally Compatible Productionof Bleached Pulp***

- ***Oxygen Bleaching Pretreatments***
- ***Dioxins and Organochlorine Minimization***

3675: ***Effects of Process Changes on Formation of Dioxins and Organochlorine (Privately Funded)***

3649: ***Oxygen Bleaching of Incompletely Washed Sulfite Pulp (Privately Funded)***

Ph.D.: ***(Schwantes) Organochlorine Character and Kinetics of Formation During Pulp Bleaching***

Ph.D.: ***(Burns) Kinetics of Three-Phase Chlorination of Medium Consistency Pulp***

CHEMICAL PULPING AND RELATED AREAS

M.S.: *(McDonald) Alkaline Sulfite-AQ-Methanol Pulping*

M.S.: *(Kramer) Eucalyptus Pulping*

3716: *Semichemical Yield Determination (API Funded)*

3699: *Conductivity Sensor Evaluation (API Funded)*

3712: *Evaluation of a Fibrous Sheet Additive (Privately Funded)*

MECHANICAL PULPING AND PULP PROPERTIES

3566: *Strong, Intact High-Yield Fibers*

3697: *Interstage Chemical Treatment (Privately Funded)*

3712: *Evaluation of a Fibrous Sheet Additive (Privately Funded)*

M.S.: *(Morra) Fiber Morphology and Sheet Strength*

MECHANICAL PULP BLEACHING

3694: High-Brightness High-Yield Pulps

3701: Peroxide Bleaching (Privately Funded)

PROJECT 3474
ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

Part 1: Minimization of Organochlorine
Part 2: Pretreatments for Oxygen Bleaching

FACTORS AFFECTING FORMATION OF PCDD/PCDF IN KRAFT PULP BLEACHING

* *Effect of Chlorine Dioxide on Precursors*
* *Mixing Effects*
* *Effects of Chlorination Stage Variables*

TABLE 1. DIOXIN FORMATION IN (CDC) SEQUENCE

STAGE 2 ClO_2/ KAPPA	STAGE 3 Cl_2/ KAPPA	STAGES 1+3 CHLORINE FACTOR	STAGE 3 EXIT pH	2378 TCDD	2378 TCDF	1278 TCDF
0.00	0.00	0.12	1.6	0.3	1.7	1.5
0.08	0.00	0.12	1.5	0.3	0.6	0.5
0.00	0.06	0.18	1.4	0.8	3.5	2.8
0.08	0.06	0.18	1.4	0.6	3.1	2.9
0.00	0.08	0.20	1.4	1.0	8.7	6.8
0.08	0.08	0.20	1.3	13.9	50.3	24.6
0.00	0.12	0.24	1.4	10.1	30.3	14.5
0.08	0.12	0.24	1.4	21.3	105.5	49.9
0.00	0.16	0.28	1.3	15.1	64.2	28.0
0.08	0.16	0.28	1.2	40.4	331.9	152.2

Note: Exit pH's For stages 1 and 2 were all in the range 1.4-1.5

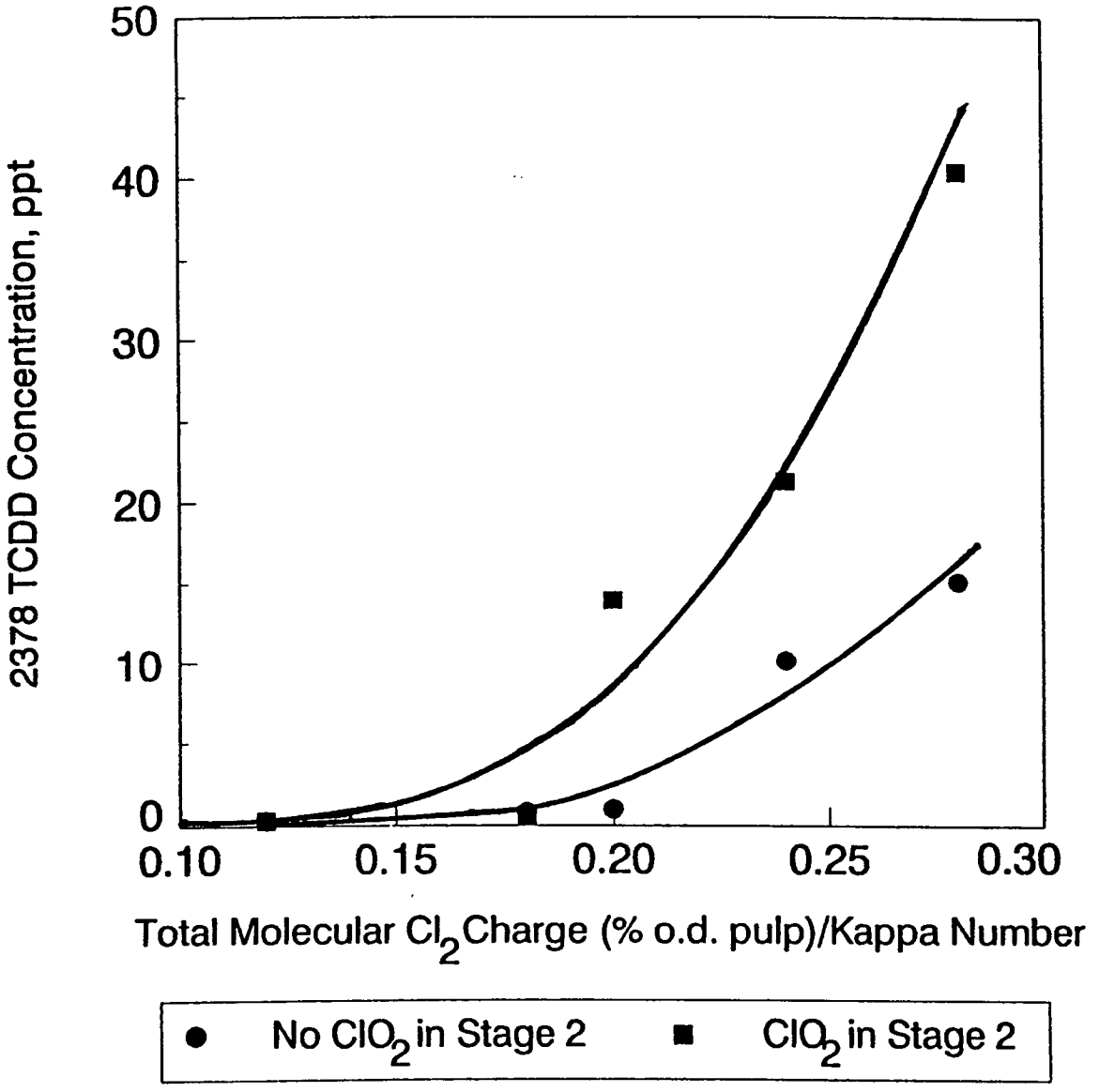


Figure 1: Formation of 2378-TCDD in CDC Sequence

MIXING EFFECTS

MIXING QUALITY	*CONSIS-TENCY*	*CE KAPPA NUMBER*	*TOTAL TCDD*
GOOD	*4*	*3.4*	*115*
		2.8	*120*
POOR		*4.4*	*73*
		4.0	*88*
GOOD	*6*	*3.4*	*132*
		3.0	*126*
POOR		*4.7*	*86*
		4.1	*89*

$$D_{mixed} = D_{av}$$

$$D_{unmixed} = \frac{D_{hi} + D_{lo}}{2} > D_{av}$$

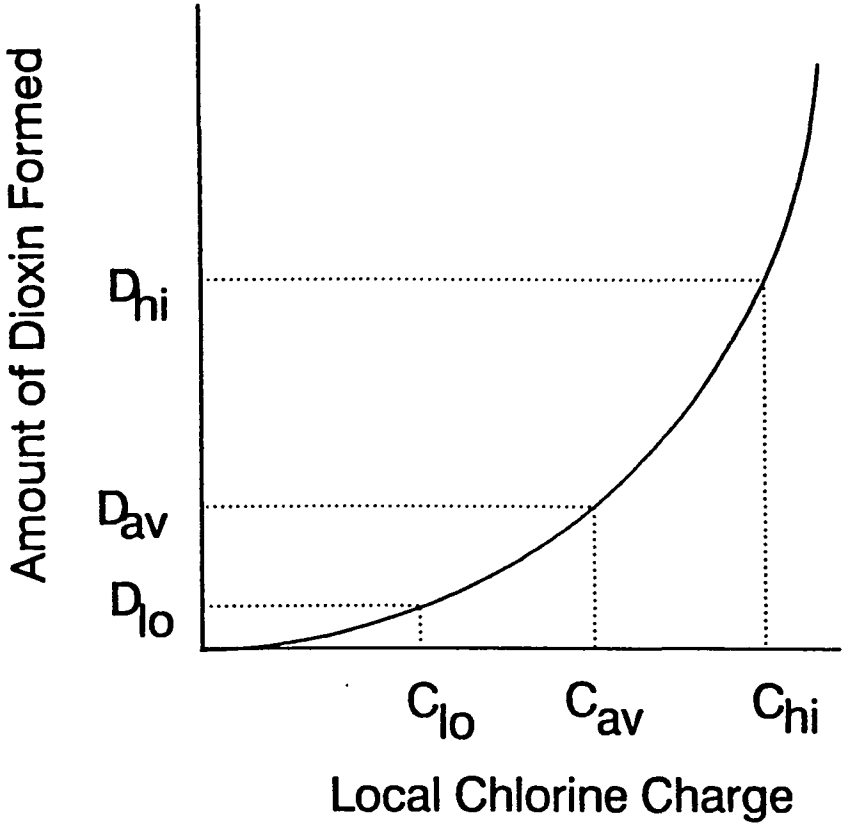


Figure 2a: Hypothetical dioxin - chlorine charge relationships and the corresponding predicted effects of poor mixing.

$$D_{mixed} = D_{av}$$

$$D_{unmixed} = \frac{D_{hi} + D_{lo}}{2} < D_{av}$$

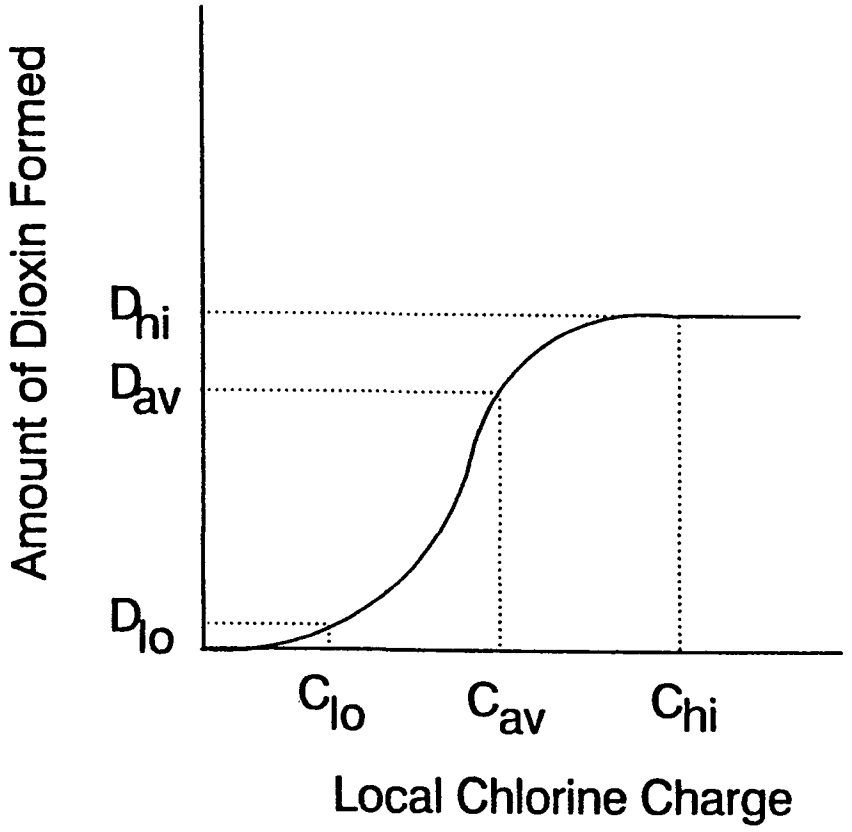


Figure 2b: Hypothetical dioxin - chlorine charge relationships and the corresponding predicted effects of poor mixing.

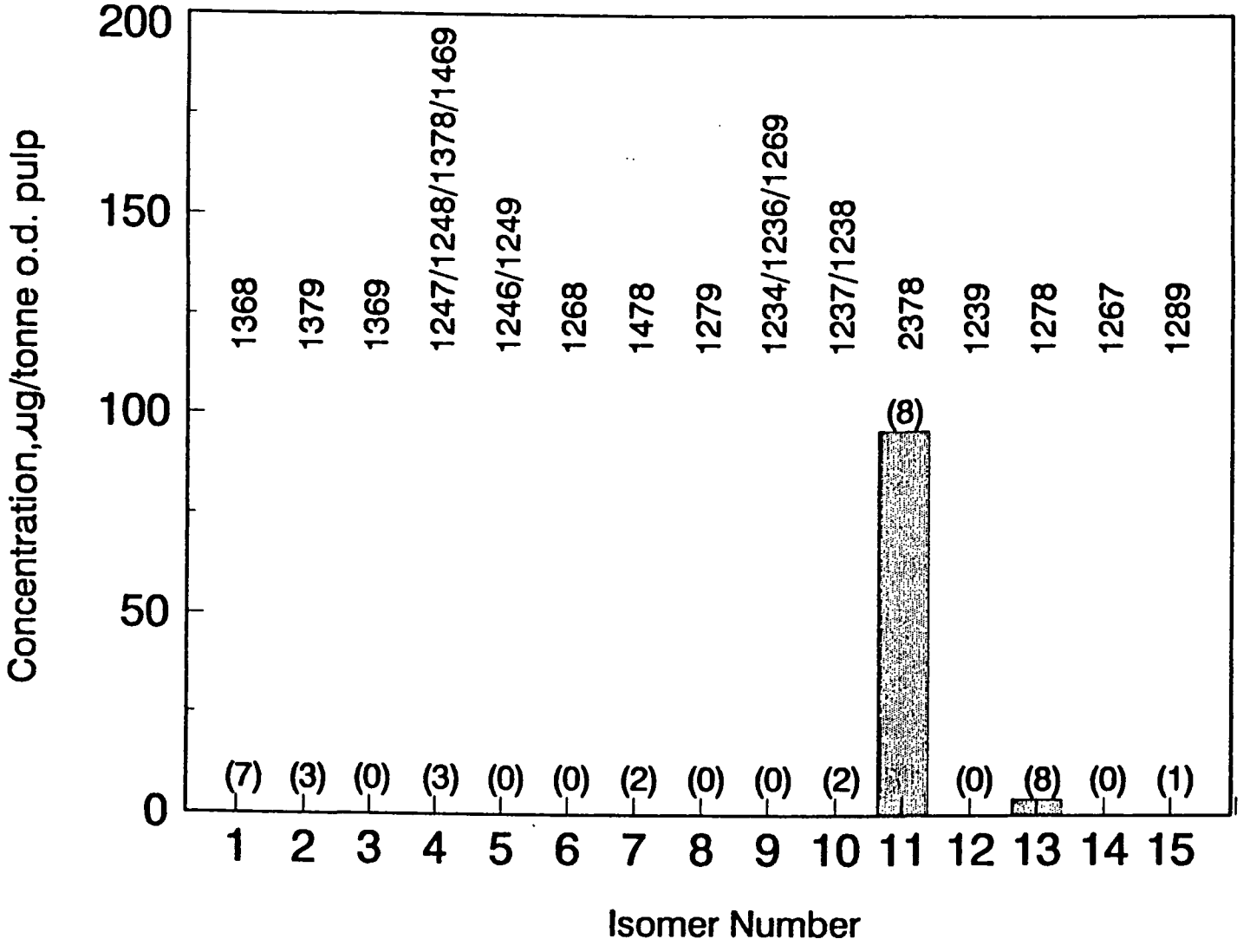


Figure 3: Average TCDD concentrations in chlorinated pulps of mixing study. Averages less than 1µg/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.

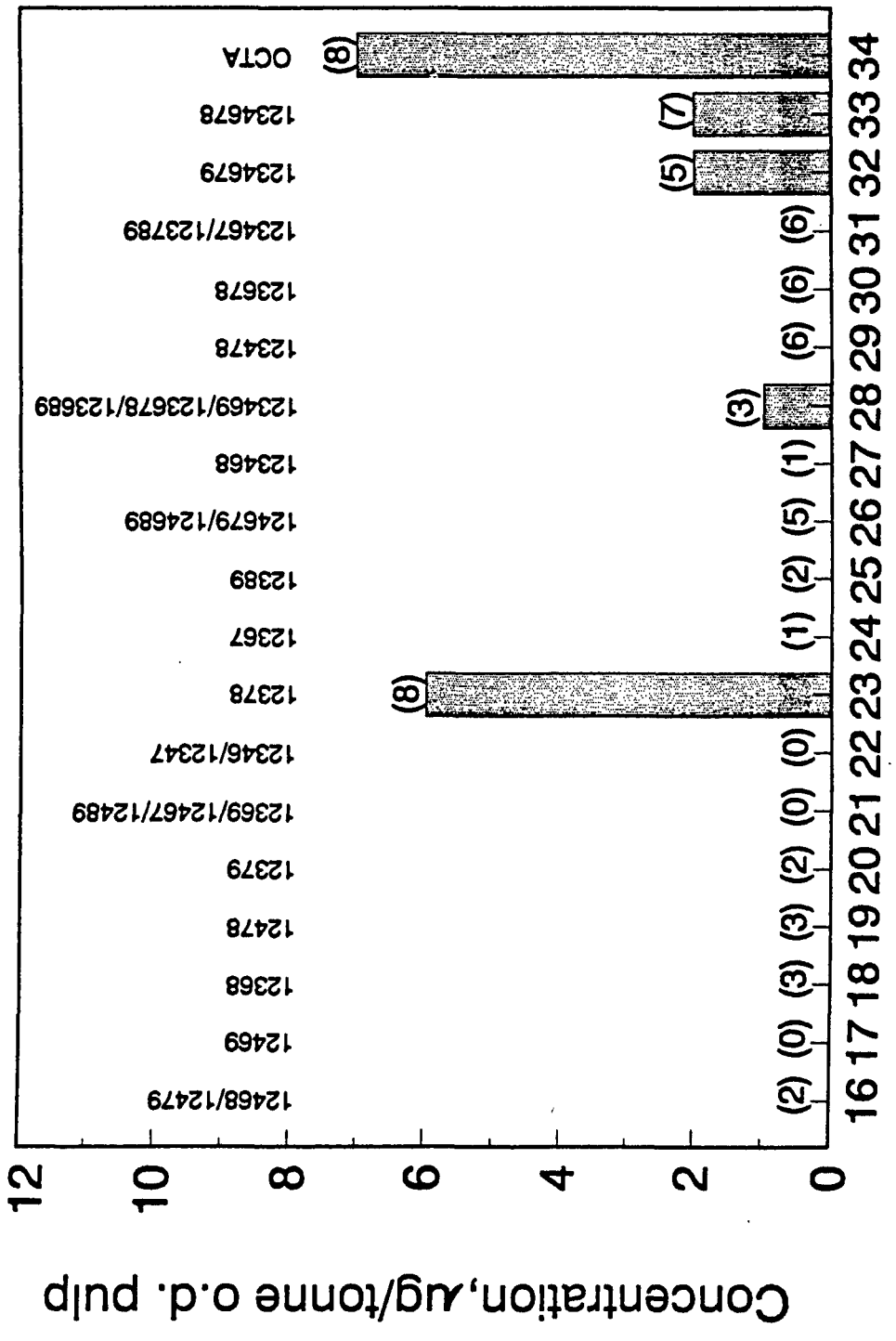


Figure 4: Average penta-, hexa-, hepta and octa- CDD concentrations in chlorinated pulps of mixing study. Averages less than 1µg/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.

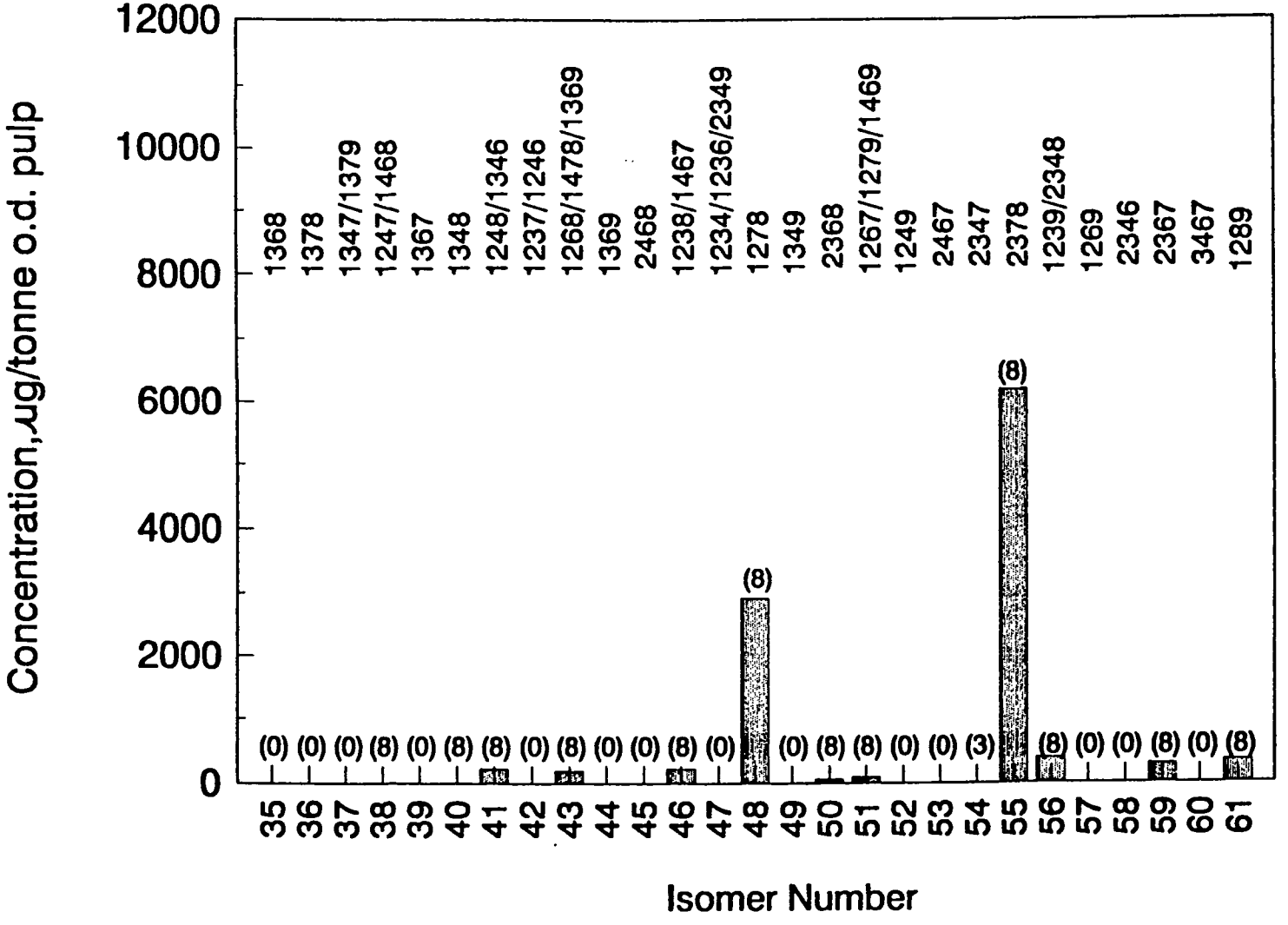


Figure 5: Average TCDF concentrations in chlorinated pulps of mixing study. Averages less than 50ug/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.

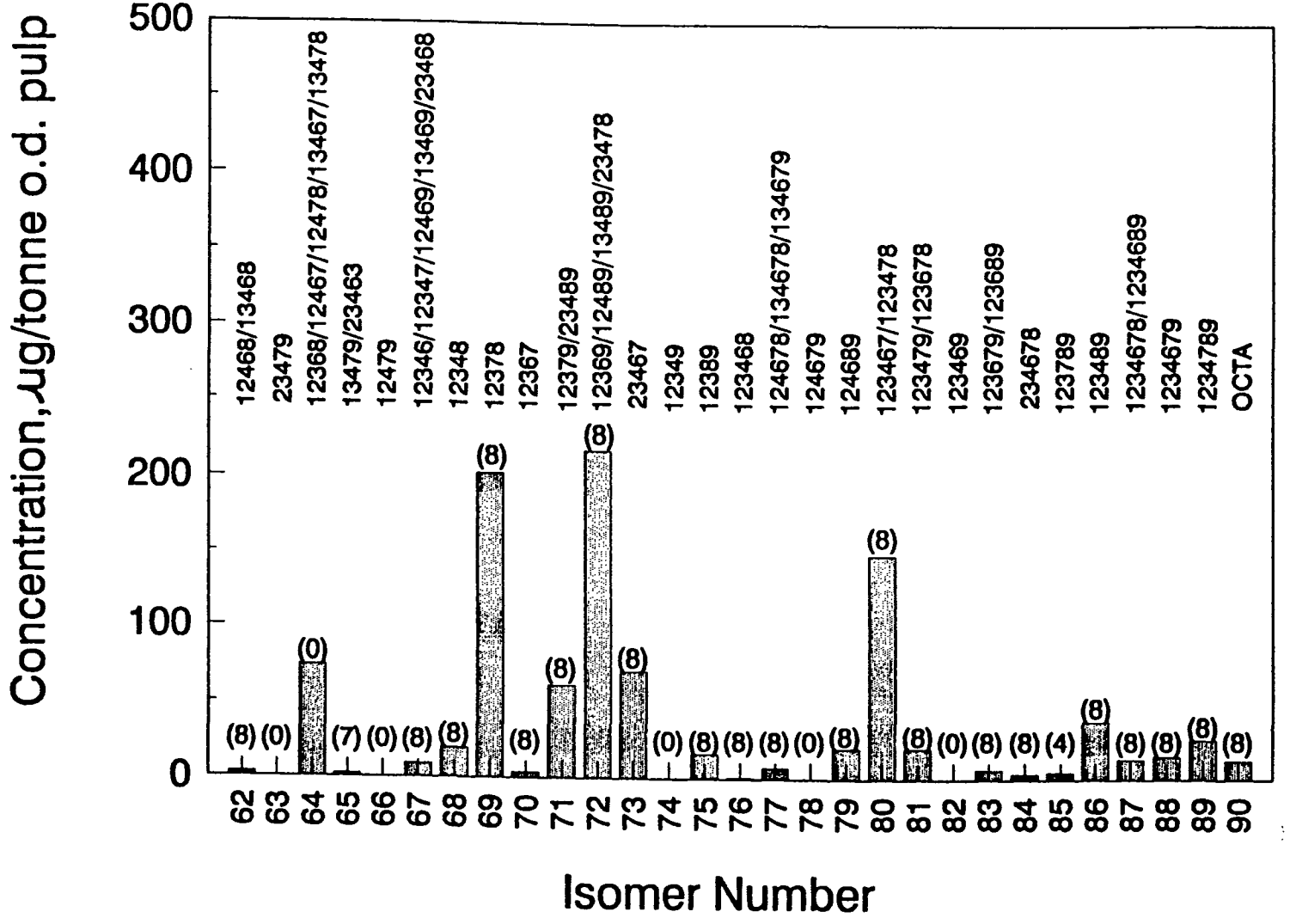


Figure 6: Average penta-, hexa-, hepta- and octa- CDF concentrations in chlorinated pulps of mixing study. Averages less than 1 ug/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.

TABLE 7A: C-STAGE FACTORIAL EXPERIMENT MEANS FOR SIGNIFICANT EFFECTS*

ISOMER	ISOMER NO.	GRAND MEAN	TREATMENT MEANS							
			ClO_2 FIRST	Cl_2 FIRST	TEMPERATURE LOW	TEMPERATURE HIGH	RECYCLE -	RECYCLE +	OXYGEN -	OXYGEN +
2378 TCDD	11	1.8	2.5	1.1	2.4	1.2			3.2	0.4
OCDD	34	5.6	5.1	6.2	4.7	6.5				
1248/1346 TCDF	41	1.1							1.5	0.6
2468 TCDF	45	9.0					7.6	10.5	12.4	5.7
1278 TCDF	48	6.3	8.1	4.6					9.9	2.8
2368 TCDF	50	0.3	0.4	0.3					0.5	0.2
1267/1279/1469 TCDF	51	0.2	0.3	0.1					0.3	0.1
2347 TCDF	54	0.3			0.3	0.2			0.4	0.1
2378 TCDF	55	9.5	13.1	5.9	12.6	6.4			16.1	2.9
1239/2348 TCDF	56	1.5	1.8	1.1	2.0	0.9			2.6	0.4
2346 TCDF	58	0.2	0.2	0.1	0.2	0.1			0.2	0.1
2367 TCDF	59	0.5	0.6	0.3	0.6	0.3			0.8	0.2
1289 TCDF	61	1.8	2.4	1.3					2.9	0.7

* All treatment means shown represent effects that are statistically significant (=>90% confidence)

TABLE 7B: C-STAGE FACTORIAL EXPERIMENT MEANS FOR SIGNIFICANT EFFECTS*

	ISOMER	ISOMER NO.	GRAND MEAN	RECYCLE -	RECYCLE +	OXYGEN -	OXYGEN +
12468/13468	PeCDF	62	0.8	0.6	0.9	1.0	0.5
12368/12467/12478/13467/13478	PeCDF	64	1.4			2.1	0.8
12346/12347/12469/13469/23468	PeCDF	67	0.8	0.7	1.0	1.2	0.4
12378	PeCDF	69	3.5	2.7	4.3	5.1	1.8
12379/23489	PeCDF	71	0.9			1.3	0.5
12369/12489/13489/23478	PeCDF	72	1.2			1.7	0.7
23467	PeCDF	73	2.1	1.6	2.5	3.0	1.2

* All treatment means shown represent effects that are statistically significant (=>90% confidence)

TABLE 7C: C-STAGE FACTORIAL EXPERIMENT MEANS FOR SIGNIFICANT EFFECTS*

	ISOMER	ISOMER NO.	GRAND MEAN	TEMPERATURE LOW	TEMPERATURE HIGH	RECYCLE -	RECYCLE +	OXYGEN -	OXYGEN +
123468	HxCDF	76	0.2			0.2	0.2	0.3	0.1
124678/134678	134679 HxCDF	77	0.5	0.6	0.4			0.7	0.3
124689	HxCDF	79	1.1	1.4	0.9			1.4	0.8
123467/123478	HxCDF	80	7.5	9.3	5.6			9.5	5.4
123479/123678	HxCDF	81	1.0	1.2	0.8			1.4	0.7
123679/123689	HxCDF	83	0.3			0.3	0.4	0.4	0.2
123789	HxCDF	85	0.2	0.3	0.2	0.2	0.3	0.3	0.2
123489	HxCDF	86	2.0	2.5	1.6			2.7	1.4
1234789	HpCDF	89	1.6	2.0	1.3				

* All treatment means shown represent effects that are statistically significant (=>90% confidence)

TABLE 7D: C-STAGE FACTORIAL EXPERIMENT MEANS FOR SIGNIFICANT EFFECTS*

ISOMER	GRAND MEAN	TREATMENT MEANS							
		ClO_2 FIRST	Cl_2 FIRST	TEMP. LOW	TEMP. HIGH	RECYCLE -	RECYCLE +	OXYGEN -	OXYGEN +
TOTAL TCDD	2.0	2.7	1.3	2.6	1.4				
TOTAL TCDF	30.6	36.7	24.5	35.1	26.1			47.5	13.7
TOTAL PeCDF	10.9					8.8	13.1	15.8	6.1
TOTAL HxCDF	12.9			15.8	9.9			16.6	9.1
TOTAL HpCDF	4.0								
OCDF	1.3								

* All treatment means shown represent effects that are statistically significant (=>90% confidence)

CONCLUSIONS: CHLORINE DIOXIDE AND PRECURSORS

* *Chlorine dioxide does not readily destroy dioxin precursors in kraft pulp.*

CONCLUSIONS: MIXING EFFECTS

* *At kappa factor 0.25, improved mixing improved delignification, but did not decrease dioxins.*

* *It is therefore likely that the rate of formation of dioxins levels off sharply as the chlorine concentration is increased beyond the range of exponential increase*

CONCLUSIONS: EFFECTS OF CHLORINATION STAGE VARIABLES

* *Oxygen bleaching sharply reduces formation of all dioxin and furan congeners.*

* *Adding chlorine before chlorine dioxide significantly reduces formation of TCDD and TCDF.*

* *Increasing chlorination stage temperature decreases the formation of 2378-TCDD and 2378-TCDF.*

* *Effects of black liquor carryover and chlorination stage filtrate recycle are smaller than the above effects.*

PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

PART 2: EFFECTS OF MIXING AND CONSISTENCY ON AOX FORMATION DURING SOFTWOOD KRAFT PULP CHLORINATION

April 2, 1991

Amy R. Malcolm

EFFECTS OF

MIXING AND CONSISTENCY ON AOX FORMATION

DURING

SOFTWOOD KRAFT PULP CHLORINATION

- **Define Mixing Conditions**

- **Effect of Mixing and Consistency on AOX Formation**

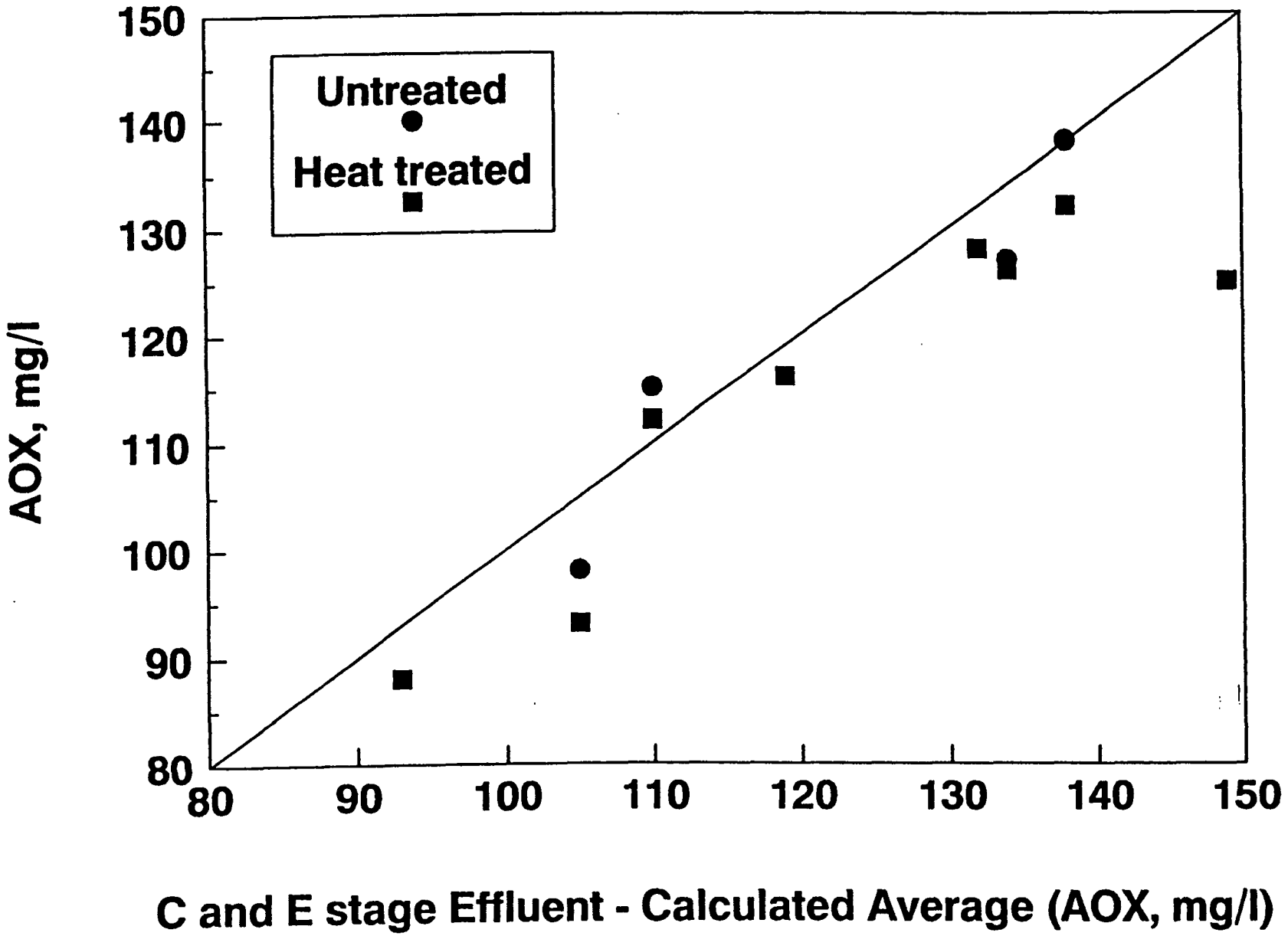
- **Effect of Chlorine Charge and Mixing on AOX Formation**

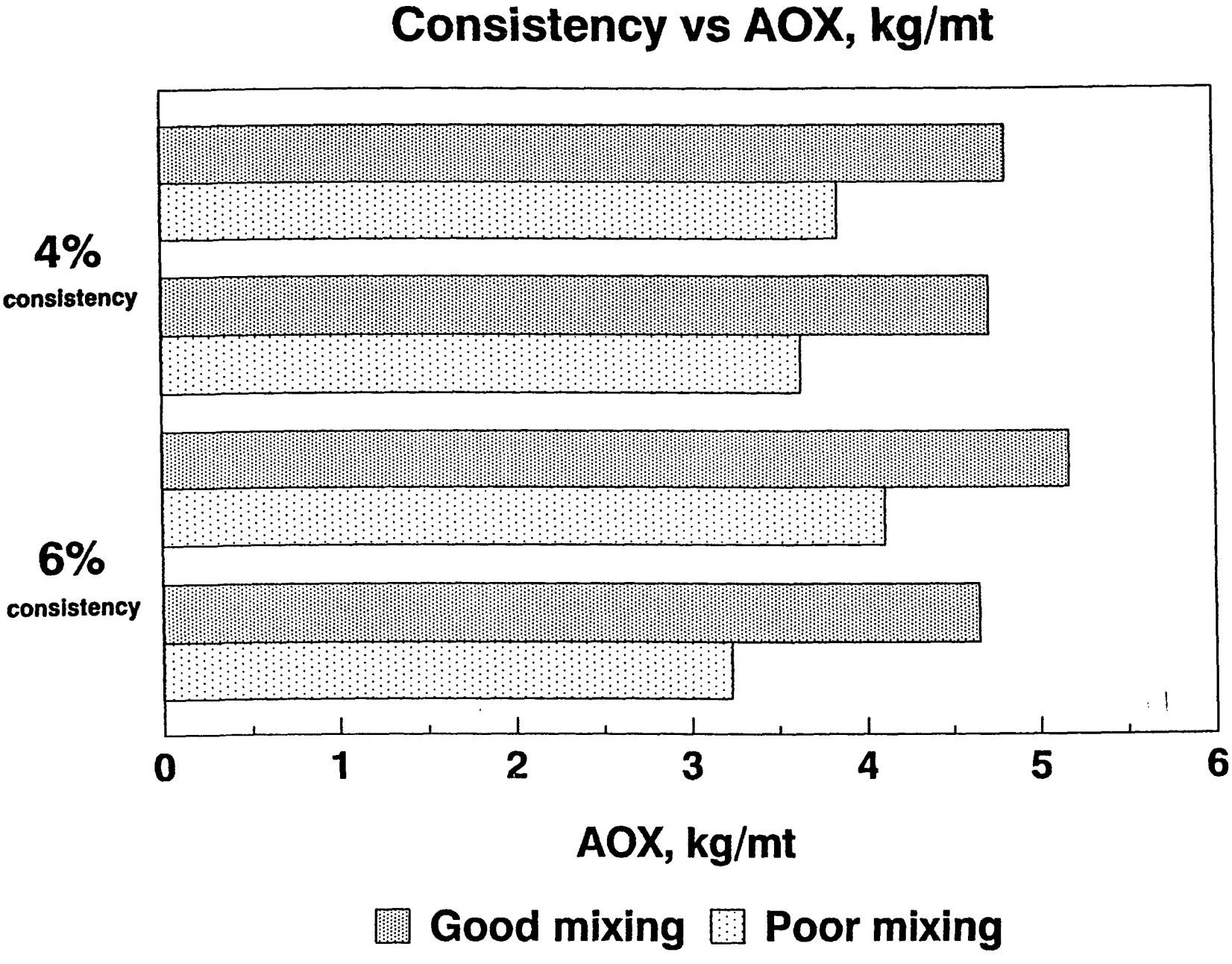
- **Define Mixing Conditions**

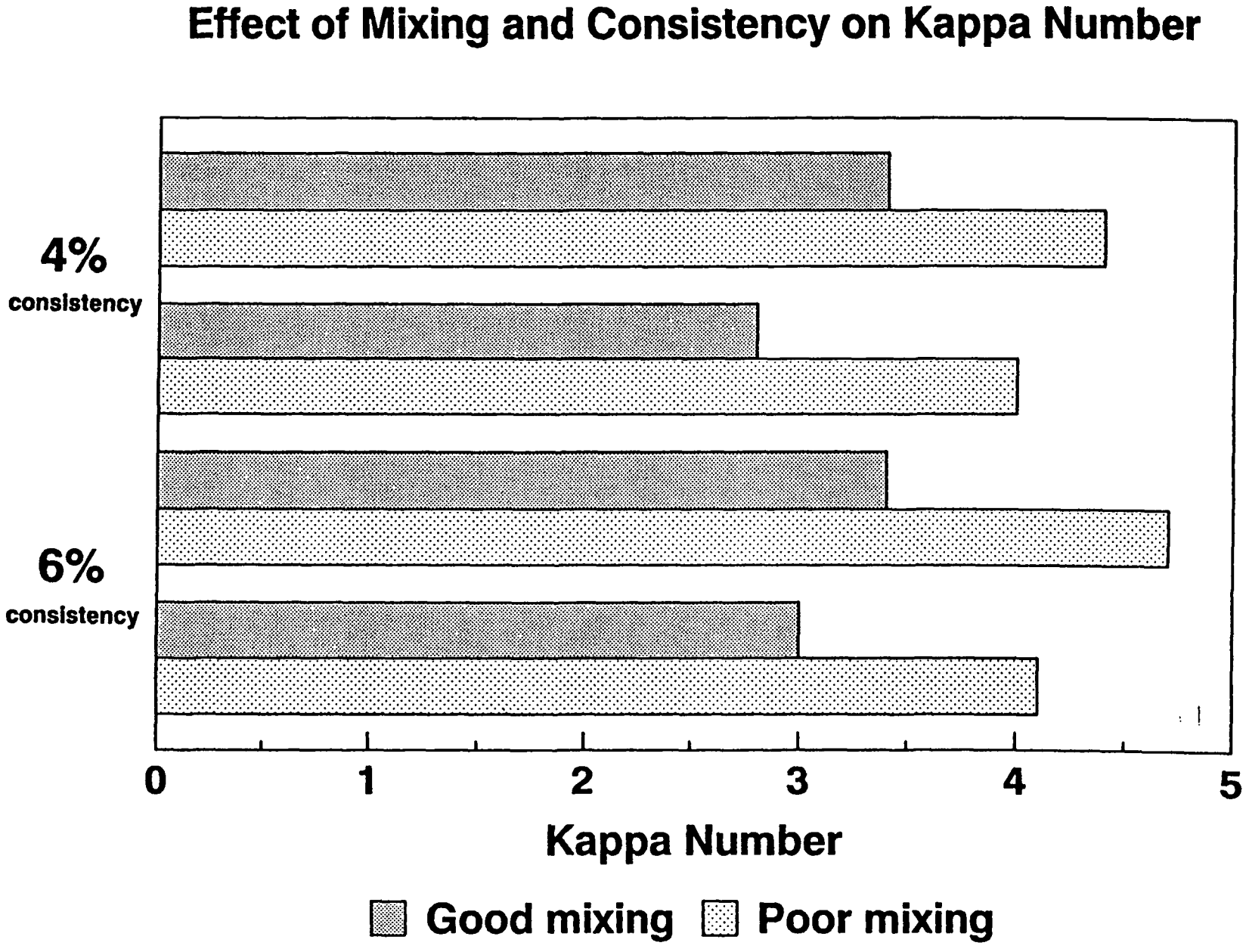
MIXING CONDTIONS

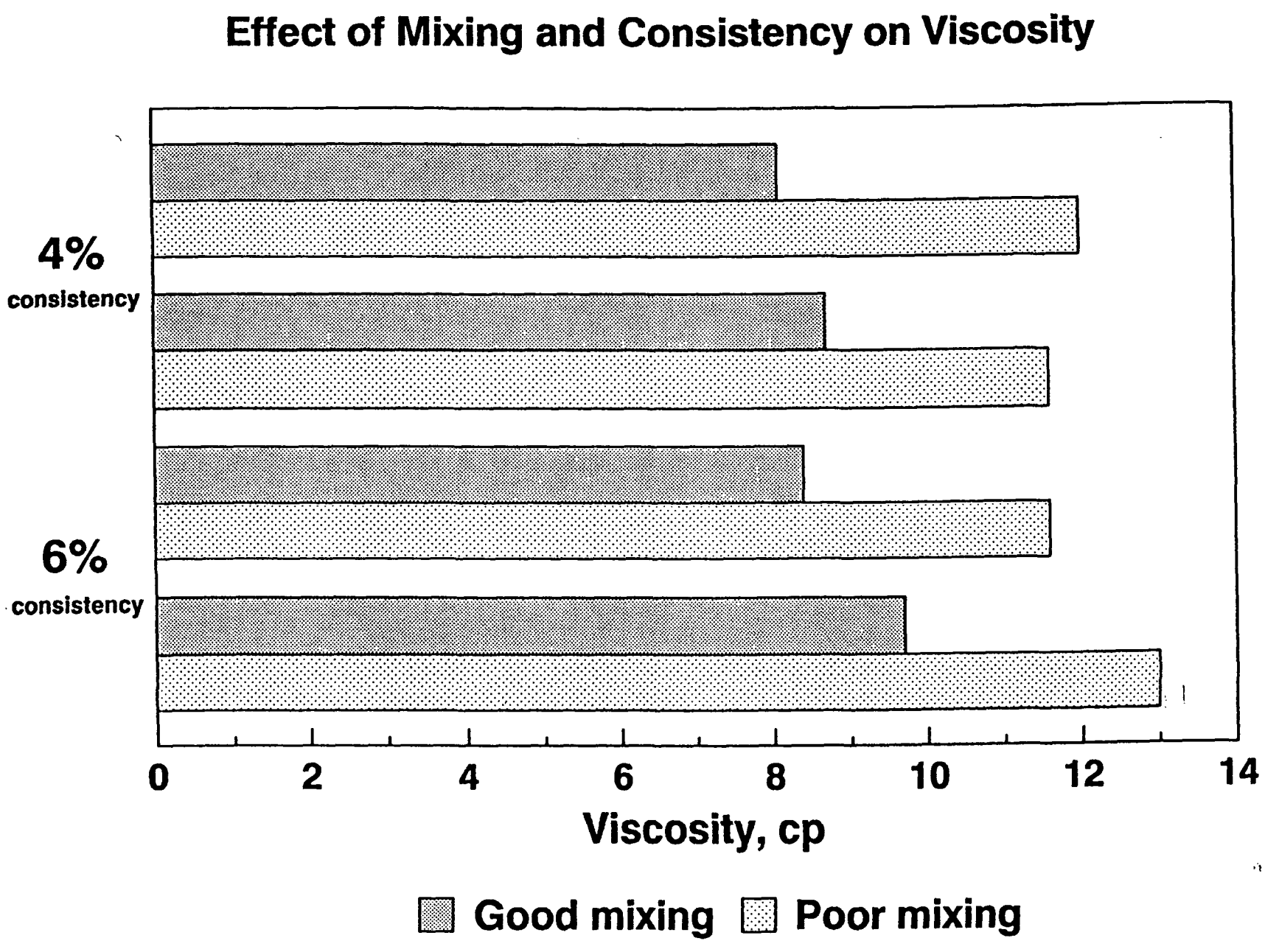
	Shaft Speed (RPM)	Total Injection Time (Seconds)
POOR:	60	13
GOOD:	1800	180

- **Effect of Mixing and Consistency on AOX Formation**


Untreated
Heat treated
AOX, mg/l
150
140
130
120
110
100
90
80
80
90
100
110
120
130
140
150
C and E stage Effluent - Calculated Average (AOX, mg/l)

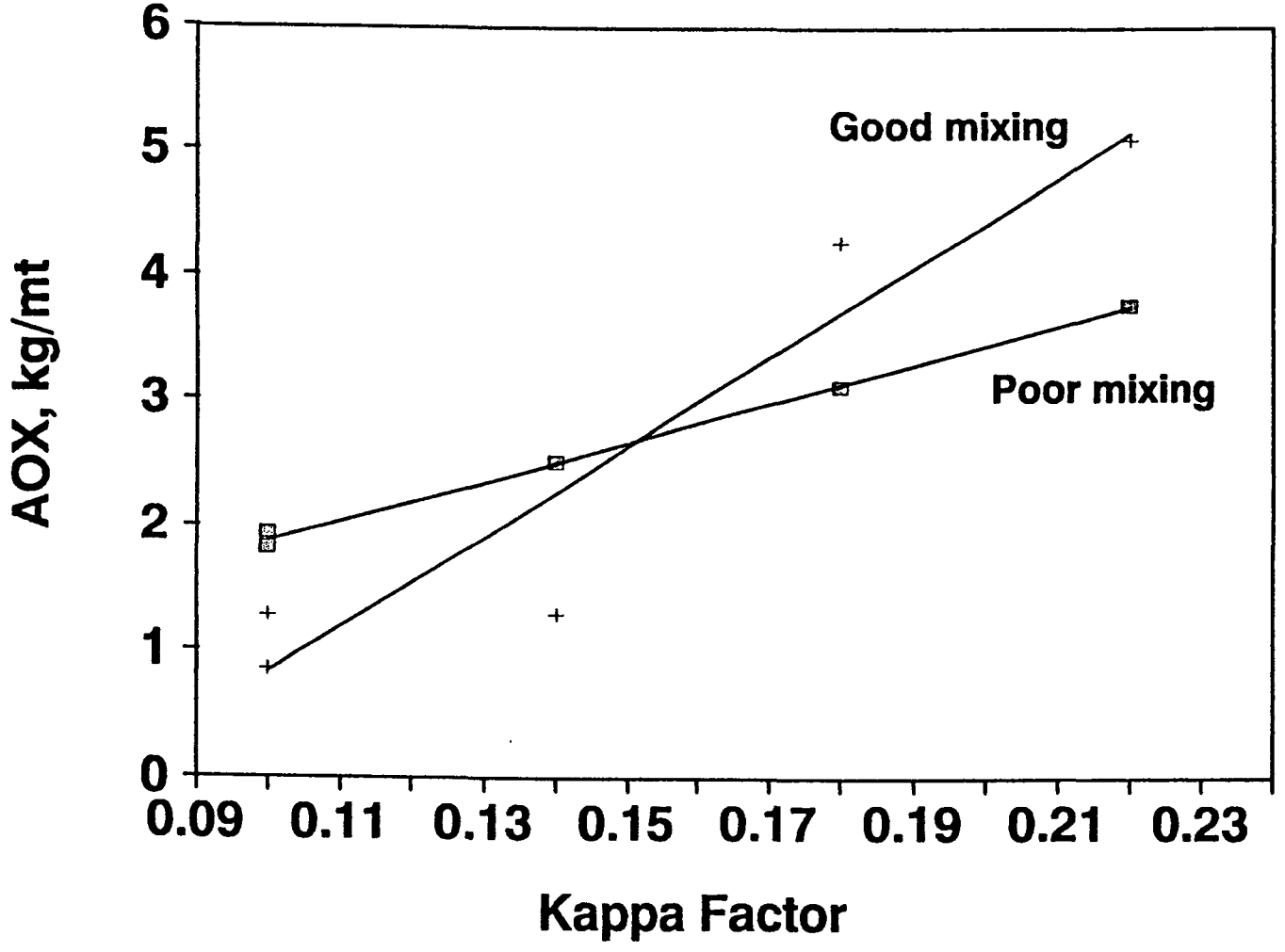

Consistency vs AOX, kg/mt
4%
consistency
6%
consistency
0
1
2
3
4
5
6
AOX, kg/mt
Good mixing
Poor mixing


Effect of Mixing and Consistency on Kappa Number
4%
consistency
6%
consistency
0
1
2
3
4
5
Kappa Number
Good mixing
Poor mixing

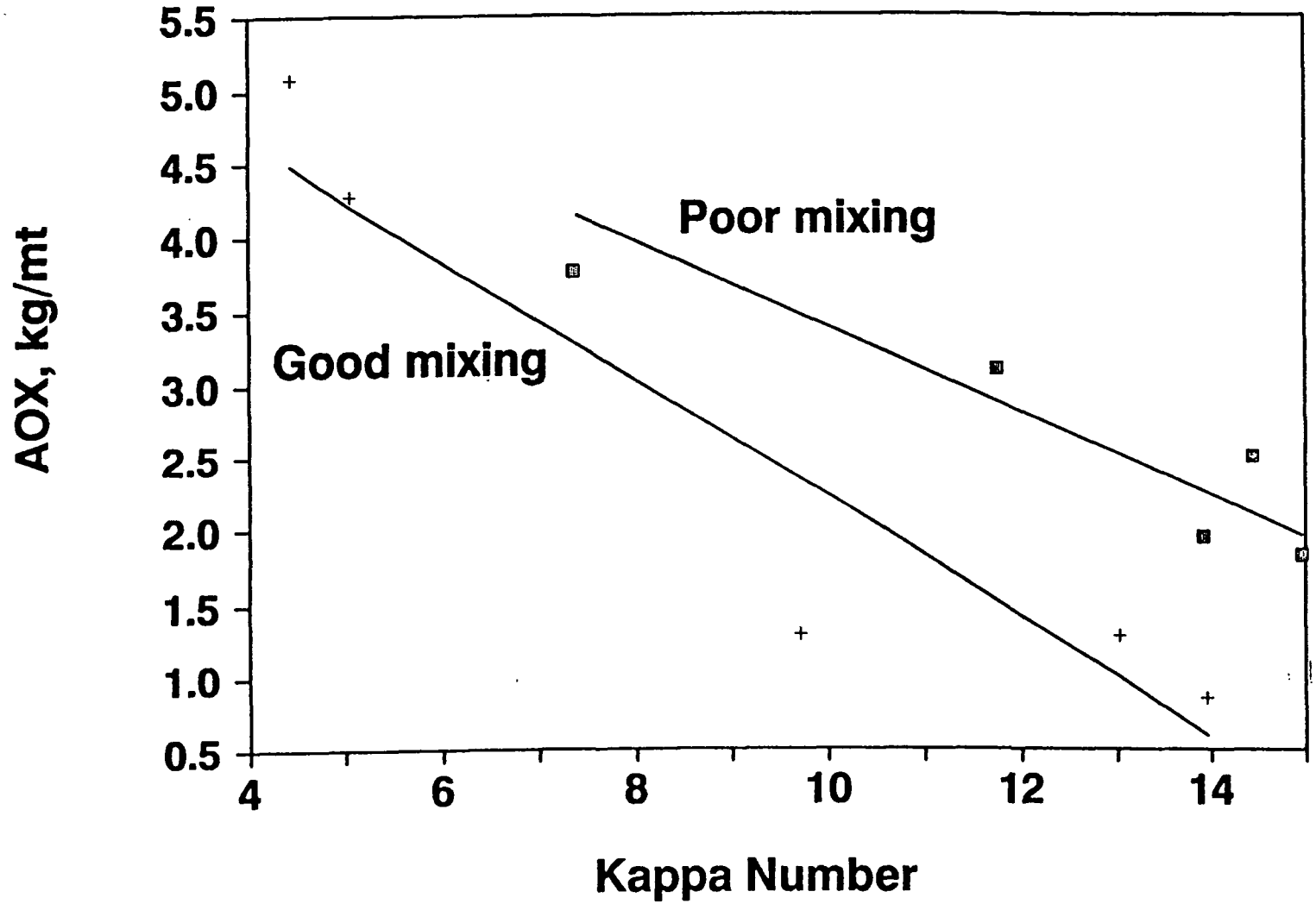

Effect of Mixing and Consistency on Viscosity
4%
consistency
6%
consistency
0
2
4
6
8
10
12
14
Viscosity, cp
Good mixing
Poor mixing

- **Effect of Chlorine Charge and Mixing on AOX Formation**

KAPPA FACTOR VS AOX



KAPPA NUMBER VS AOX



CONCLUSIONS

- No reaction when C and E stage effluents combined
- At kappa factors < 0.15, poor mixing AOX levels were higher
- At kappa factors > 0.15, good mixing AOX levels were higher
- For a given CE kappa number, good mixing uses less chlorine and produces lower AOX levels

FUTURE

WORK

PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

PART 3: PRETREATMENTS TO IMPROVE OXYGEN BLEACHING SELECTIVITY

April 2, 1991

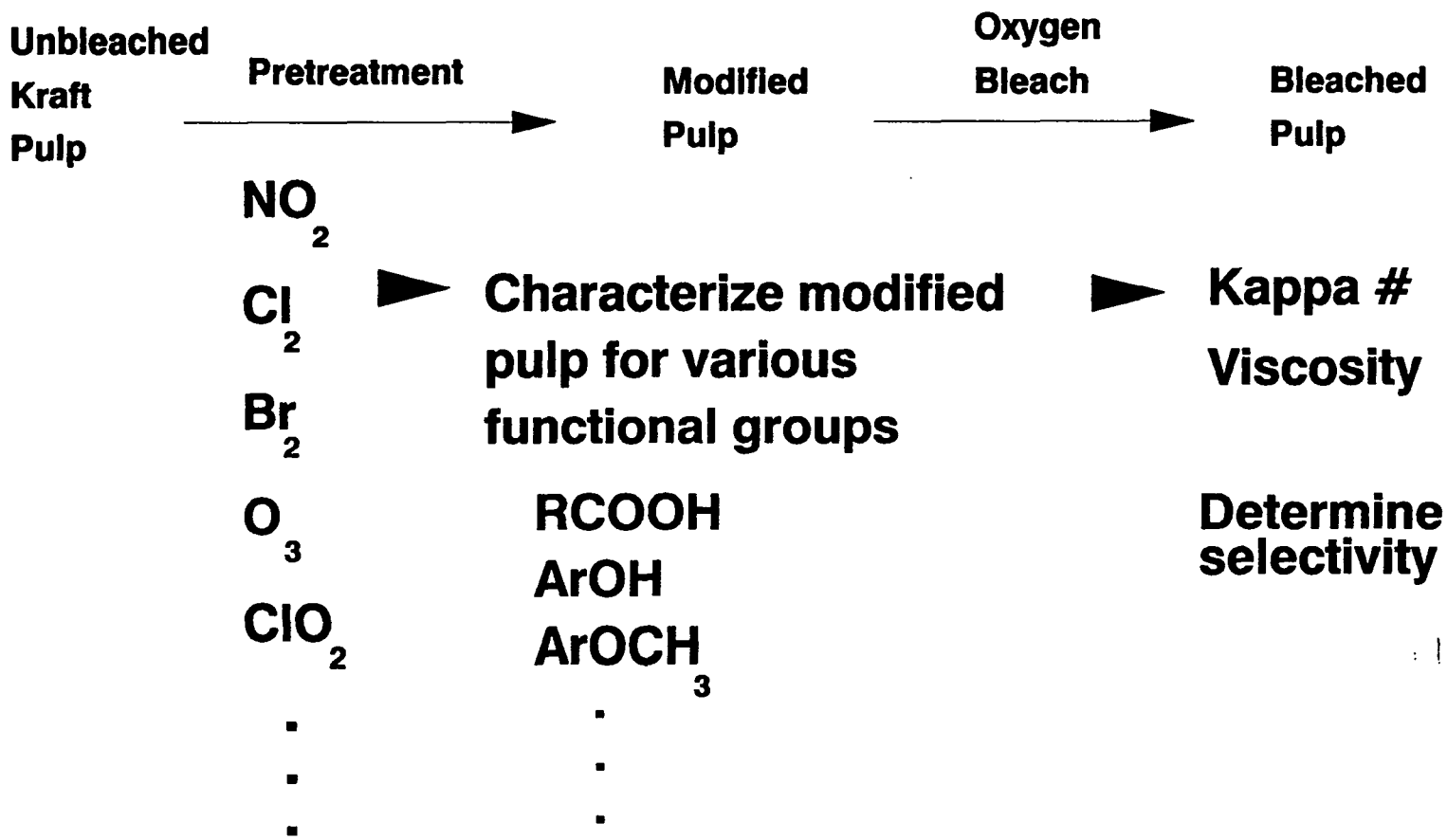
Kyle R. Reed

Project 3474

Enviromentally Compatible Production of Bleached Pulp

Pretreatments to Improve Oxygen Bleaching Selectivity

Experimental strategy:



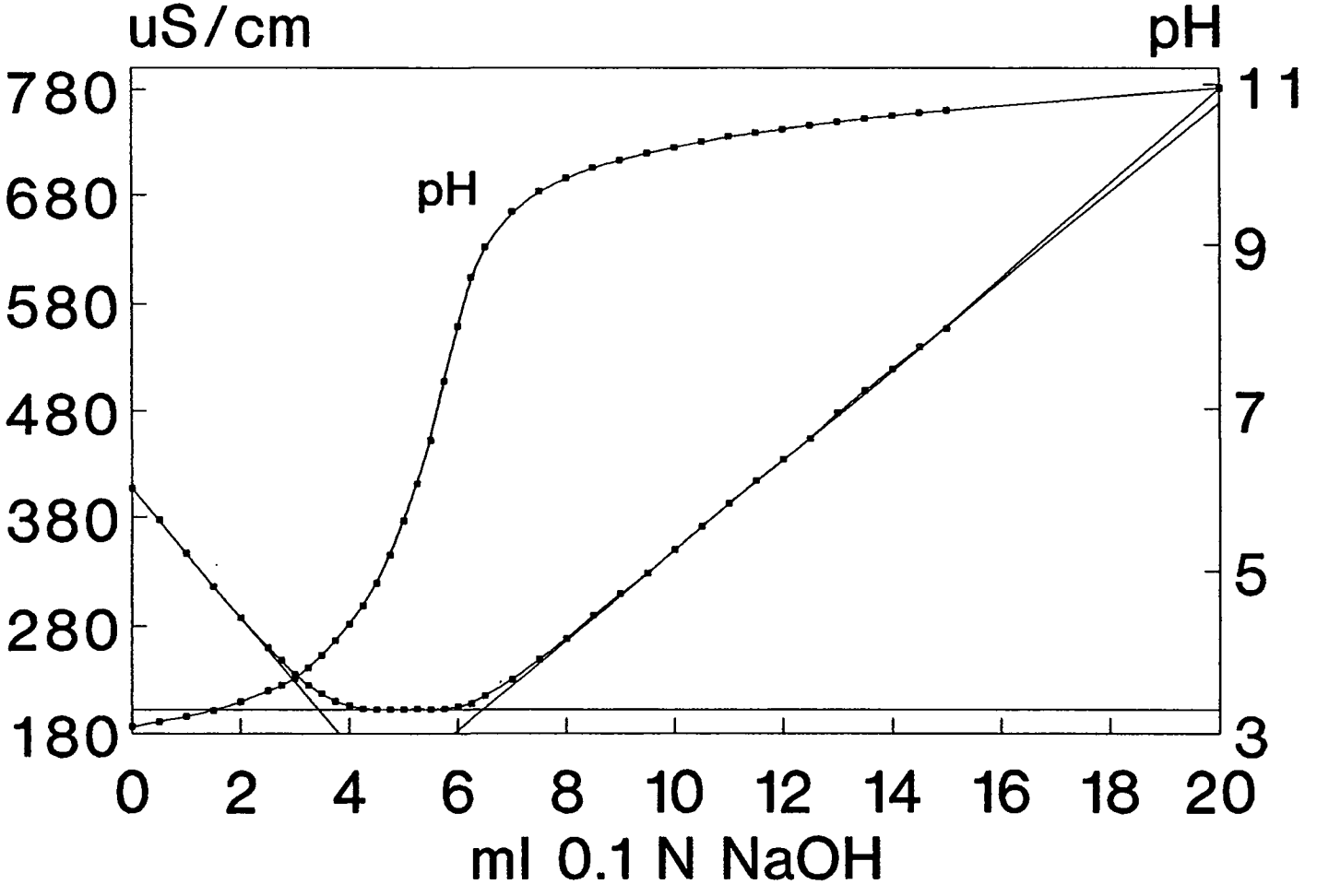
Factors which may influence bleaching selectivity:

A) Carbohydrate protection

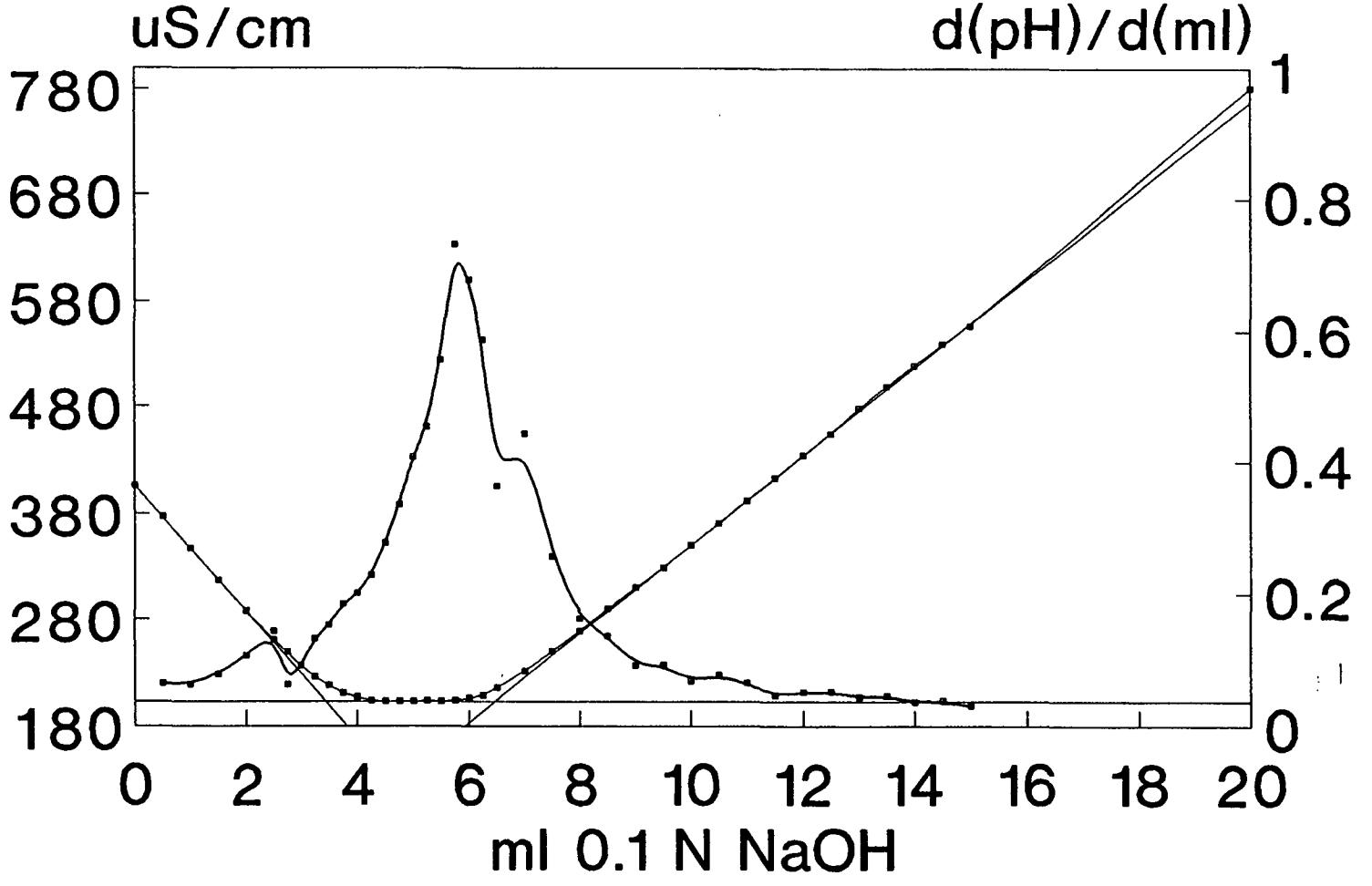
B) Decreased lignin stability

C) Hydrophilic properties of residual lignin

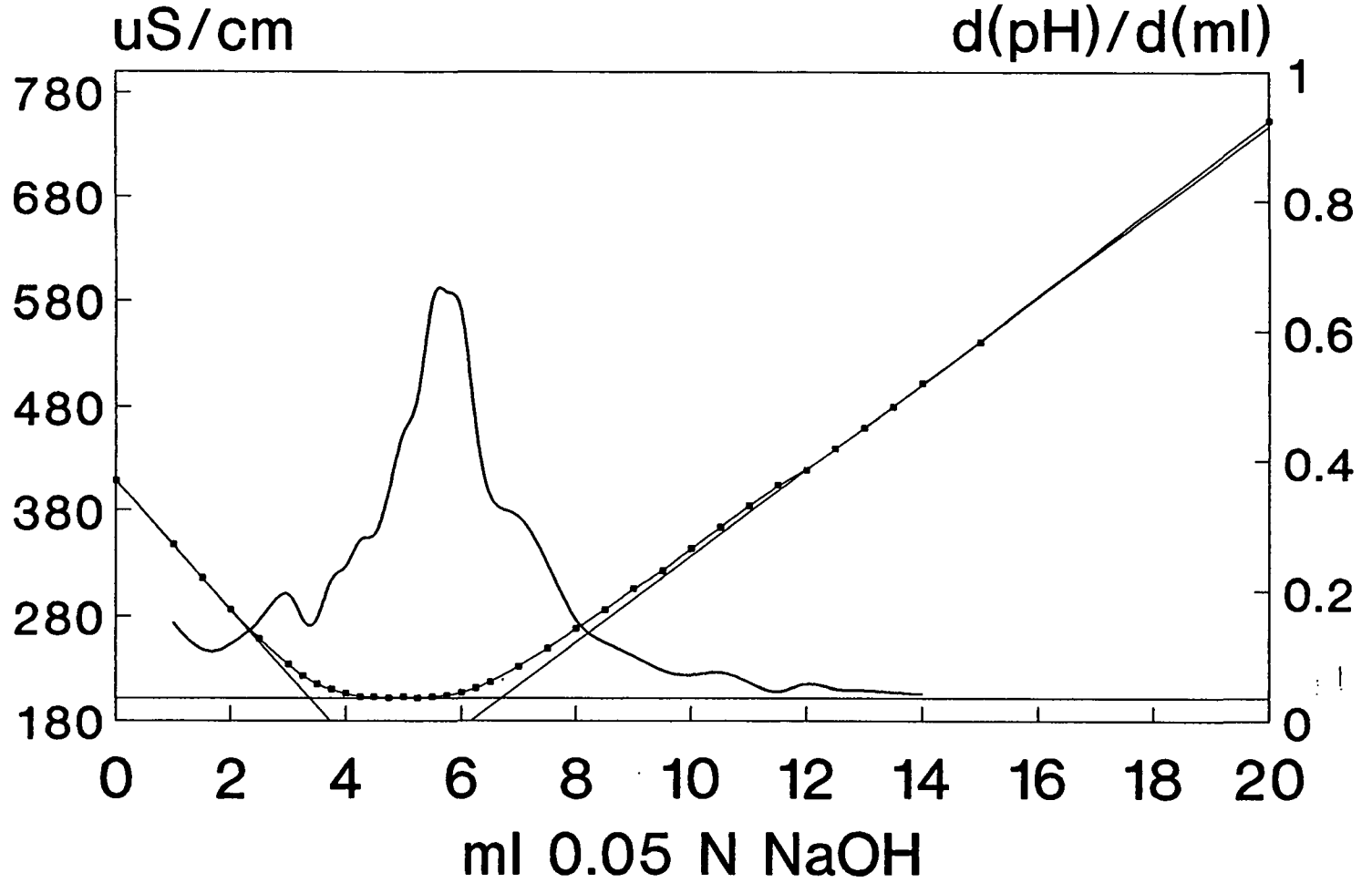
Conductometric Titration of Untreated Kraft Pulp



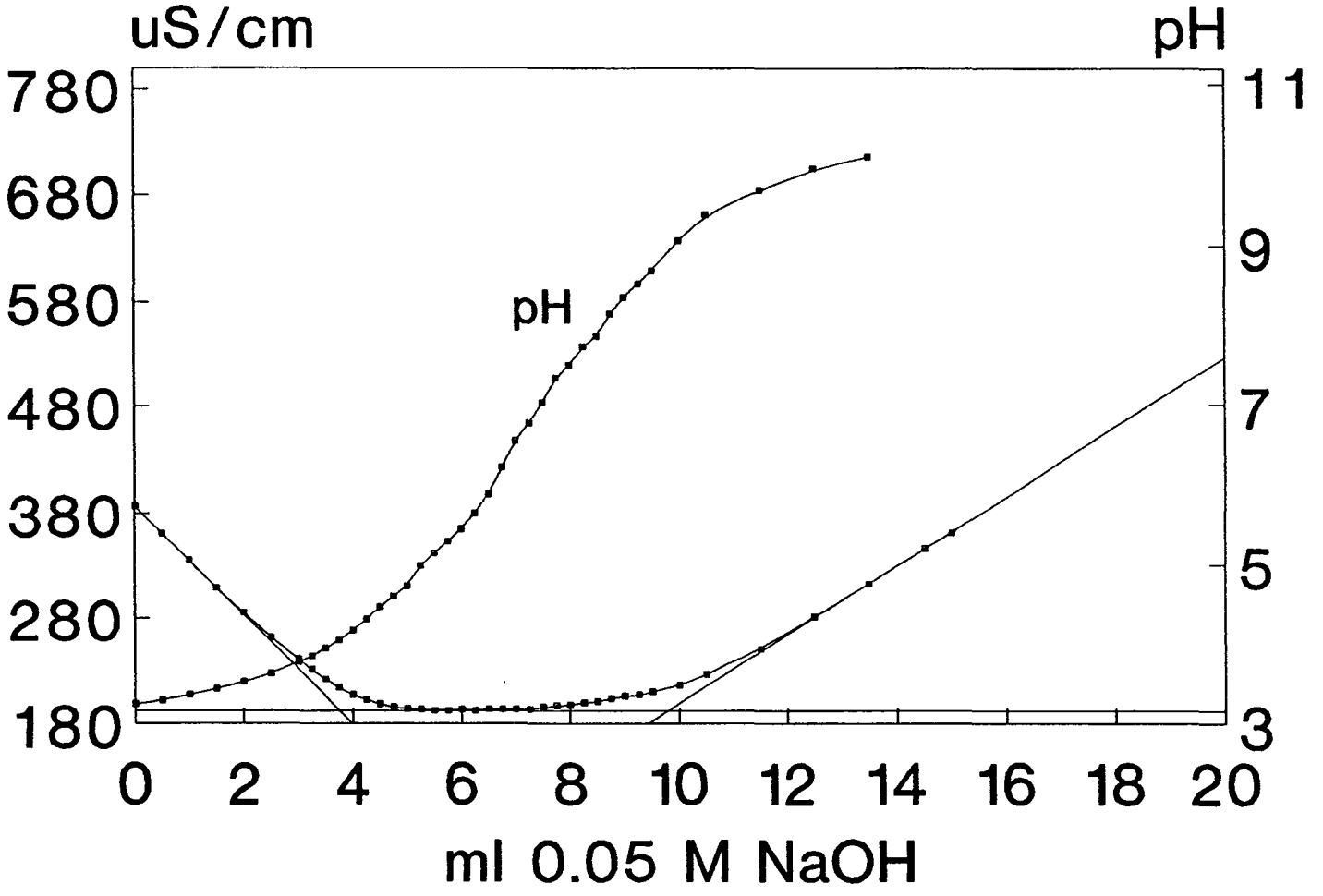
1st Derivative of pH Curve
Untreated Kraft Pulp



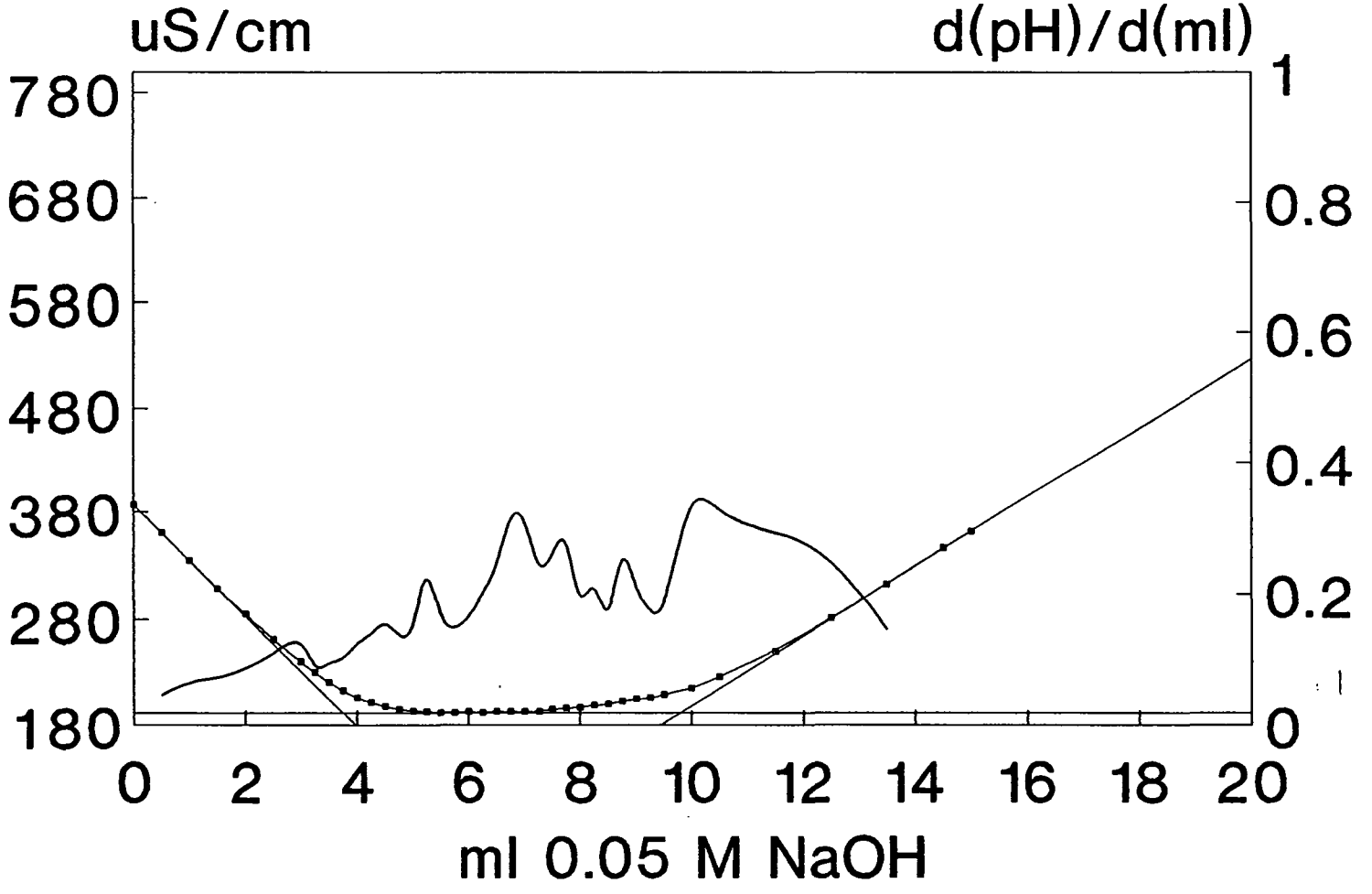
1st Derivative of pH Curve
Untreated Kraft Pulp

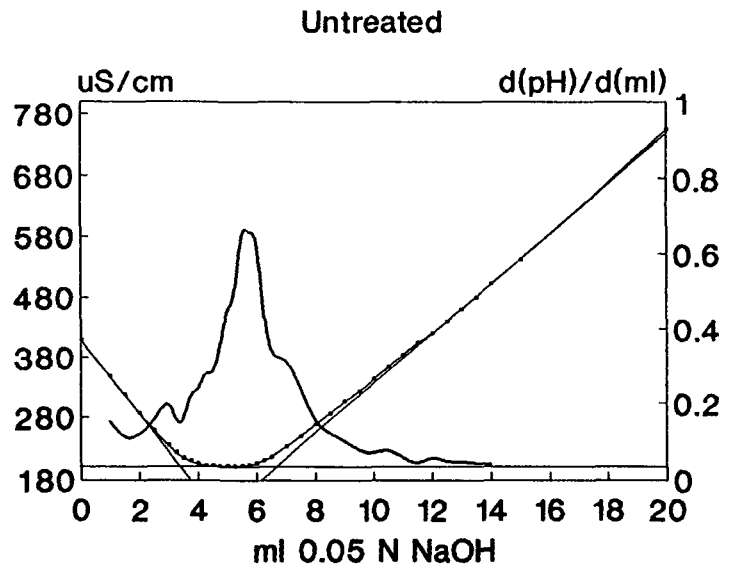


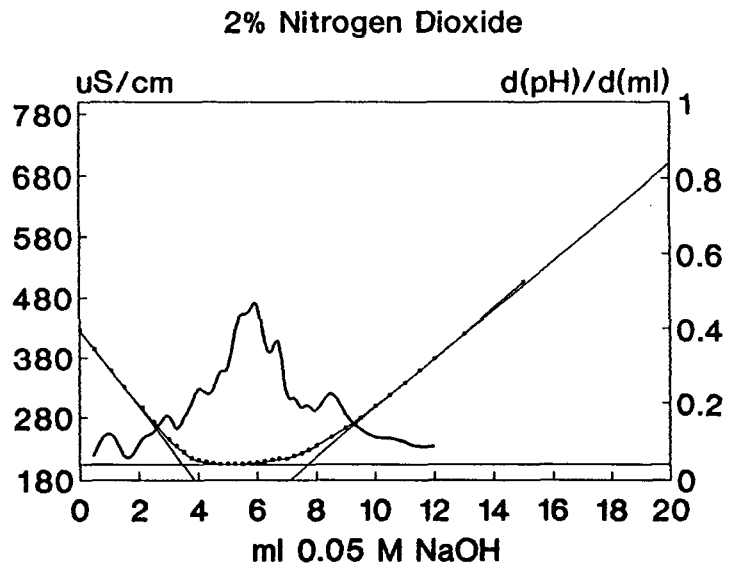
Conductometric Titration of Treated Pulp
8% Nitrogen Dioxide

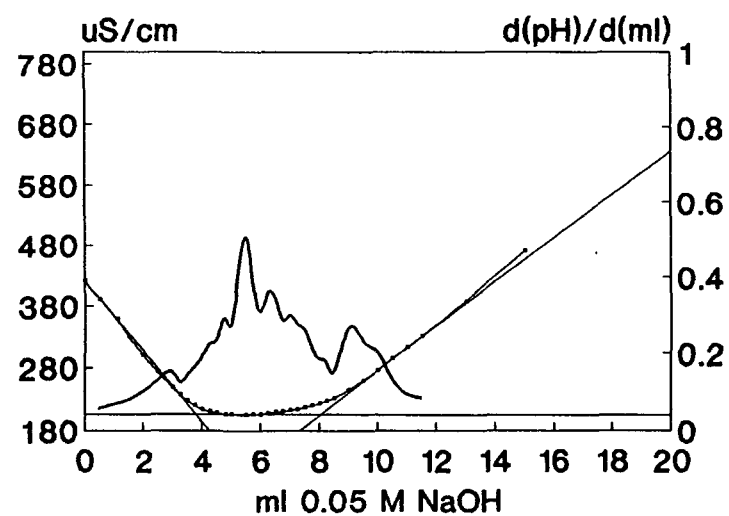


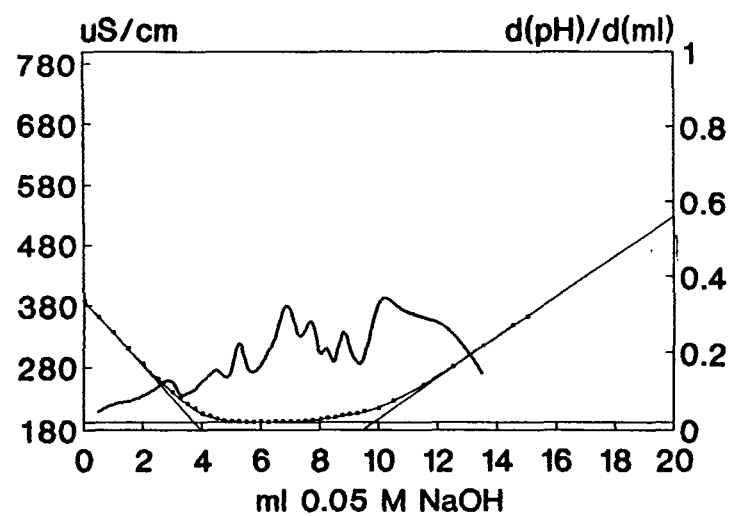
1st Derivative of pH Curve
8% Nitrogen Dioxide




Untreated
uS/cm
d(pH)/d(ml)
780
680
580
480
380
280
180
1
0.8
0.6
0.4
0.2
0
0 2 4 6 8 10 12 14 16 18 20
ml 0.05 N NaOH


2% Nitrogen Dioxide
uS/cm
d(pH)/d(ml)
780
680
580
480
380
280
180
1
0.8
0.6
0.4
0.2
0
0 2 4 6 8 10 12 14 16 18 20
ml 0.05 M NaOH

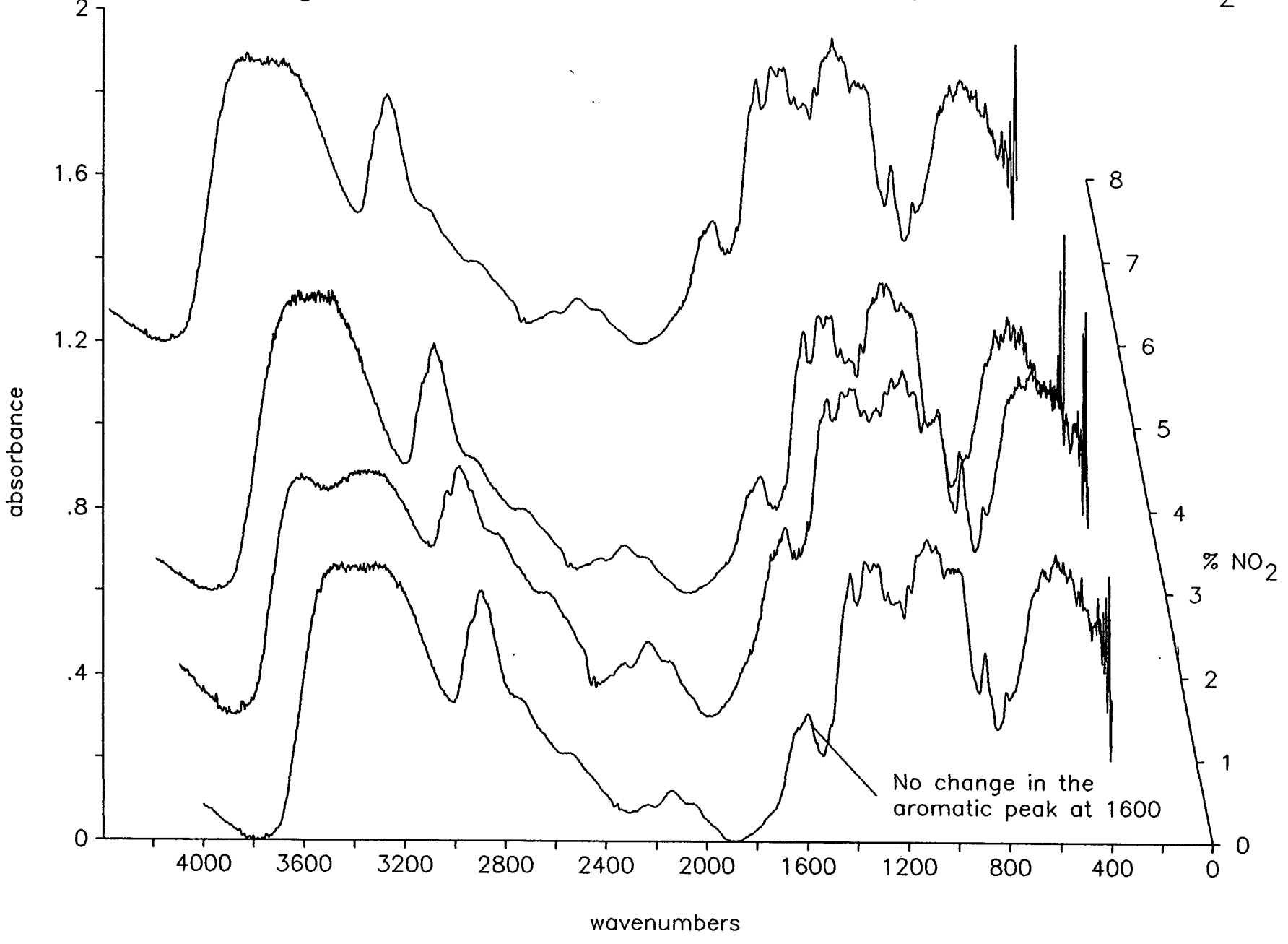

4% Nitrogen Dioxide
uS/cm
d(pH)/d(ml)
780
680
580
480
380
280
180
1
0.8
0.6
0.4
0.2
0
0 2 4 6 8 10 12 14 16 18 20
ml 0.05 M NaOH


8% Nitrogen Dioxide
uS/cm
d(pH)/d(ml)
780
680
580
480
380
280
180
1
0.8
0.6
0.4
0.2
0
0 2 4 6 8 10 12 14 16 18 20
ml 0.05 M NaOH

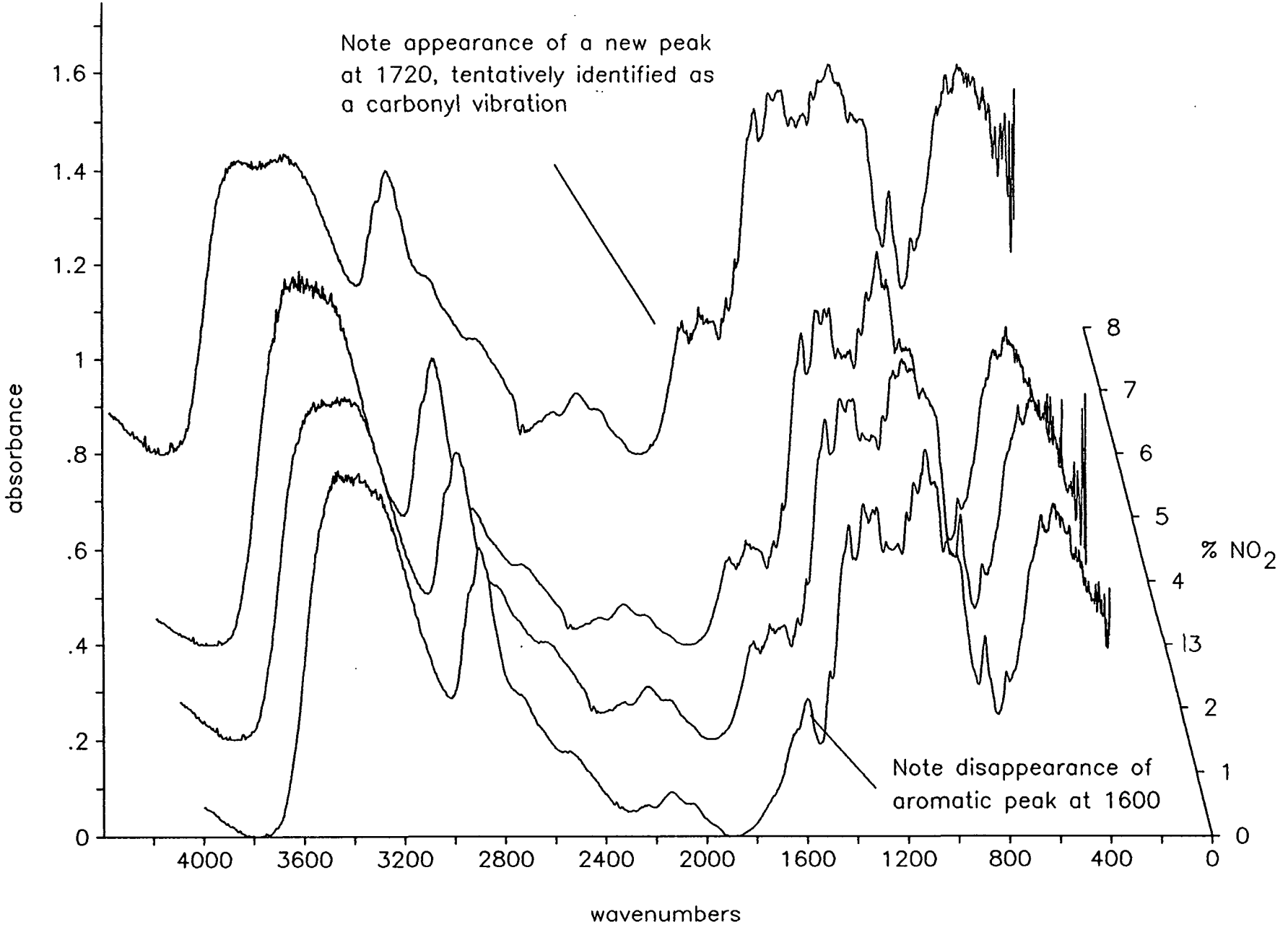
Acid Content of Treated Kraft Pulps

Treatment	Acidity meq/kg
None	106
2% Nitrogen Dioxide	155
4% Nitrogen Dioxide	138
8% Nitrogen Dioxide	153

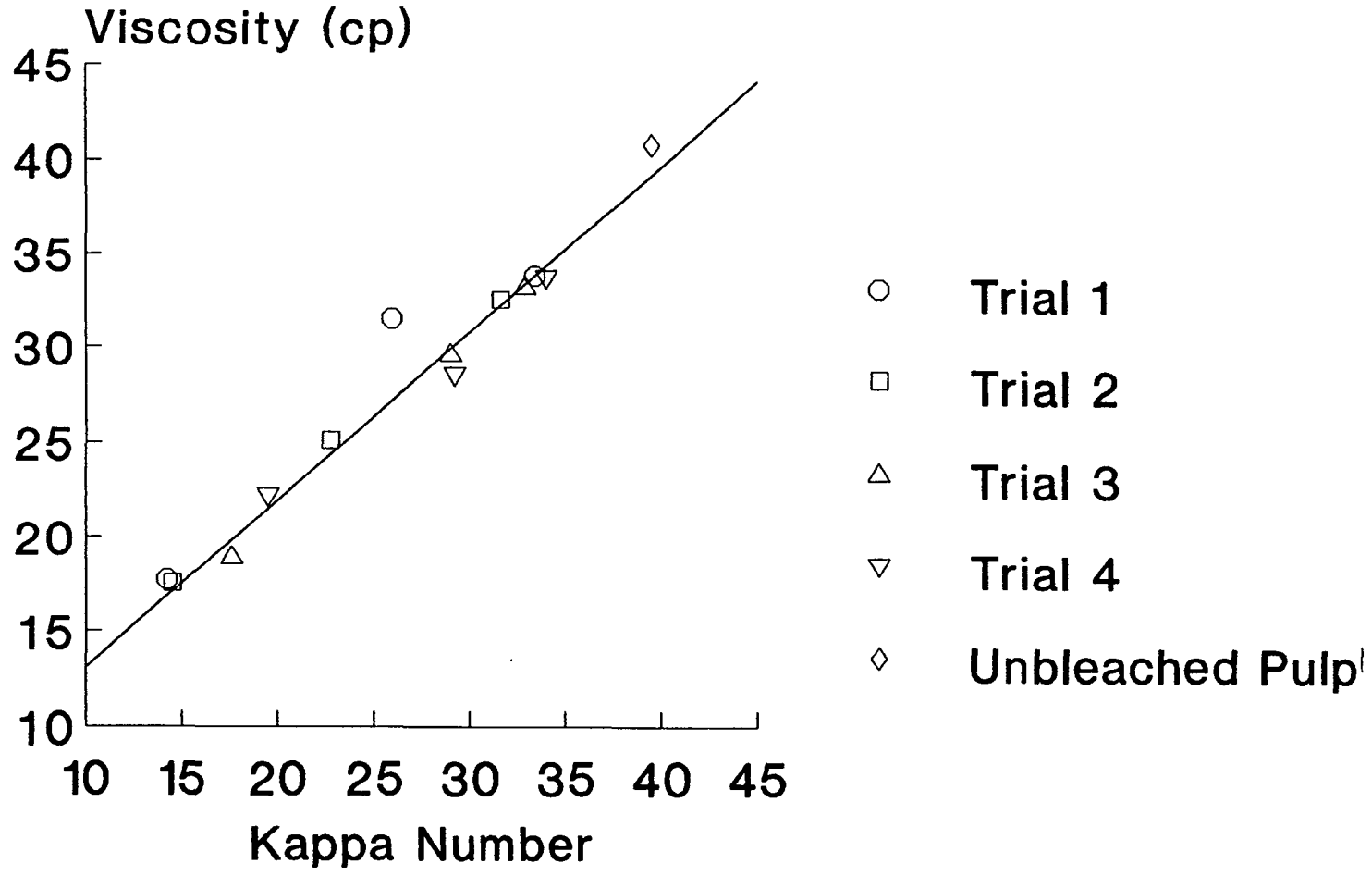
Drift Spectra of Bleached Loblolly Pine Pulp Following Treatment With 0, 2, 4, and 8% NO_2



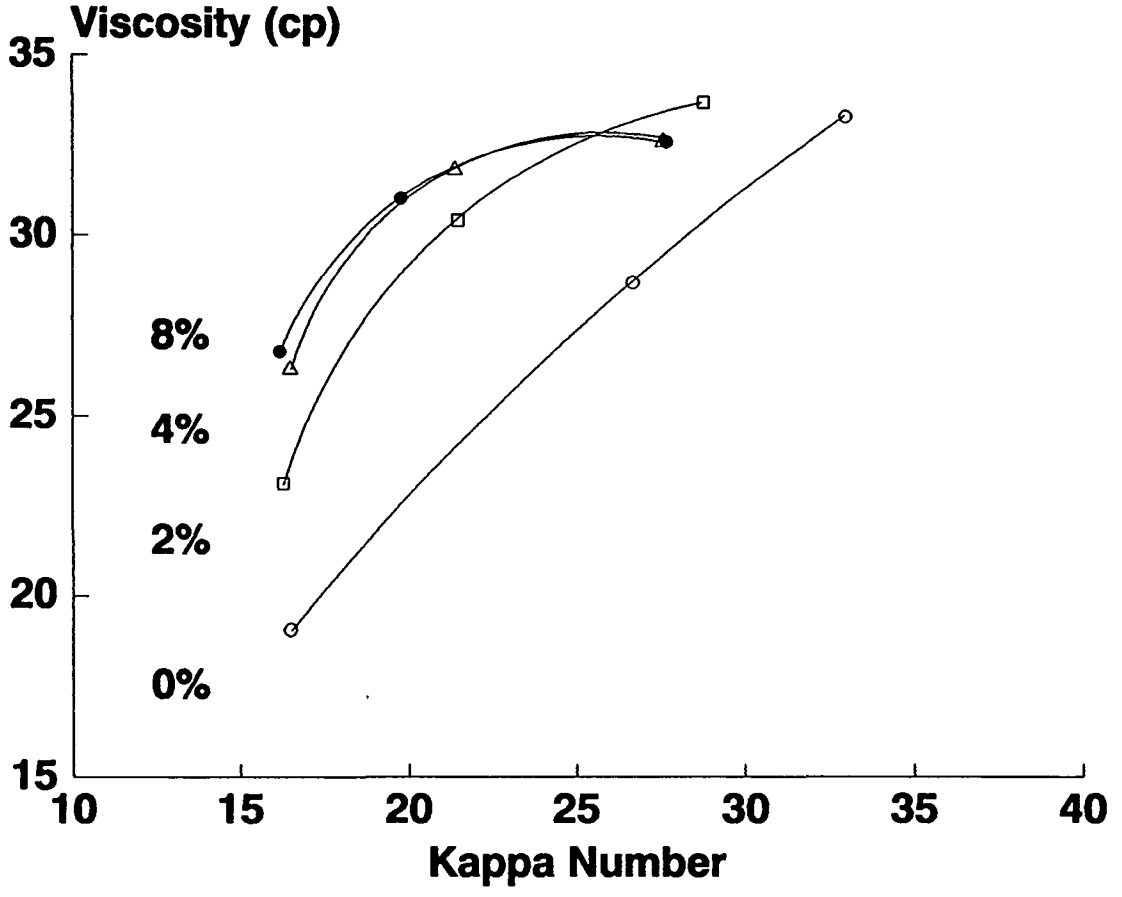
DRIFT Spectra of Unbleached Loblolly Pine Pulp Following Treatment With 0, 2, 4, and 8% NO_2



Viscosity/Kappa # Plot for Oxygen Bleaching of Untreated Kraft Pulp



Viscosity/Kappa # Plots for Nitrogen Dioxide Pretreatment



Conclusions

- introduction of nitrophenolic groups likely
- acid content of pulps increased significantly by nitrogen dioxide
- technique which will follow "pKa spectrum" of pulp is possible

PROJECT 3699

EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS

April 2, 1991

Charles E. Courchene

IPST

Project 3699

CONDUCTIVITY SENSOR EVALUATION

IPST

Project 3699

CONDUCTIVITY SENSOR EVALUATION

- OBJECTIVE -

TO EVALUATE COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS FOR THEIR ABILITY TO ACCURATELY AND REPRODUCIBLY MONITOR ALKALI CONCENTRATION IN PROCESS STREAMS

IPST

Project 3699

PROJECT PERSONNEL

SAM SUH

Director Process Control Technology - Champion International

KAREL CERNY

Senior Control Systems Engineer - Georgia Pacific Corp.

EARL MALCOLM - DIVISION DIRECTOR - IPST

TOM MCDONOUGH

Group Leader Pulping and Bleaching - IPST

CHUCK COURCHENE - Supervisor Pulping Laboratory - IPST

LEE THAMES - Technician - IPST

SUPPLIER REPRESENTATIVES

IPST

Project 3699

COMMERCIALLY AVAILABLE INDUSTRIAL SENSORS

TYPES

- FOUR ELECTRODE
- INSERTION ELECTRODELESS
- FLOW THROUGH ELECTRODELESS

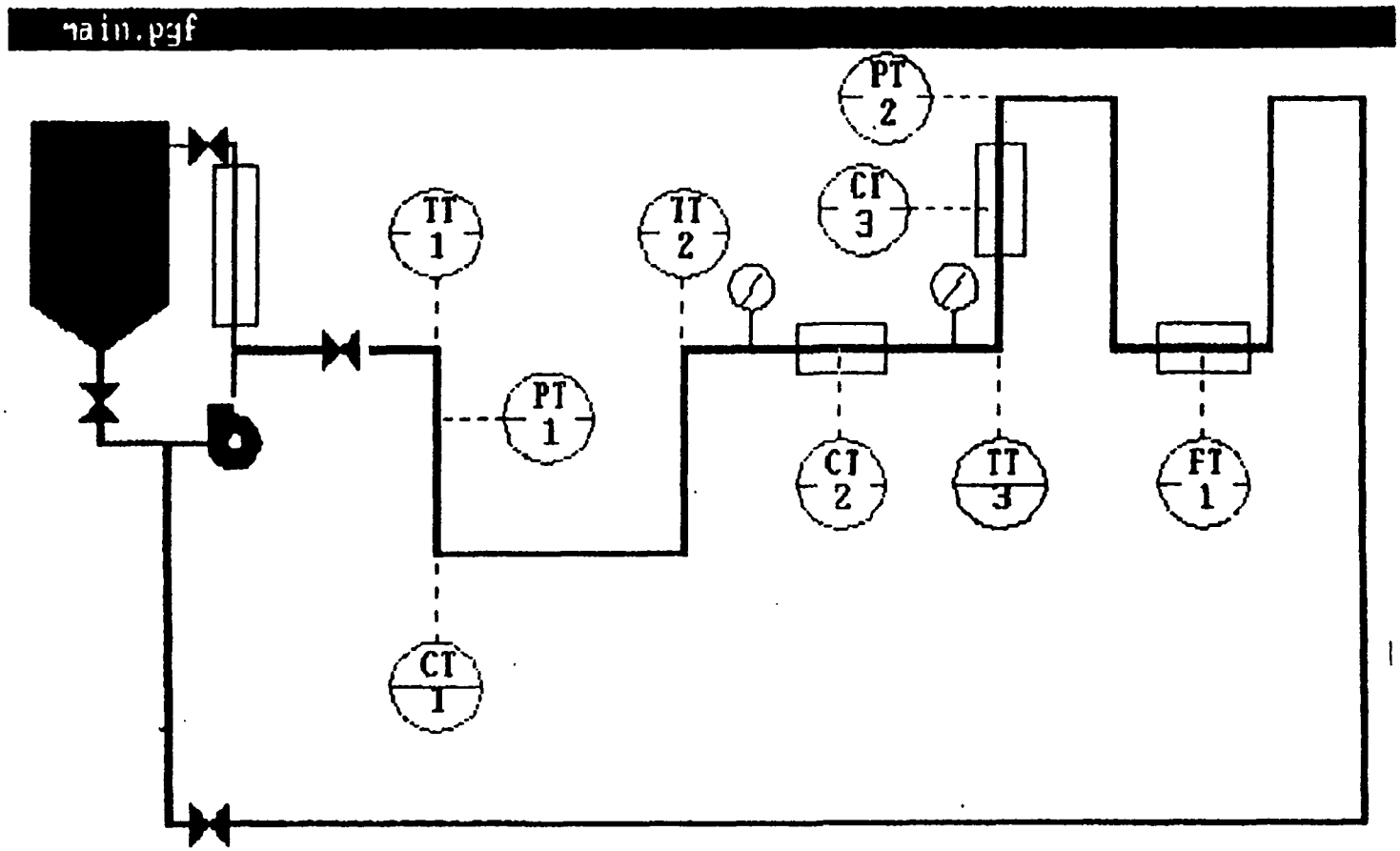
IPST

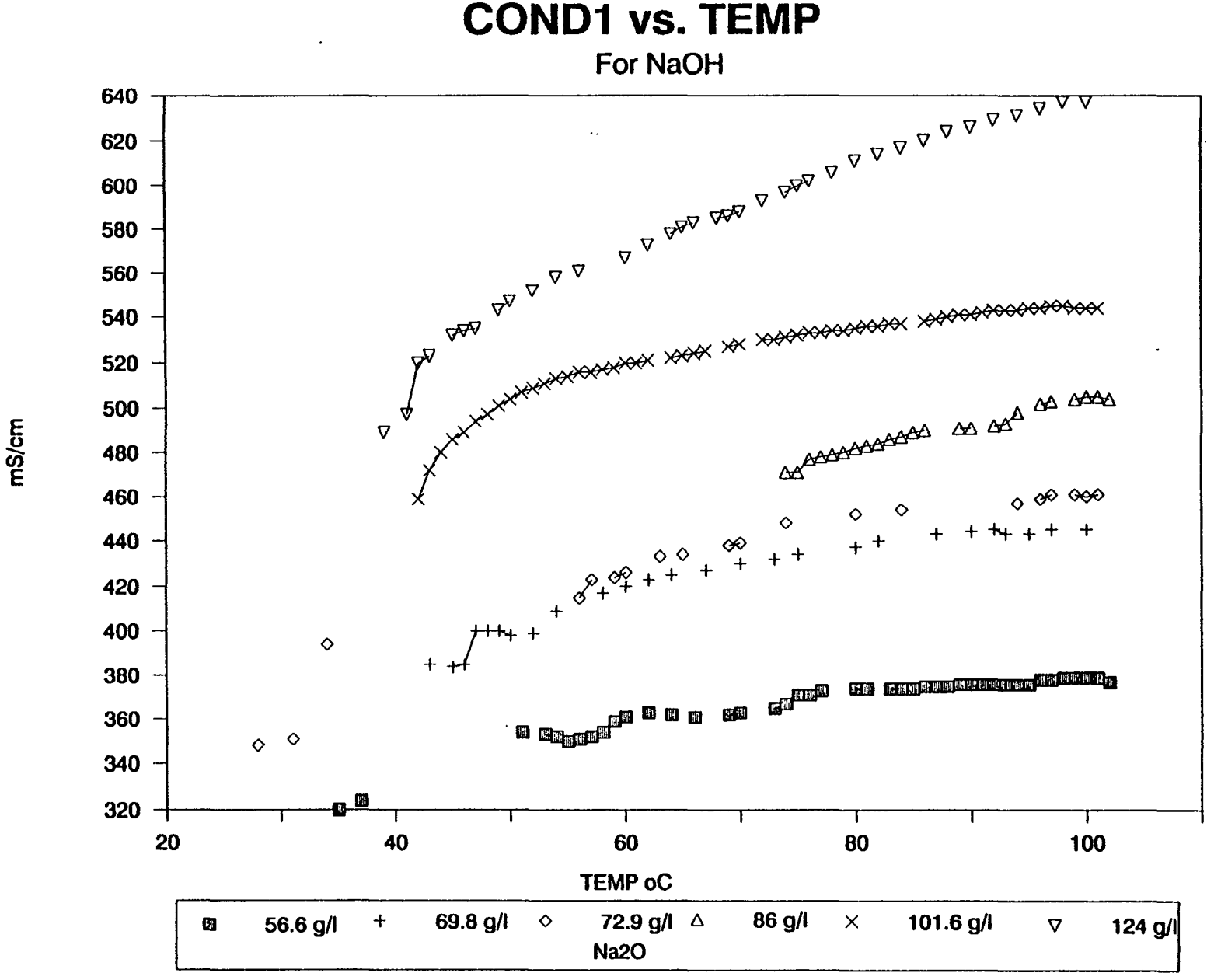
Project 3699

PHASE I TESTING

- SYNTHETIC WHITE LIQUOR
- VARIABLES
  - TEMPERATURE
  - CHEMICAL CONCENTRATION
  - VELOCITY

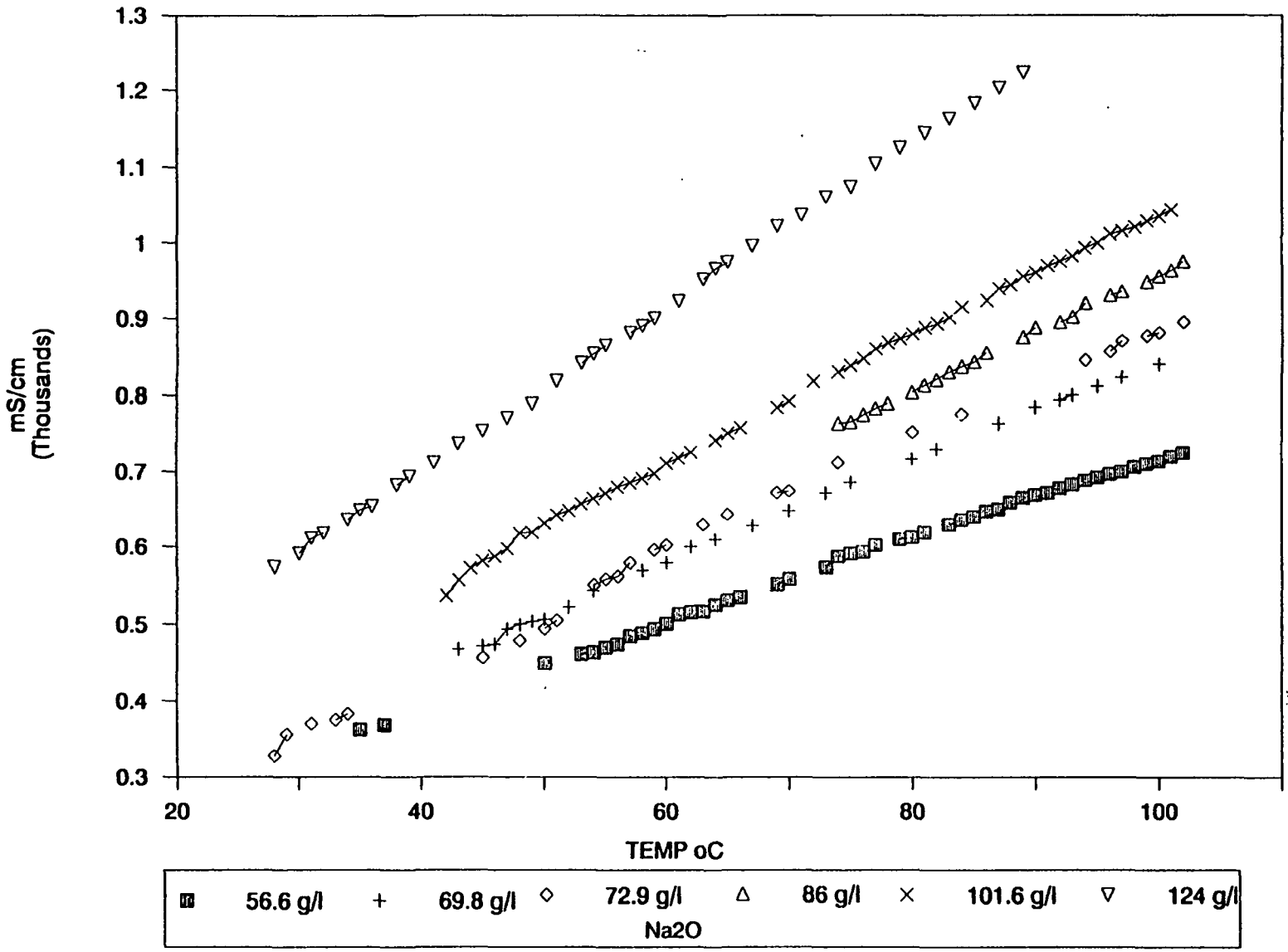
IPST
Project 3699

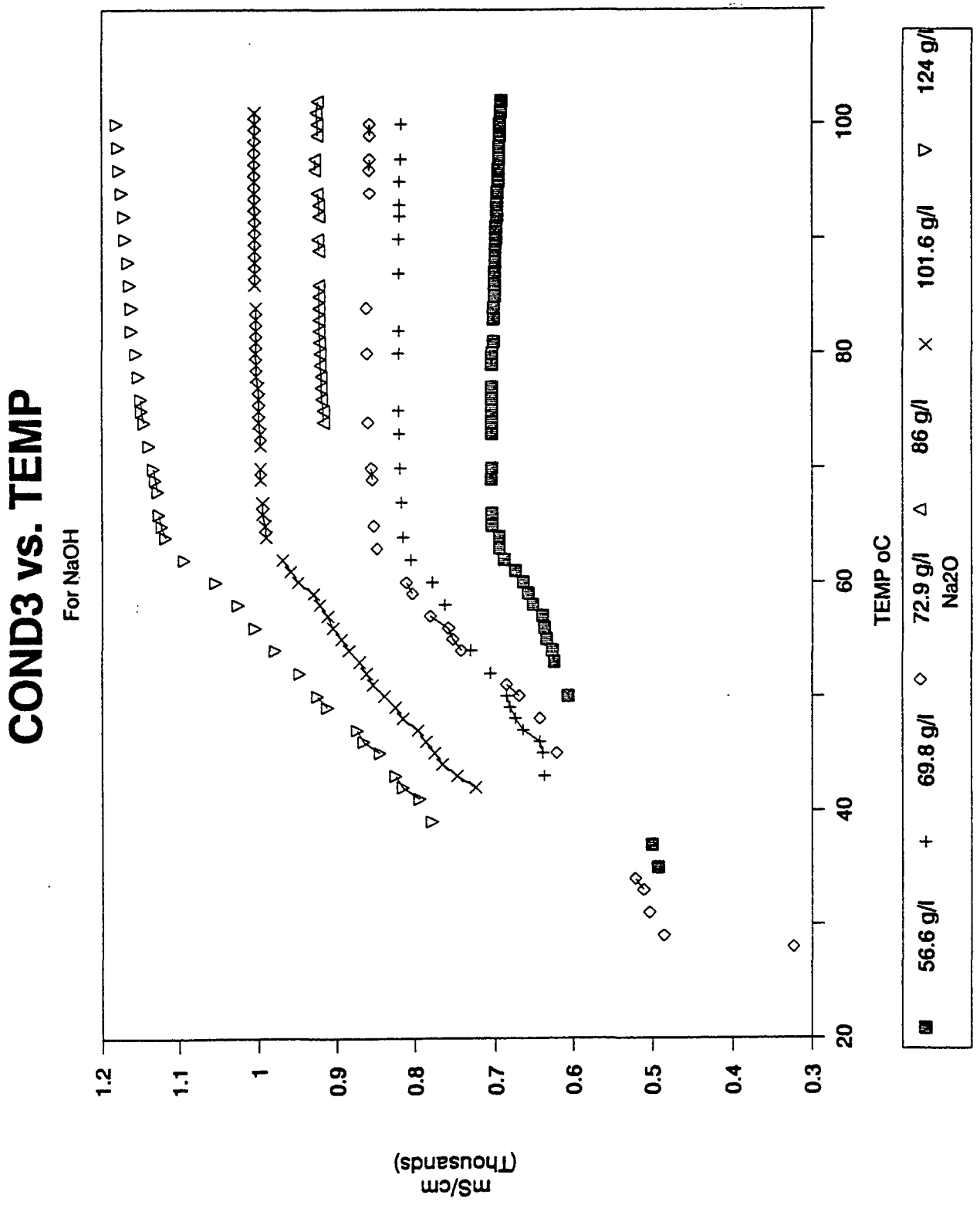



COND1 vs. TEMP
For NaOH
mS/cm
640
620
600
580
560
540
520
500
480
460
440
420
400
380
360
340
320
20
40
60
80
100
TEMP oC
56.6 g/l
69.8 g/l
72.9 g/l
86 g/l
101.6 g/l
124 g/l
Na2O

COND2 vs. TEMP

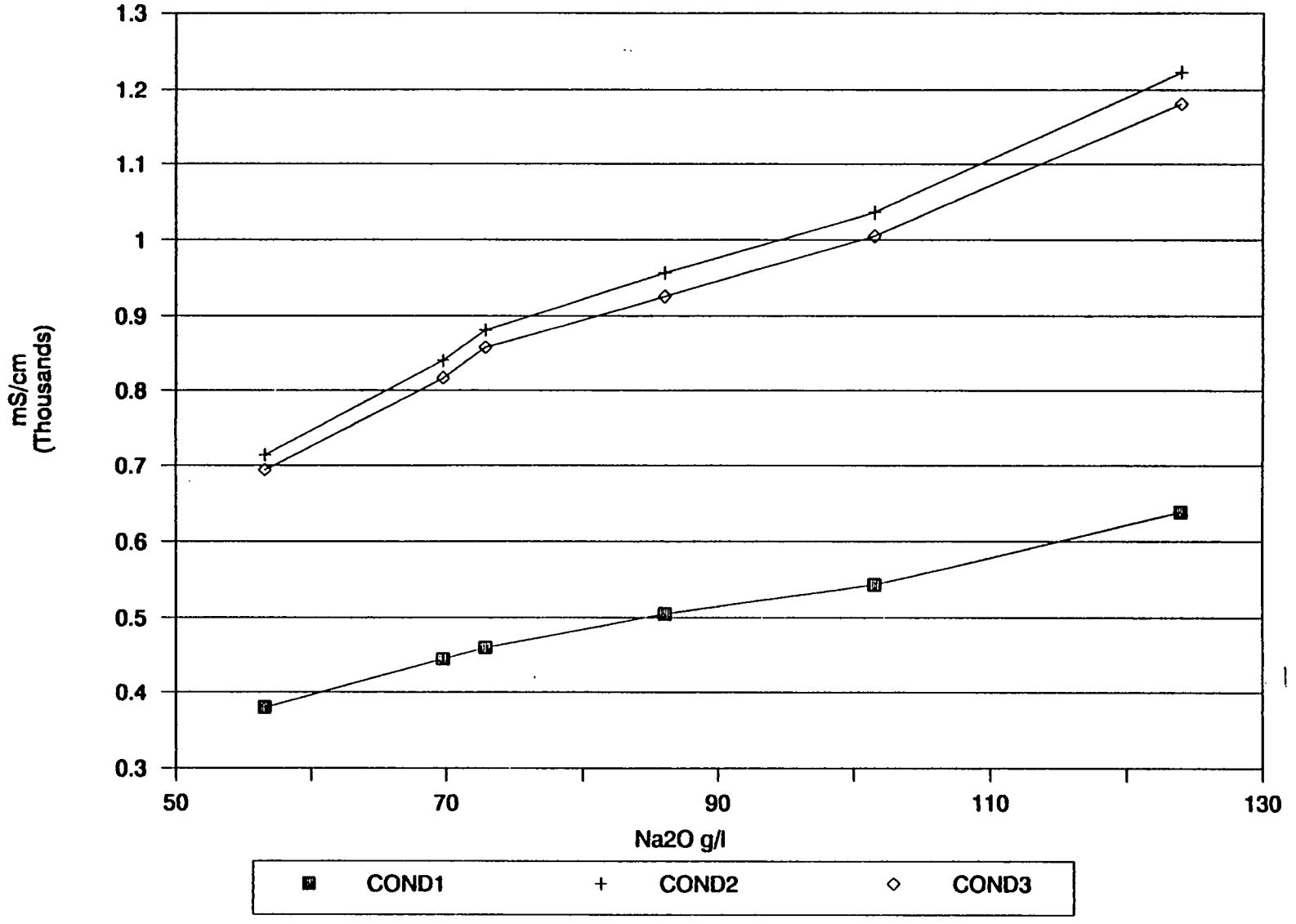
For NaOH



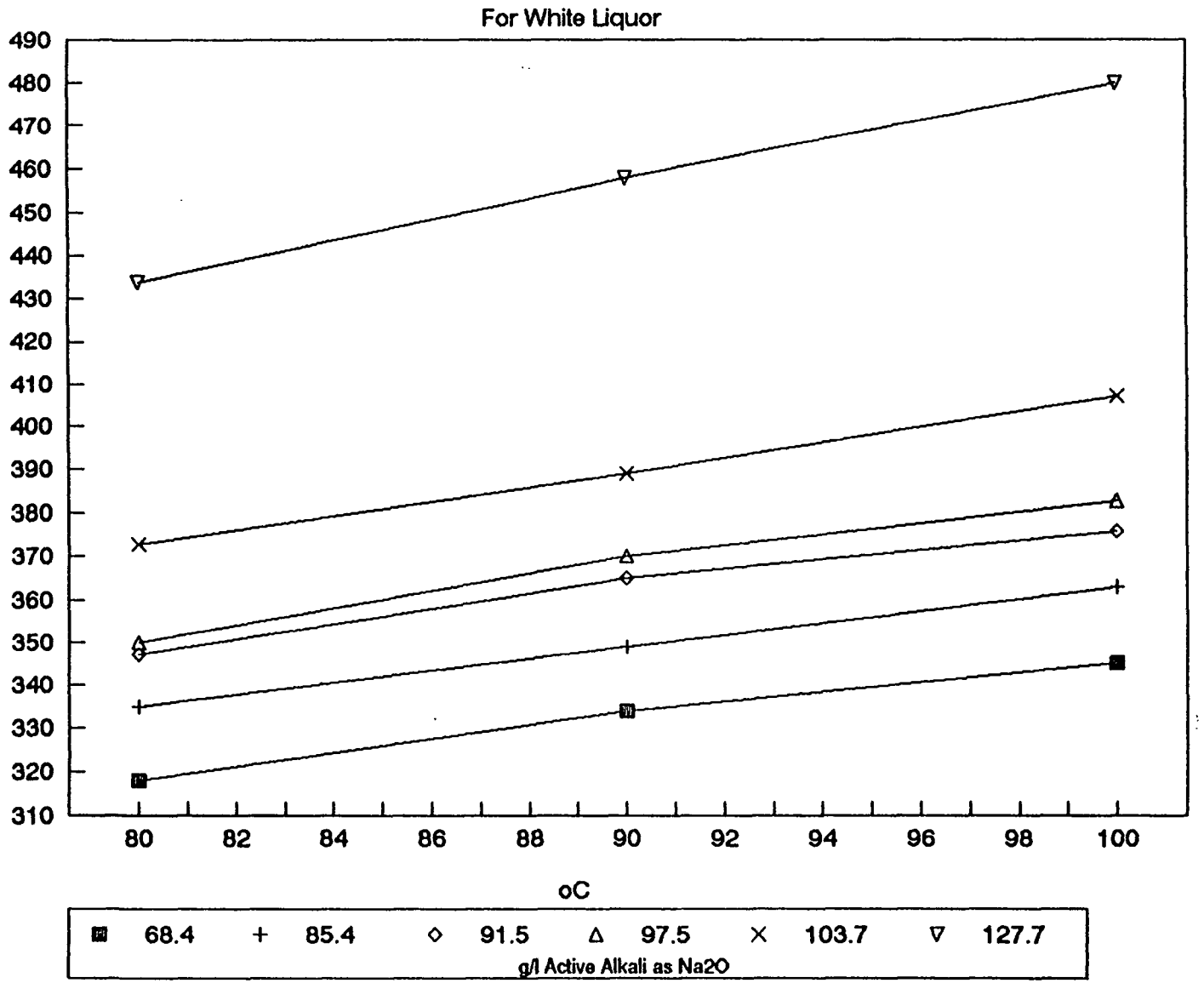

COND3 vs. TEMP
For NaOH
mS/cm
(Thousands)
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
20
40
60
80
100
TEMP oC
56.6 g/l
69.8 g/l
72.9 g/l
86 g/l
101.6 g/l
124 g/l
Na2O

CONDUCTIVITY vs. ALKALI

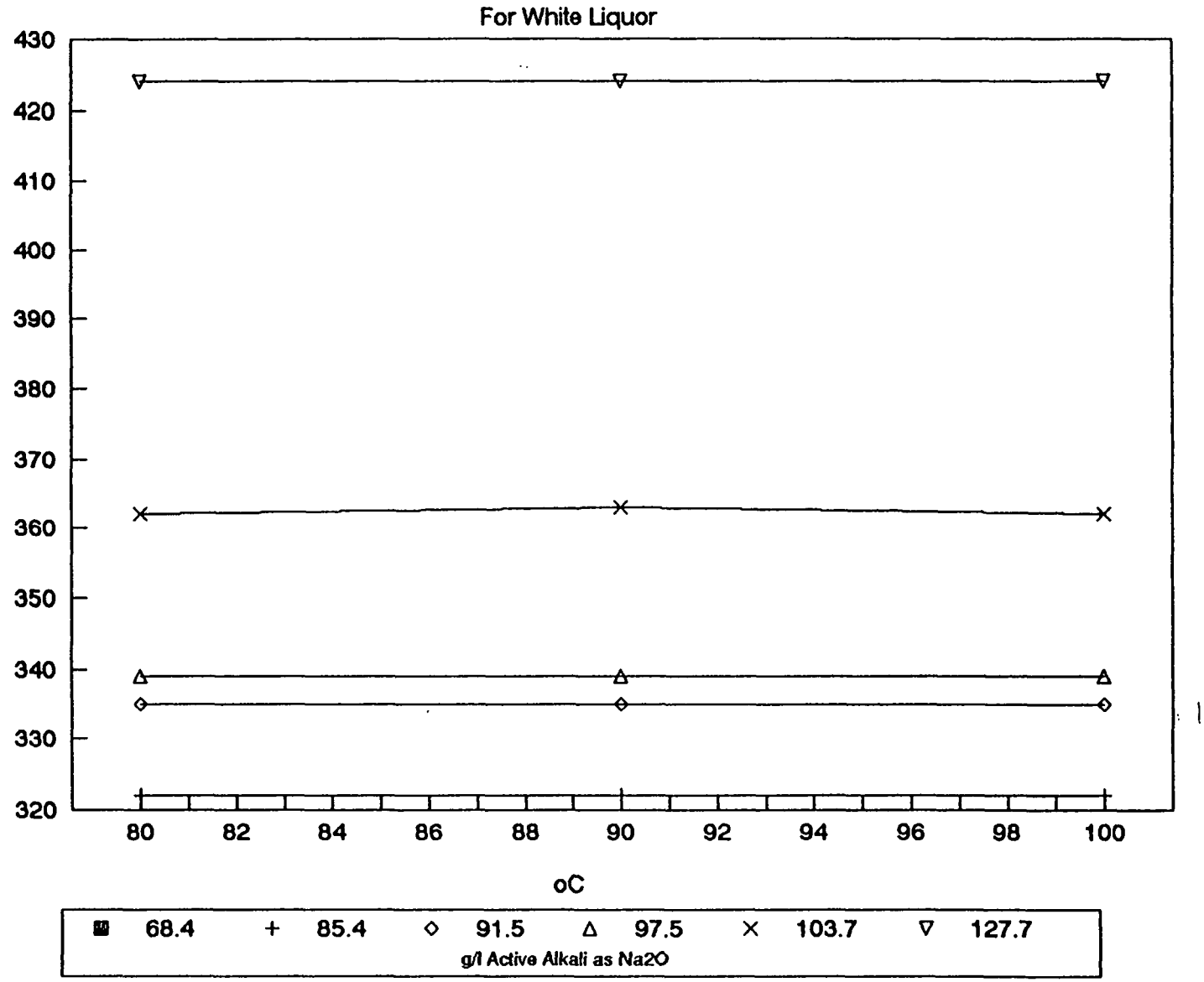
Values at 100 oC for NaOH



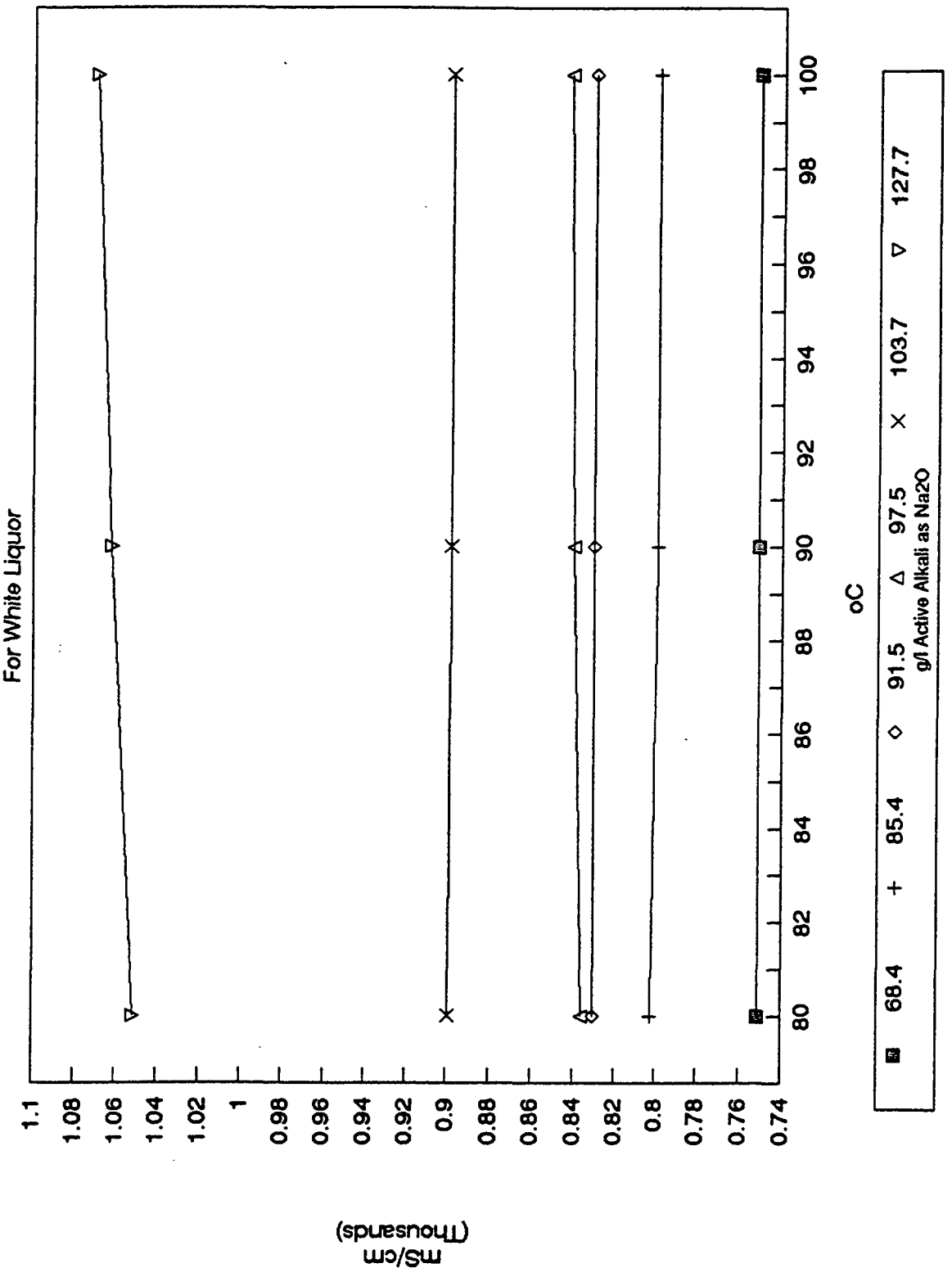
COND1 VS TEMP



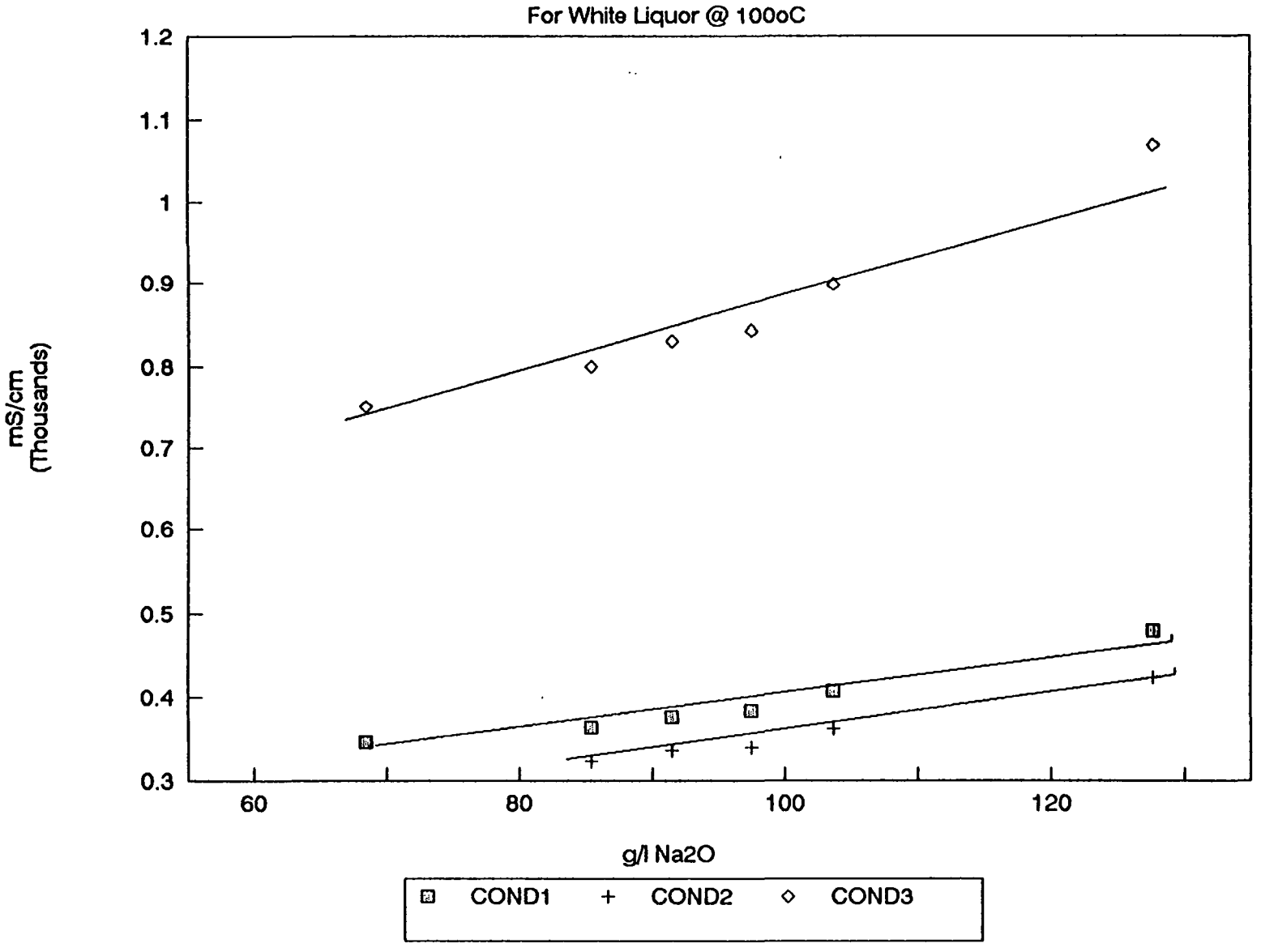
COND2 VS TEMP



COND3 VS TEMP



CONDUCTIVITY VS AA



IPST

Project 3699

PHASE II TESTING

- COOKING LIQUOR
- BLACK LIQUOR
- LONG TERM RESPONSE

PROJECT 3716

ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMI-CHEMICAL PULPING

April 2, 1991

Clark P. Woitkovich

IPST PROJECT 3716

ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMI-CHEMICAL PULPING

IPST PROJECT 3716

SPONSOR: CONTAINER BOARD AND
KRAFT PAPER GROUP (CKPG)
OF
THE AMERICAN PAPER INSTITUTE (API)

BUDGET: $75,000

PULPING YIELD → PULP PHYSICAL PROPERTIES

(immeasurable) (measurable)

LIGNIN CONTENT AS A YIELD ESTIMATOR

PULPING PROCESS	YIELD	LIGNIN CONTENT
CHEMICAL	50-60%	3-7%
SEMI-CHEMICAL	60-80%	10-20%

INDUSTRY NEED

A SIMPLE ANALYSIS FOR SEMI-CHEMICAL PULP AND/OR LIQUOR THAT CAN QUICKLY AND RELIABLY:

- ESTIMATE YIELD
- PREDICT END-USE PROPERTIES

BENEFITS

IMPROVED CONTROL OF:

- PULPING PROCESSES
- PRODUCT PROPERTIES
  - REDUCED VARIABILITY
  - EASIER MANIPULATION

APPROACH

1. EVALUATE CANDIDATE METHODS:

Spectroscopic

- NEAR-INFRARED REFLECTANCE
- ULTRAVIOLET-VISIBLE LUMINESCENCE
- ULTRAVIOLET REFLECTANCE

Other

- REFRACTIVE INDEX
- TOTAL ORGANIC CARBON
- TOTAL DISSOLVED SOLIDS
- HYPO NUMBER

APPROACH (cont.)

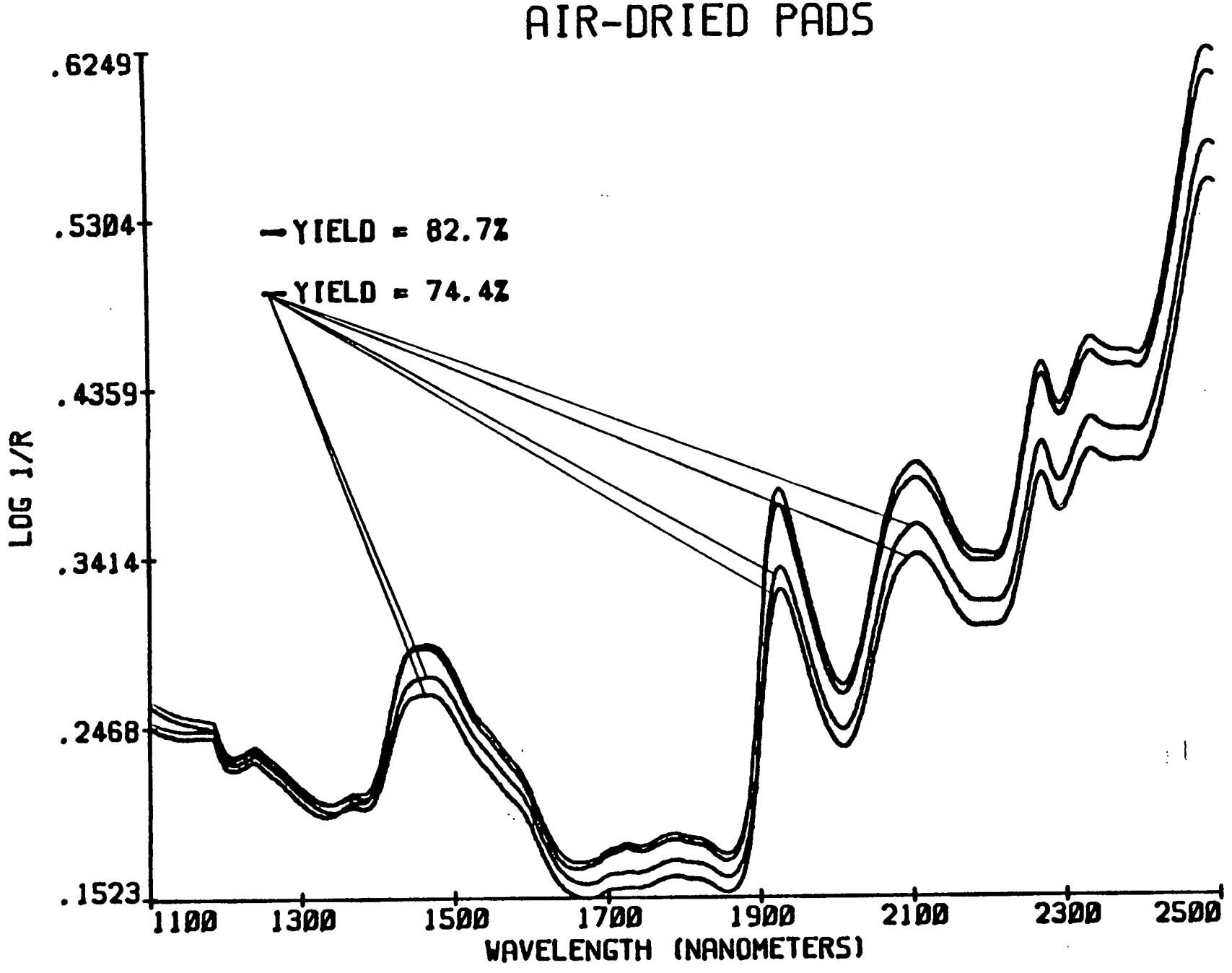
2. IDENTIFY THE METHOD(S) WITH THE HIGHEST POTENTIAL

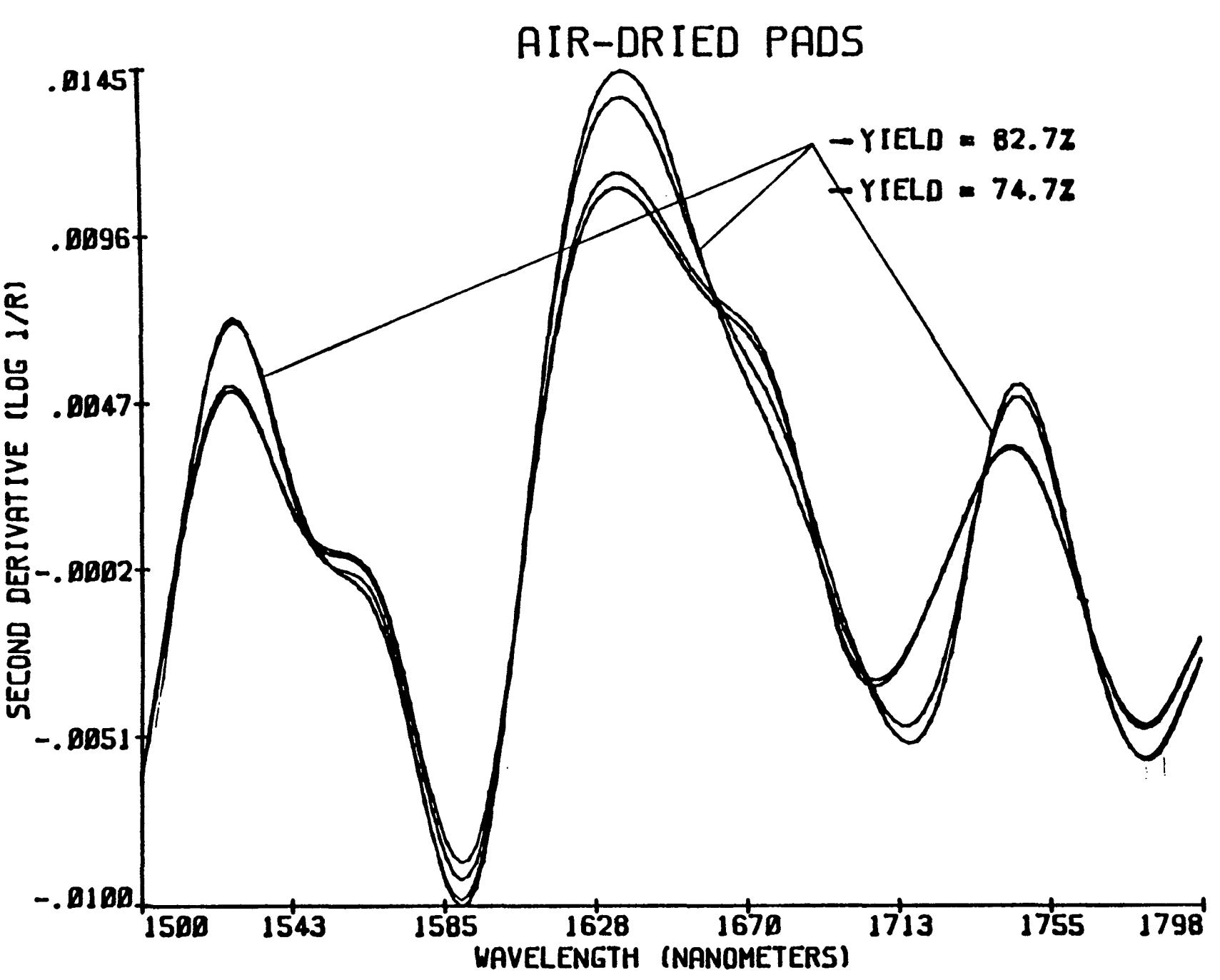
APPROACH (cont.)

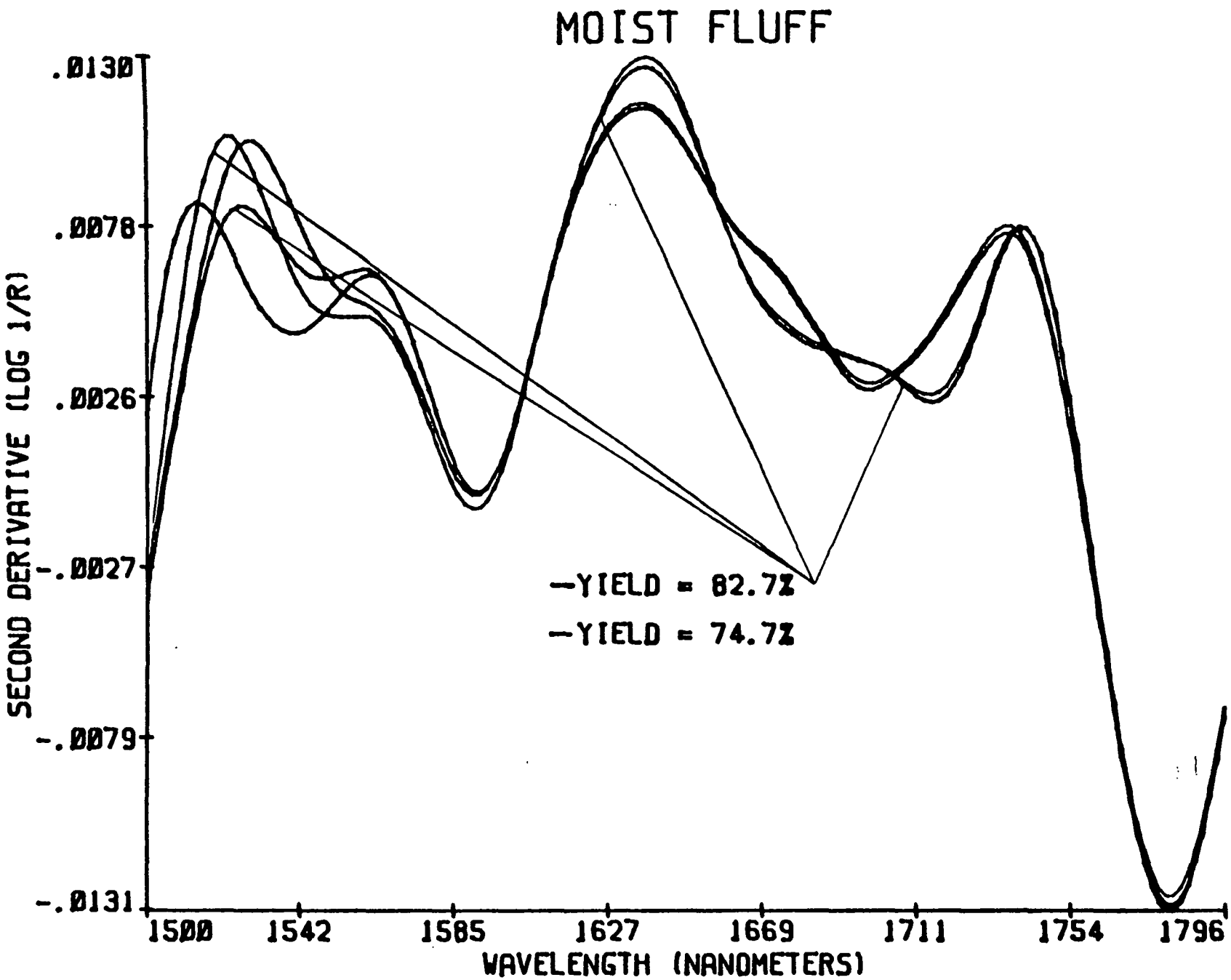
3. DEVELOP CORRELATIONS BETWEEN ANALYTICAL MEASUREMENTS, ESTIMATED YIELD, AND END-USE PROPERTIES

PRELIMINARY RESULTS

NEAR-INFRARED REFLECTANCE SPECTROSCOPY

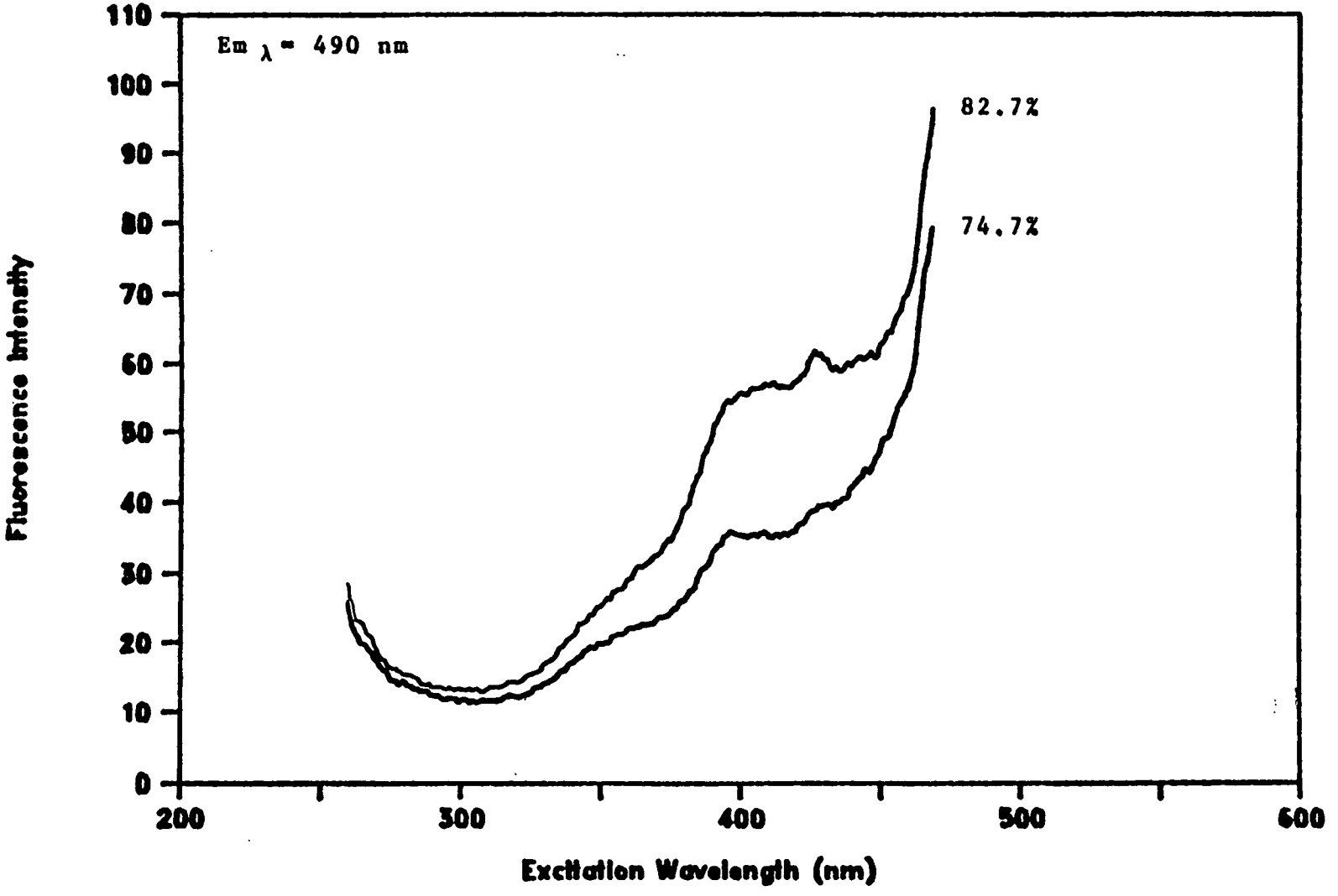

AIR-DRIED PADS
.6249
.5304
.4359
.3414
.2468
.1523
LOG 1/R
YIELD = 82.7%
YIELD = 74.4%
1100
1300
1500
1700
1900
2100
2300
2500
WAVELENGTH (NANOMETERS)


AIR-DRIED PADS
.0145
.0096
.0047
-.0002
-.0051
-.0100
SECOND DERIVATIVE (LOG 1/R)
YIELD = 82.7%
YIELD = 74.7%
1500
1543
1585
1628
1670
1713
1755
1798
WAVELENGTH (NANOMETERS)

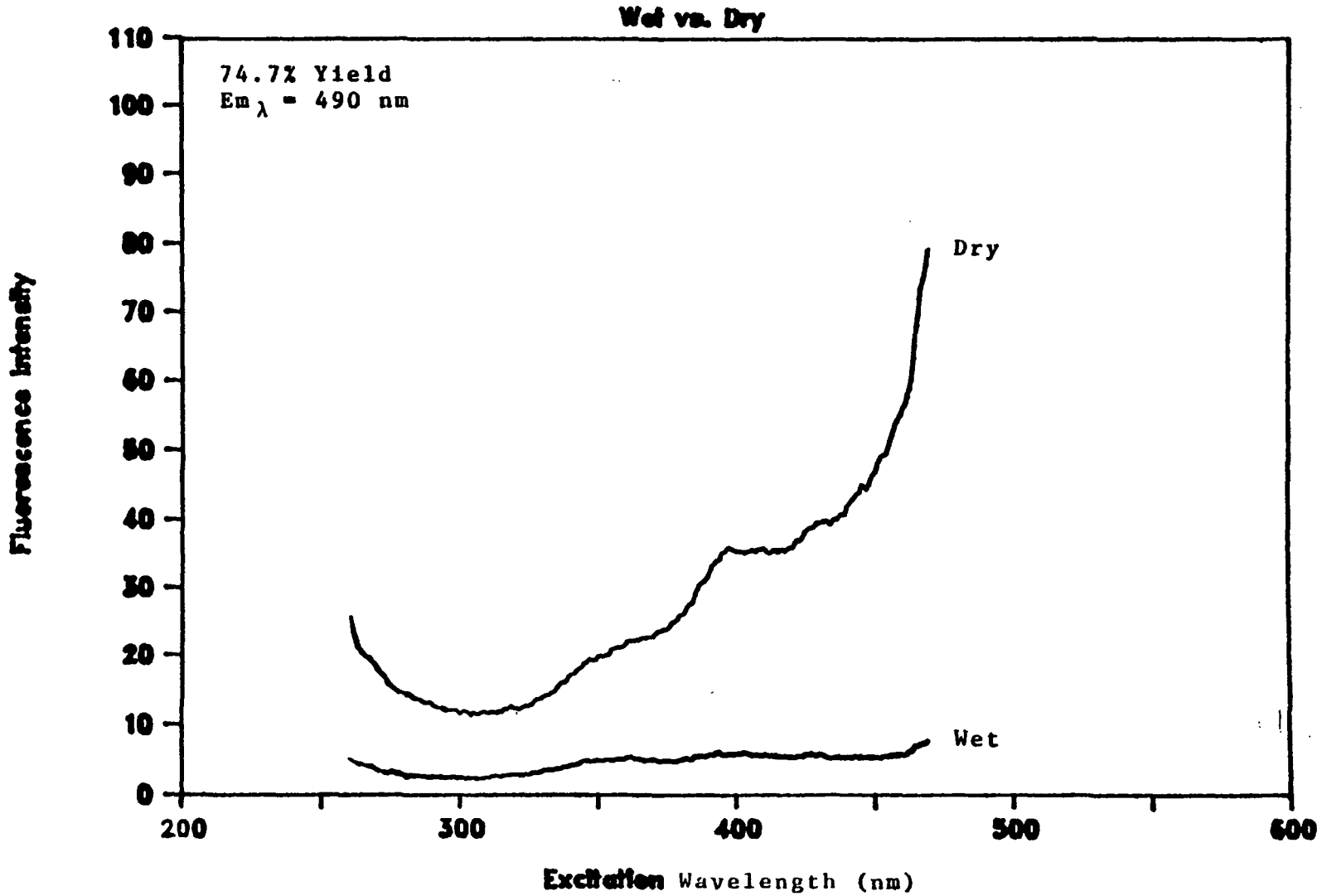

MOIST FLUFF
.0130
.0078
.0026
-.0027
-.0079
-.0131
SECOND DERIVATIVE (LOG 1/R)
—YIELD = 82.7%
—YIELD = 74.7%
1500
1542
1585
1627
1669
1711
1754
1796
WAVELENGTH (NANOMETERS)

ULTRAVIOLET-VISIBLE LUMINESCENCE SPECTROSCOPY

Excitation Spectra



Excitation Spectra



CONCLUSION

INITIAL APPLICATIONS OF NEAR-INFRARED AND FLUORESCENCE SPECTROSCOPY SHOW CONSIDERABLE PROMISE