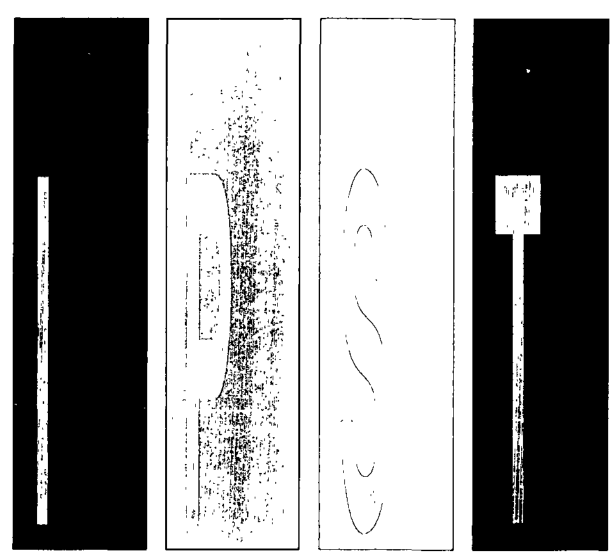
Institute of Paper Science and Technology

MECHANICAL PULPING

ANNUAL RESEARCH REVIEW

April 3, 1991



Atlanta, Georgia

MECHANICAL PULPING

HANDOUT BOOK

April 3, 1991

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PROJECT 3566

HIGH STRENGTH, HIGH YIELD PULPS

PROJECT 3566

HIGH STRENGTH, HIGH YIELD PULPS

T. J. McDONOUGH, A. W. RUDIE

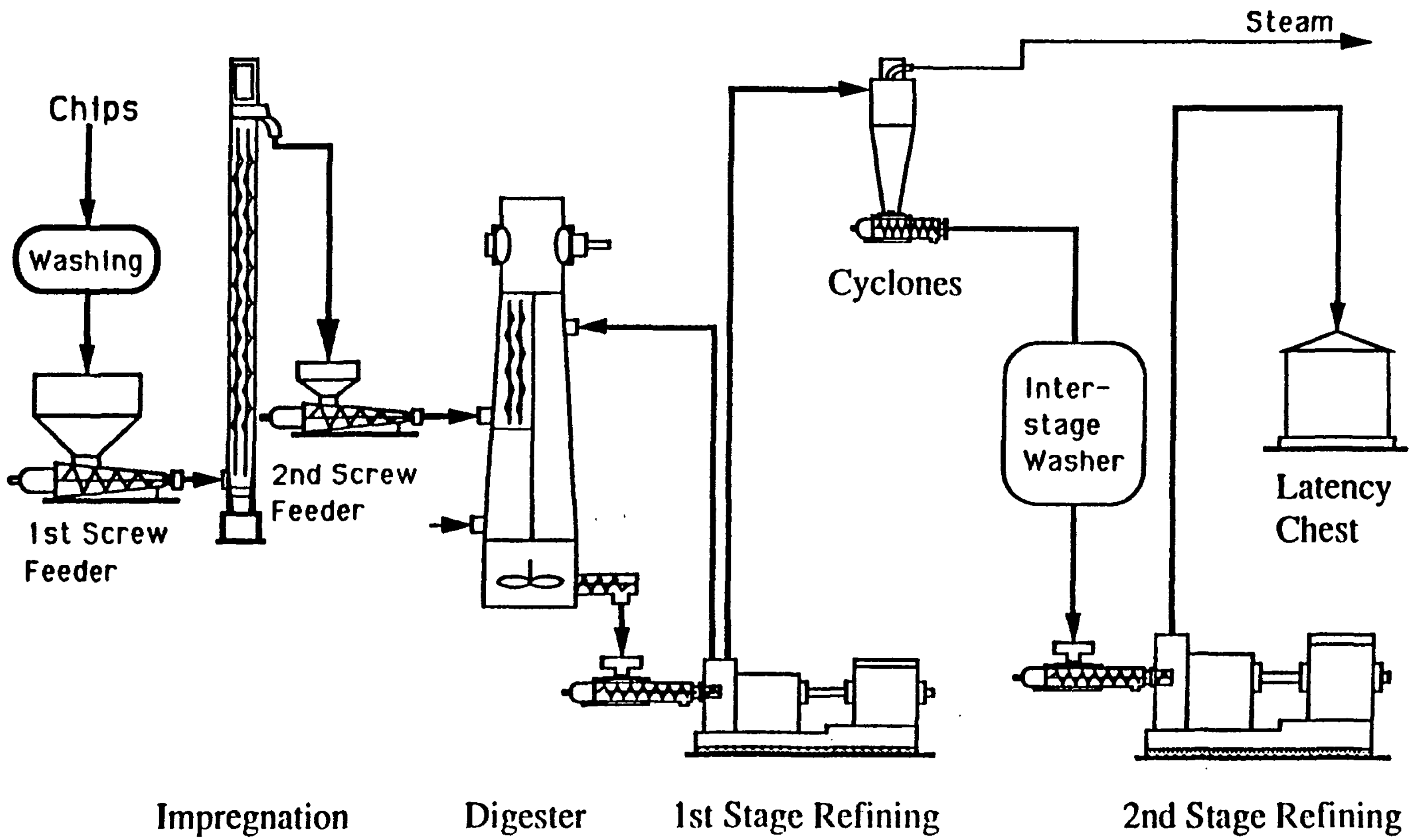
OBJECTIVES:

DEVELOP WOOD FIBER SEPARATION AND TREATMENT METHODS THAT WILL ALLOW GOOD CONTROL OF THE STRENGTH, PHYSICAL FORM AND BONDING CHARACTERISTICS OF THE RESULTING FIBERS.

CENTER FOR HIGH YIELD PULP SCIENCE

CHYPS

Two-Stage CTMP Pilot Plant



STATUS

- THE PILOT PLANT IS INSTALLED AND OPERATIONAL.
- CHYPS IS WAITING ON ADDITIONAL FUNDING TO START THE PROJECTS. PROJECT WORK IS EXPECTED TO BEGIN IN AUGUST.
- A PRELIMINARY PROJECT WAS COMPLETED IN NOVEMBER. THE RESULTS ARE BEING ANALYZED FOR USEFUL OPERATING DATA.

PRELIMINARY PROJECT:

- THE PROJECT WAS CONDUCTED AS A 2^{3-1} FRACTIONAL FACTORIAL DESIGN EXPERIMENT.
- PROCESS VARIABLES WERE:

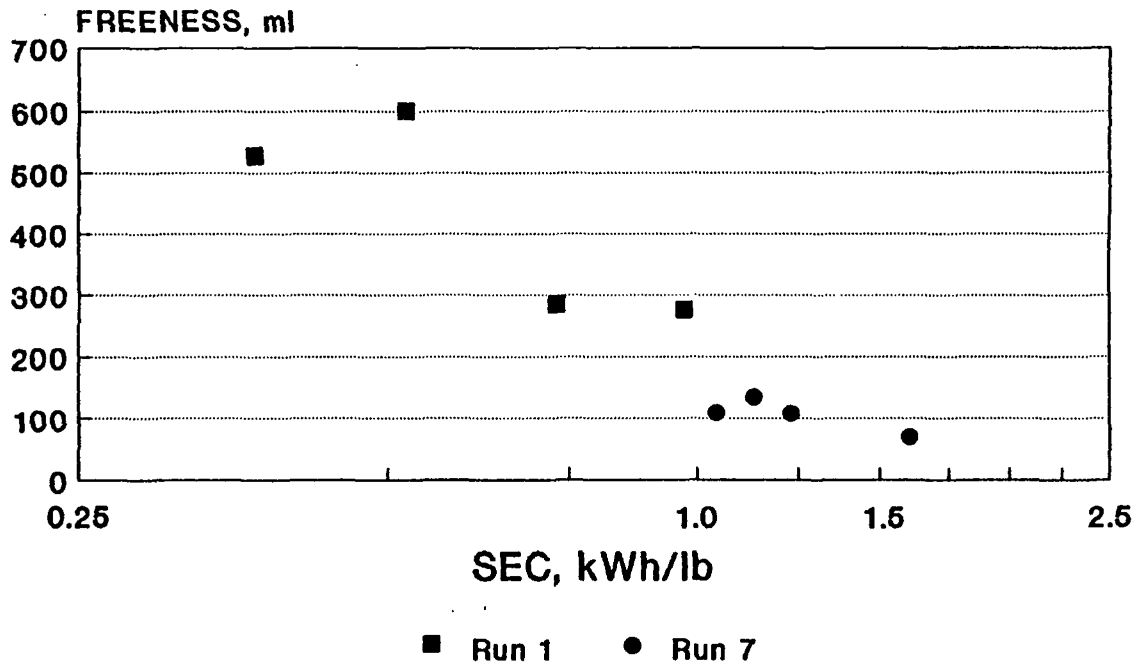
  TREE AGE, 10 YEARS AND 24 YEARS

  TREE GROWTH RATE,
  SLOW = 2.5 TO 5 GROWTH RINGS PER INCH OF DIAMETER
  FAST = 1 TO 3 GROWTH RINGS PER INCH OF DIAMETER

  CHIP SIZE,
  SMALL = 1/8 TO 3/4 INCH
  LARGE = 1/4 TO 5/4 INCH

REPEATABILITY

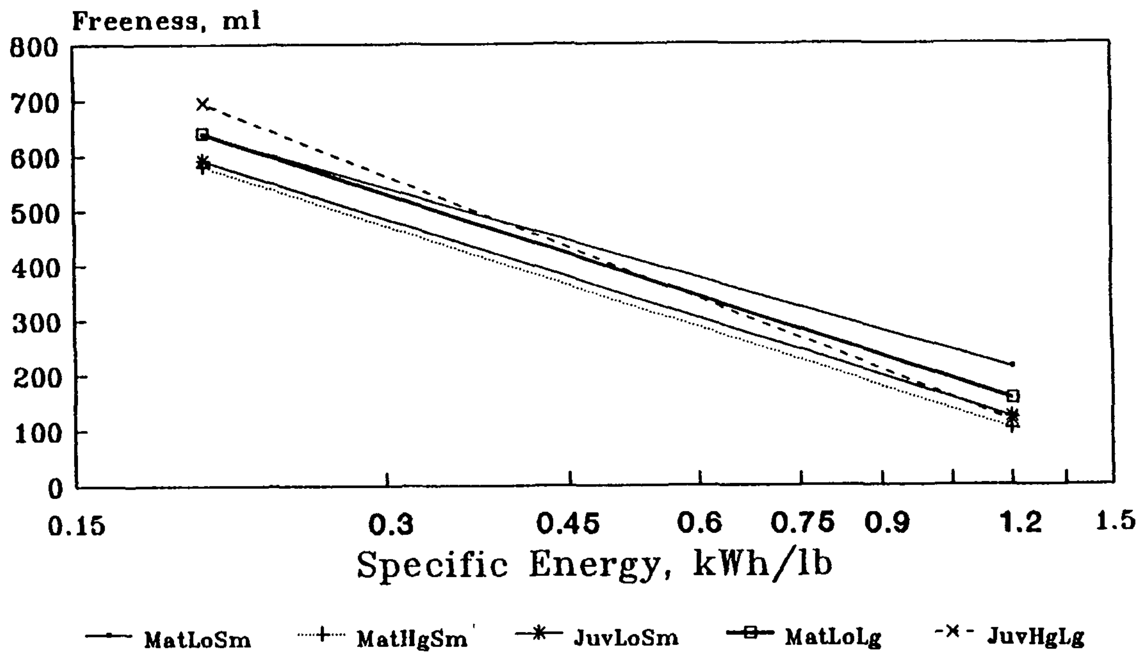
10 Year Old, Low Density, Small Chips



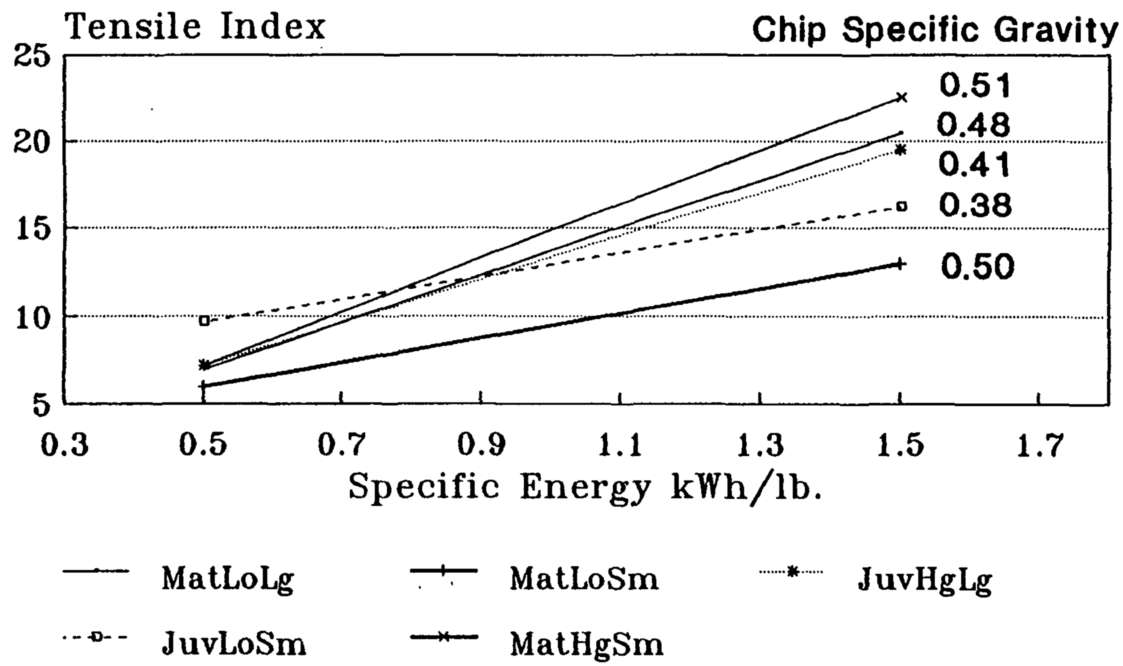
Runs 1 and 7

ENERGY vs. FREENESS

Age, Density and Chip Size

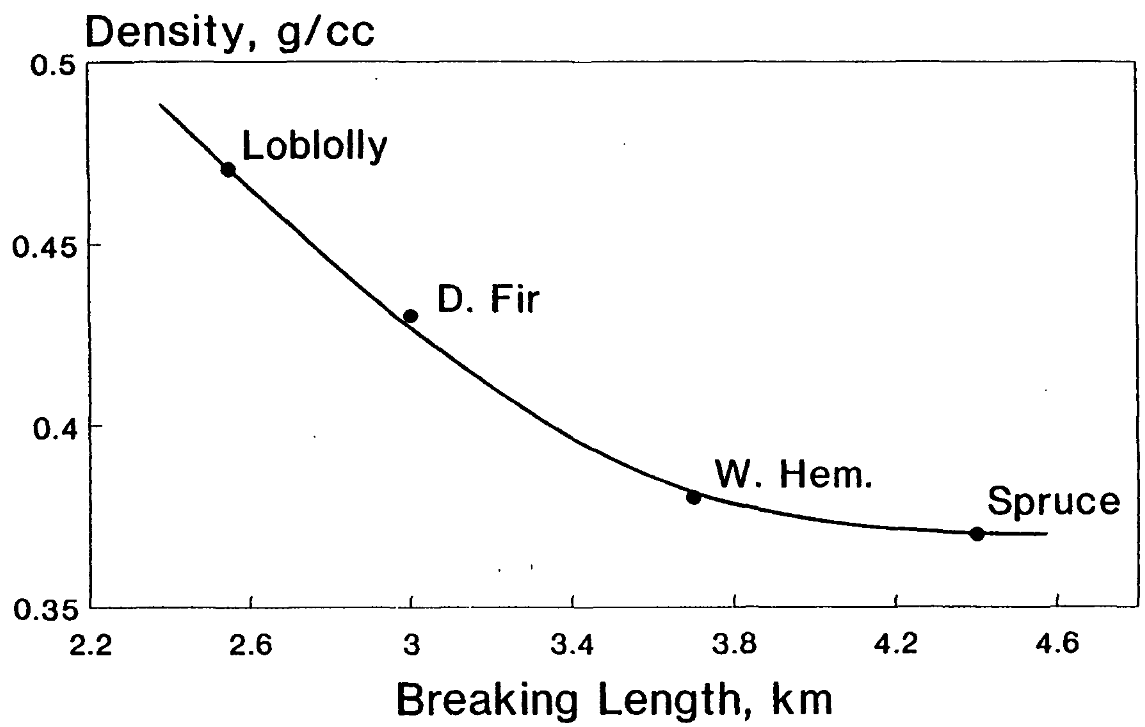


Tensile Index vs. SEC
Tree age, density and chip size



Wood Density vs BL

BL @ 2000kWh/BDT



RESULTS:

- OPERATION AND CONTROL OF THE PILOT PLANT IMPROVED SIGNIFICANTLY DURING THE PROJECT.
- TREE VARIABLES DO NOT APPEAR TO SIGNIFICANTLY AFFECT THE FREENESS/SEC RELATIONSHIP
- TREE DENSITY APPEARS TO HAVE THE LARGEST EFFECT ON THE TENSILE INDEX/SEC RELATIONSHIP. THE OBSERVED INCREASE IN TENSILE INDEX WITH INCREASED WOOD DENSITY CONTRADICTS THE USUAL INVERSE CORRELATION BETWEEN STRENGTH AND WOOD DENSITY.

ALKALINE PEROXIDE MECHANICAL PULPING

OBJECTIVES:

EVALUATE THE ALKALINE PEROXIDE MECHANICAL PULPING PROCESS FOR PRESERVING FIBER STRENGTH AND PHYSICAL FORM IN MECHANICAL PULPING.

EVALUATE APMP FOR THE PREPARATION OF HIGH YIELD PULP FROM DENSE SOUTHERN HARDWOODS.

INITIAL APPROACH

- USE OF HOLOPULPING TO DELIGNIFY AND CHARACTERIZE FIBERS AND FIBER DAMAGE:

  FIBER LENGTH

  ZERO SPAN TENSILE,

  TEAR/TENSILE RELATIONSHIP

  VISCOSITY

  FREENESS AND SURFACE AREA.

INITIAL APPROACH

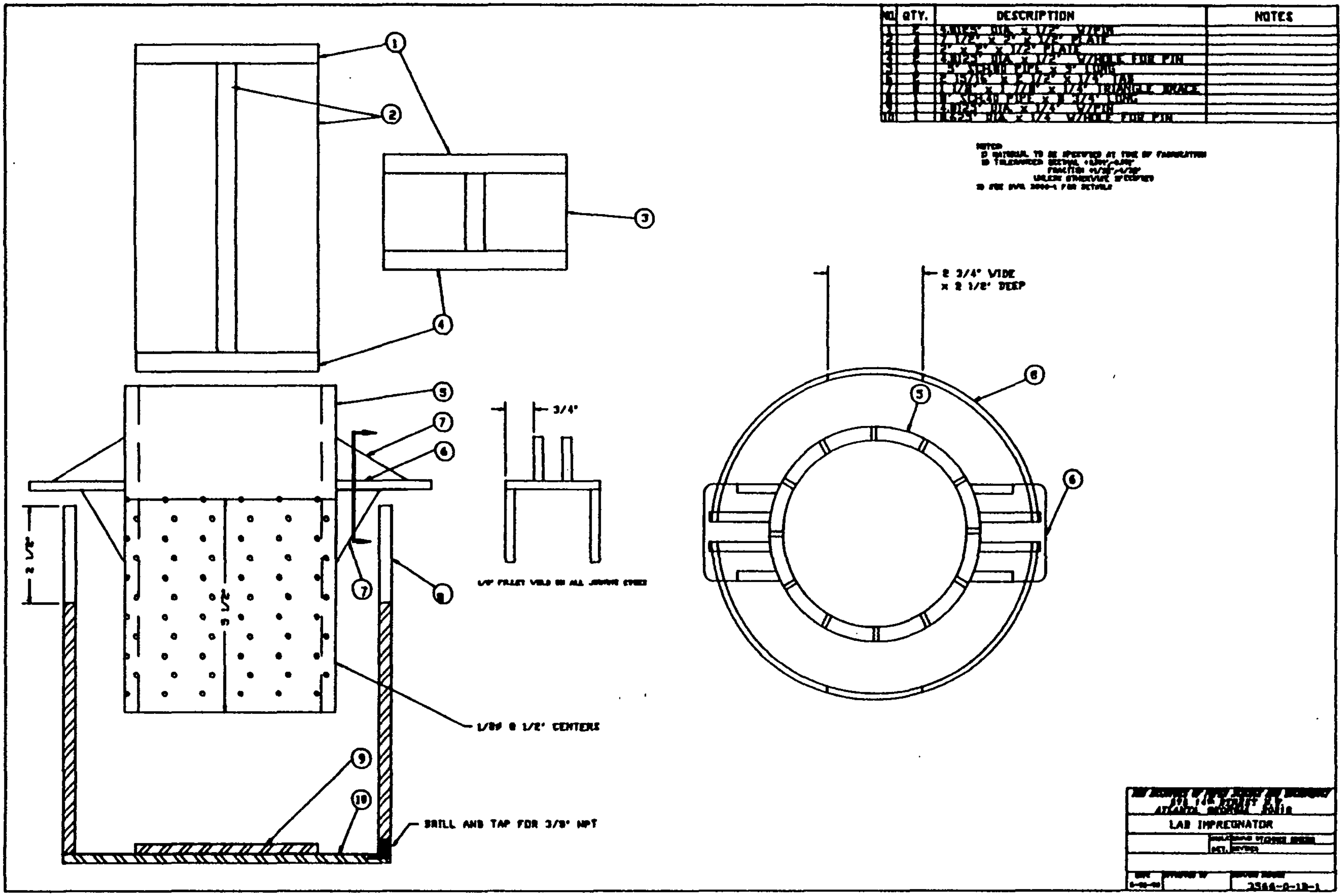
- EVALUATE THE EFFECTS OF PLUG SCREW FEEDERS ON FIBER STRENGTH AND FIBER DEVELOPMENT.

  WET STRENGTH!

  FRACTURE SURFACE?

  FIBER DEVELOPMENT MECHANISM:

  - CRUSHING
  - SHEAR
  - BI - VIS EXTRUDER
  - FROTAPULPER


NO. QTY. DESCRIPTION NOTES
1 3.8125" DIA X 1/2" W/PIN
2 7 1/2" X 2" X 1/2" PLATE
3 2" X 2" X 1/2" PLATE
4 4.8125" DIA X 1/2" W/HOLE FOR PIN
5 5" SCH40 PIPE X 5" LONG
6 2 15/16" X 2 1/2" X 1/4" TAB
7 1 7/8" X 1 7/8" X 1/4" TRIANGLE BRACE
8 8" SCH40 PIPE X 8 3/4" LONG
9 4.8125" DIA X 1/4" W/PIN
10 8.625" DIA X 1/4" W/HOLE FOR PIN
2 3/4" WIDE
X 2 1/2" DEEP
3/4"
2 1/2"
5 1/2"
1/8Ø @ 1/2" CENTERS
DRILL AND TAP FOR 3/8" NPT
LAB IMPREGNATOR
2566-0-1B-1

91 GOALS: PROJECT 3566

- COMPLETE THE EVALUATION OF CHLORITE HOLOPULPING FOR DETERMINING FIBER STRENGTH LOSSES IN HIGH YIELD PULPS.
- COMPLETE THE EVALUATION OF LABORATORY PRESSING ON FIBER STRENGTH LOSSES IN HIGH YIELD PULPS.

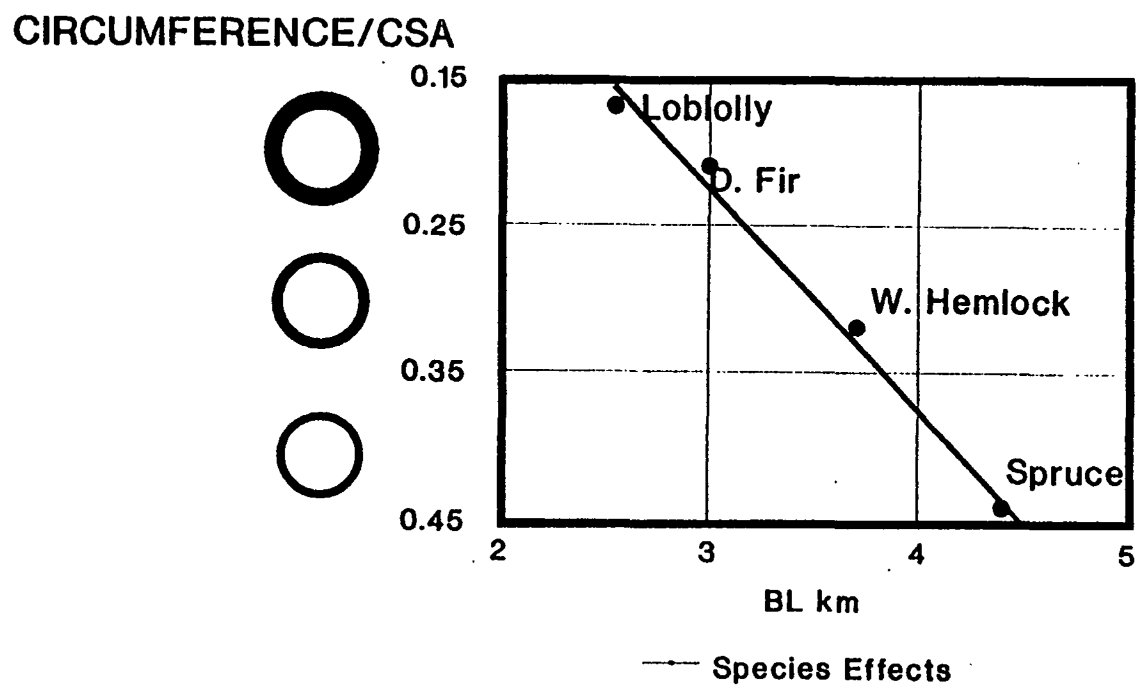
RELATED STUDENT RESEARCH:

MR. JOSEPH MORRA

MASTERS DEGREE CANDIDATE INDEPENDENT STUDY PROJECT ON THE INFLUENCE OF FIBER MORPHOLOGY ON THERMOMECHANICAL PULP PROPERTIES.

TMP STRENGTH

EFFECT OF CSA ON BL



FUTURE ACTIVITIES

- THE PROJECT IS TO BE TERMINATED AT THE END OF FISCAL YEAR 91.
- EVALUATE THE EFFECTS OF PLUG SCREW FEEDERS ON FIBER STRENGTH LOSSES IN HIGH YIELD PULPS.
- EVALUATE THE INFLUENCE OF REFINING PARAMETERS ON THE PRODUCTION OF TMP AND CTMP FROM JUVENILE SOUTHERN PINES. (CHYPS)
- EVALUATE THE INFLUENCE OF FIBER DIAMETER AND FIBER CELL WALL THICKNESS ON STRENGTH DEVELOPMENT IN MECHANICAL PULPS.

NEW PROJECT

CHYPS

OBJECTIVE:

DETERMINE THE EFFECTS OF IMPORTANT CHEMIMECHANICAL PULPING VARIABLES ON FIBER INTEGRITY, FIBER STRENGTH AND BOND STRENGTH.

PROJECT 3694

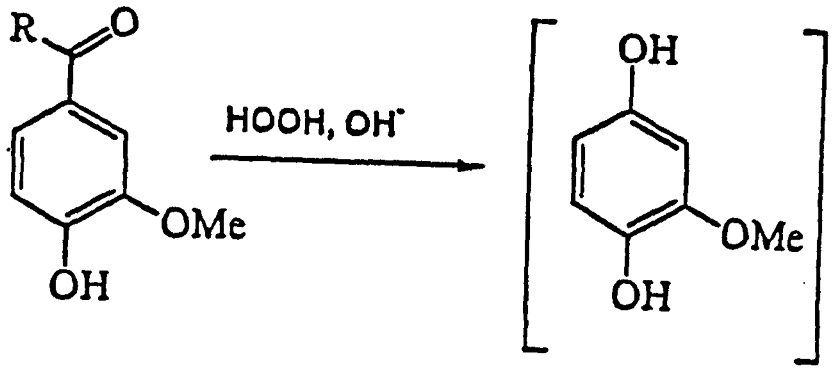
HIGH BRIGHTNESS, HIGH YIELD PULPS

PROJECT 3694

HIGH BRIGHTNESS, HIGH YIELD PULPS

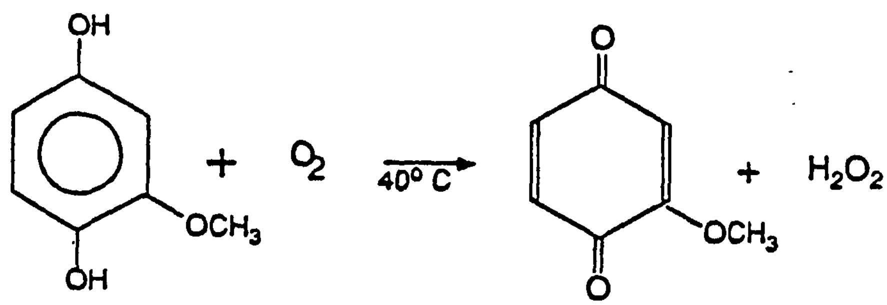
OBJECTIVE:

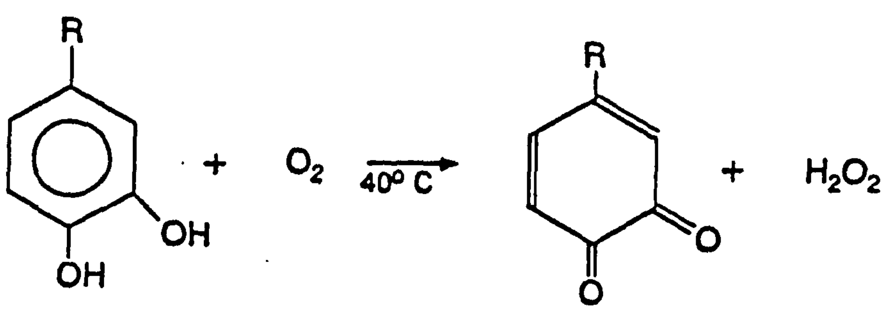
DEVELOP A COST EFFECTIVE METHOD TO PRODUCE HIGH YIELD PULPS OF HIGH AND STABLE BRIGHTNESS.



hydroquinone

Tappi, 1965, *48*, 121
Tappi, 1969, *52*, 491





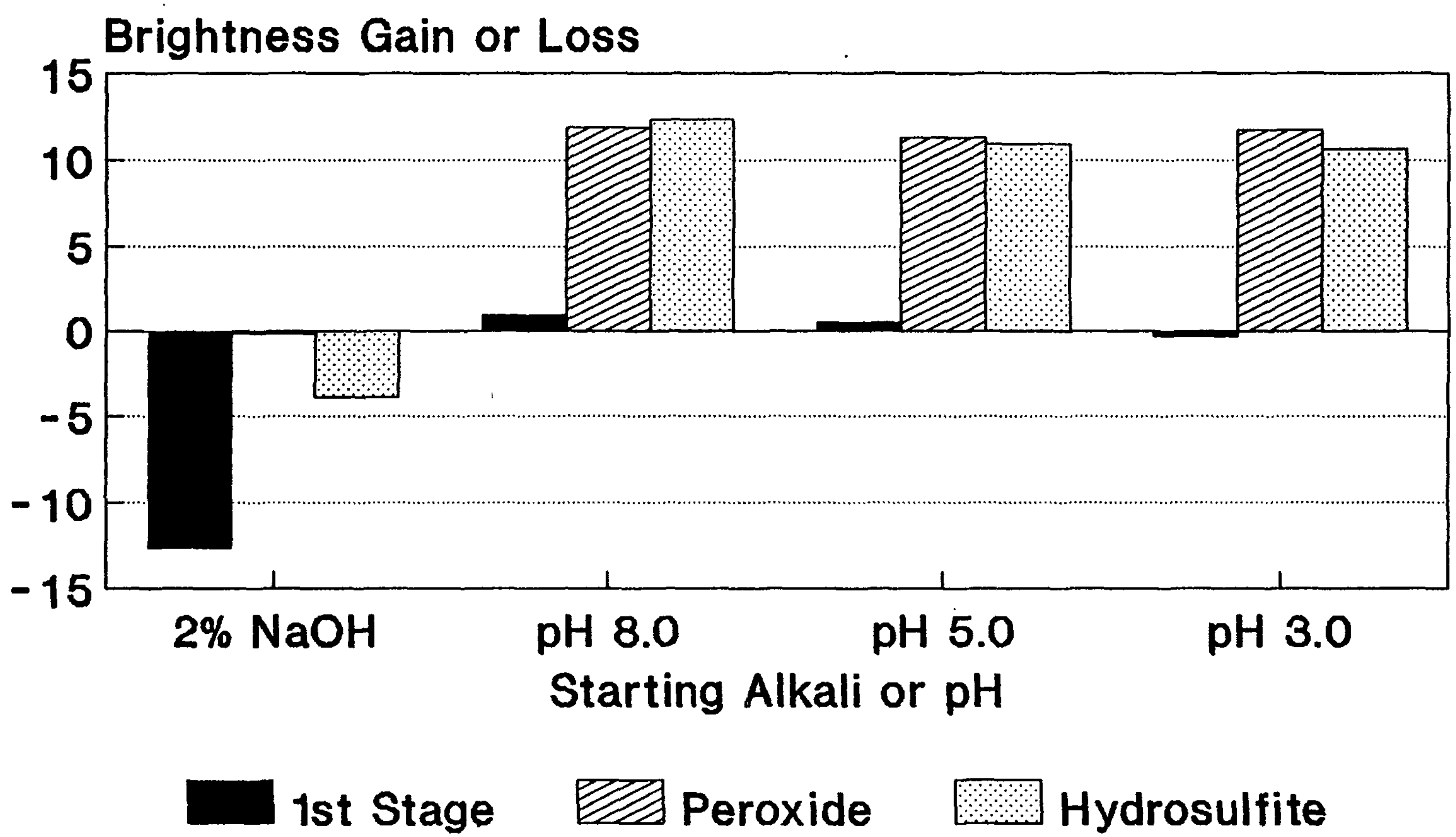
R = t - Butyl

WHY OXYGEN ?

- HYDROQUINONES AND CATECHOLS ARE PRODUCTS OF PEROXIDE BLEACHING, AND SOURCES OF PULP COLOR.
- OXYGEN REACTS READILY WITH CATECHOLS AND HYDROQUINONES.
- OXYGEN IS ACTIVE IN KRAFT PULP BLEACHING AND REVERSION OF HIGH YIELD PULPS.

OXYGEN TREATMENT of TMP

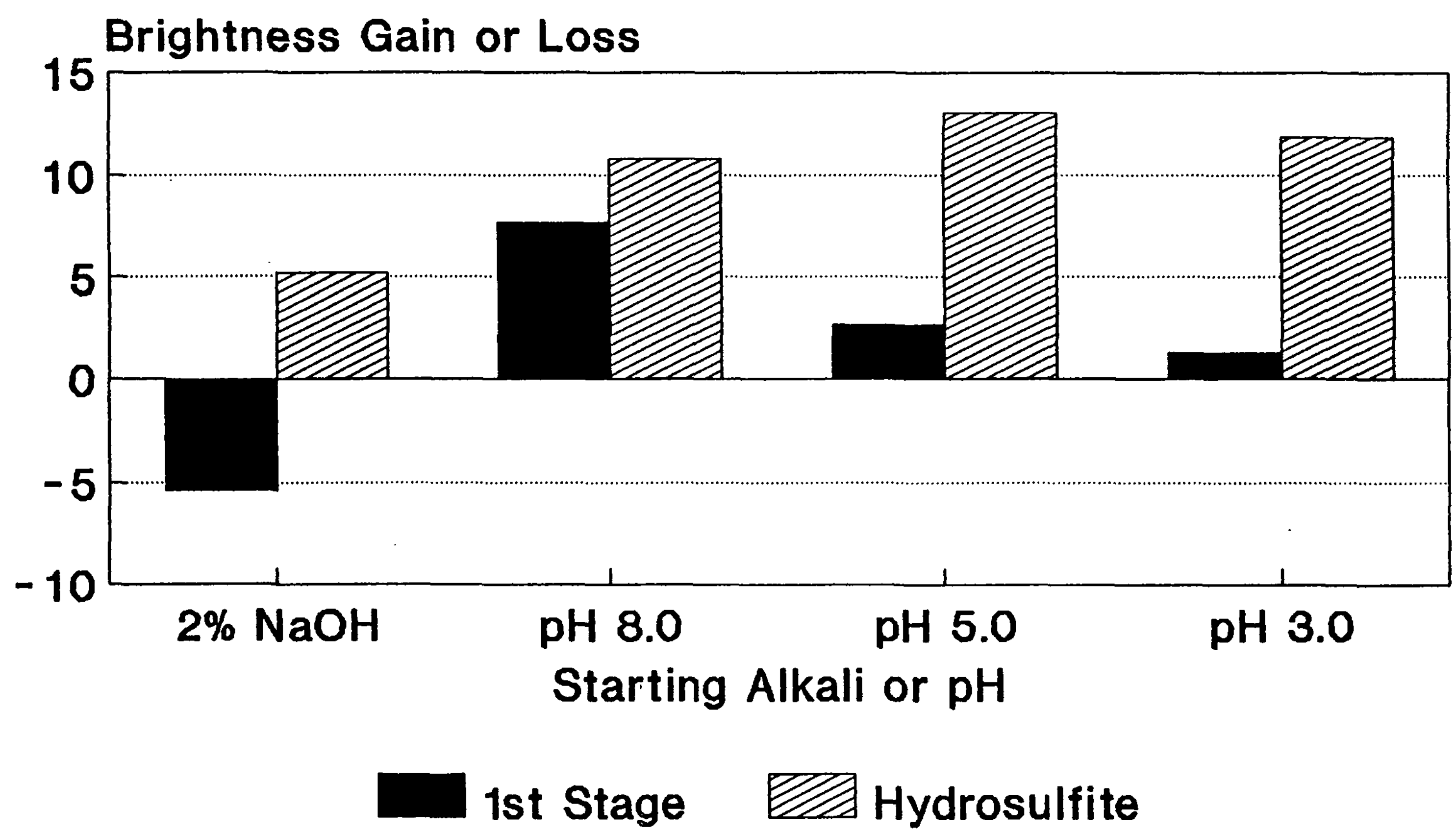
Influence of Starting Alkali or pH



2nd stage treatments with 1% hydrogen peroxide or 1% sodium hydrosulfite

OXYGEN/PEROXIDE BLEACHING

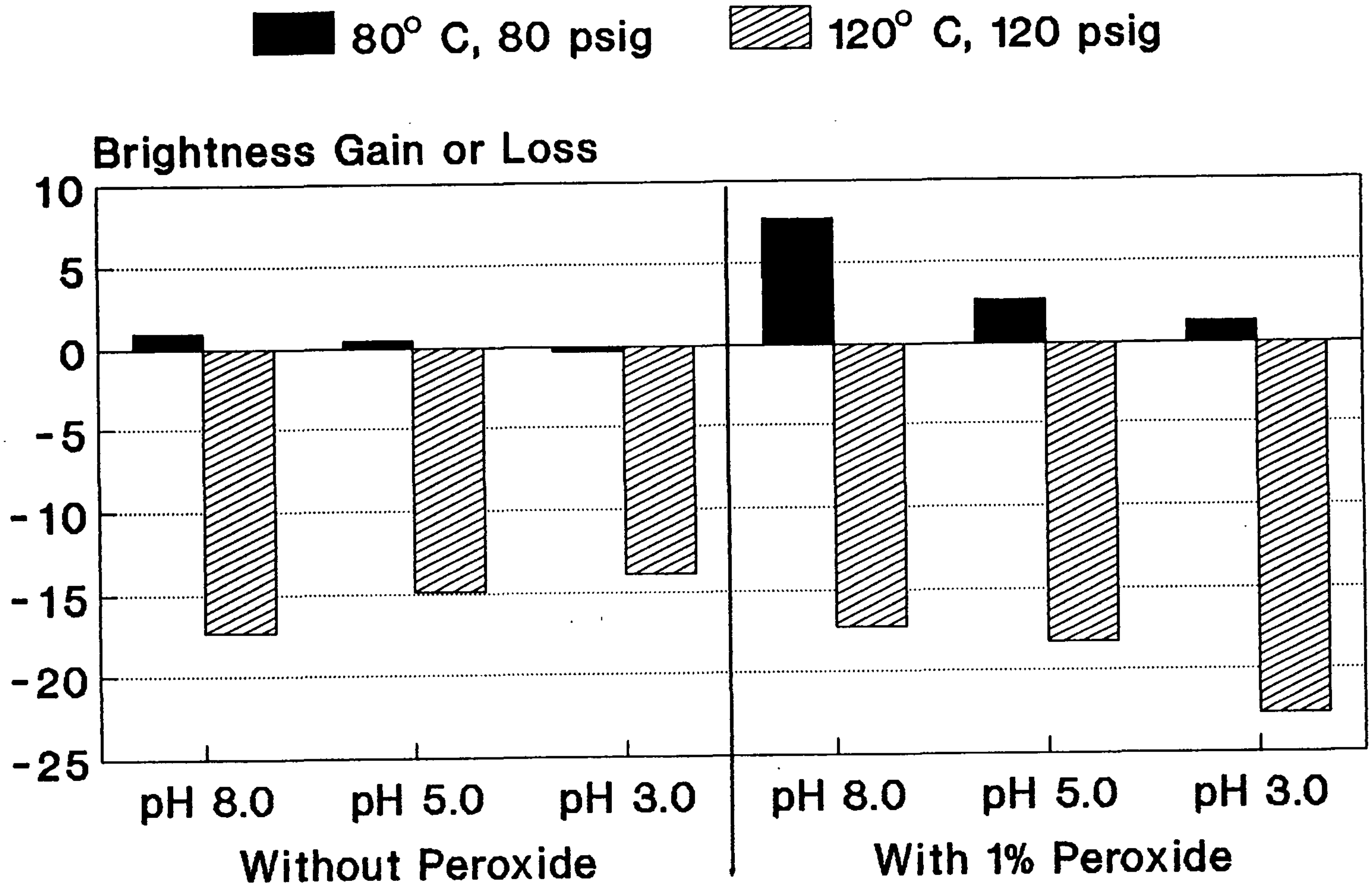
Influence of Starting Alkali or pH



1% Hydrogen Peroxide in the 1st stage
2nd Stage using 1% sodium hydrosulfite

OXYGEN TREATMENT of TMP

Effect of Temperature and Pressure

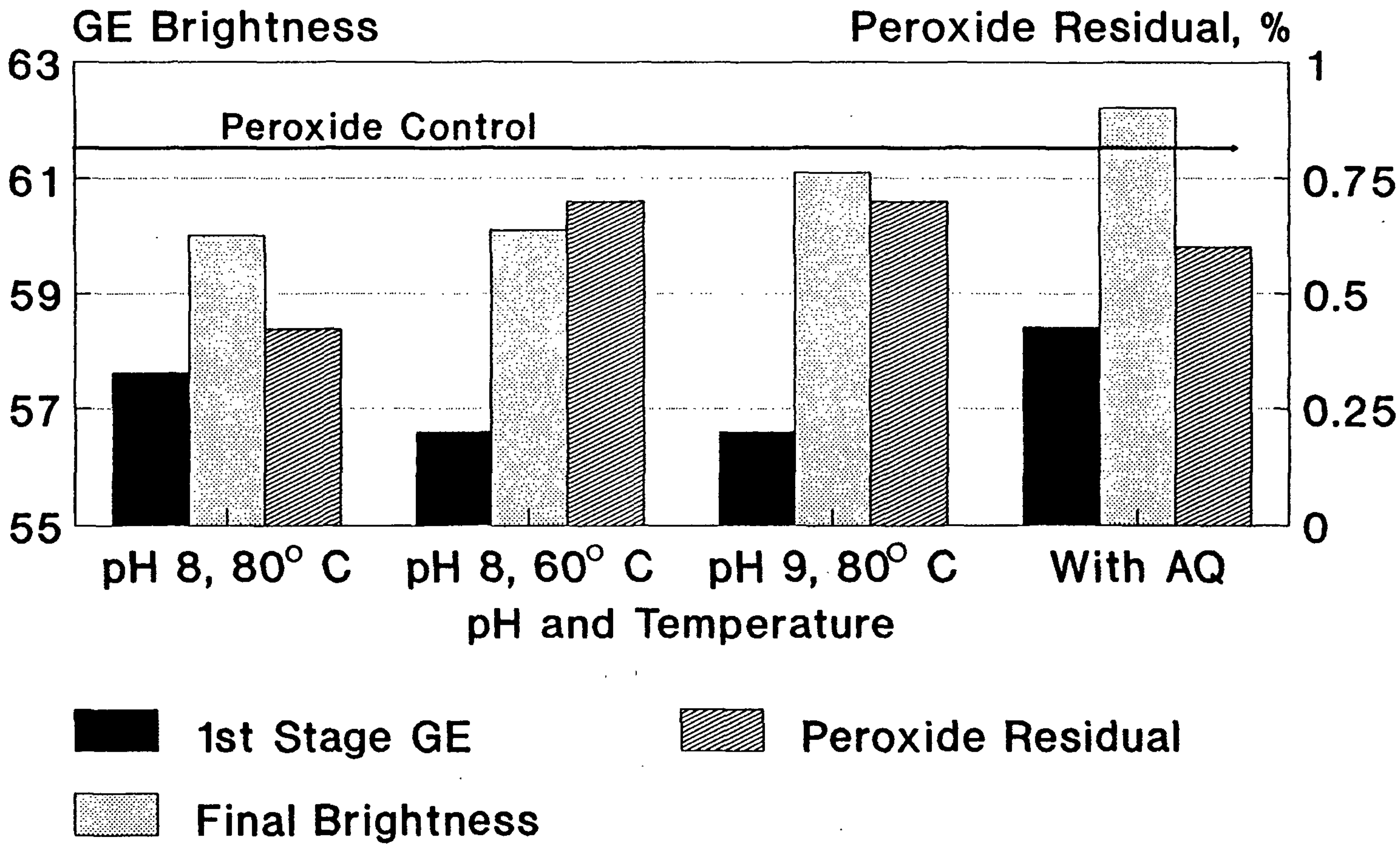


CONCLUSIONS: PRELIMINARY EXPERIMENTS

- OXYGEN CAN BLEACH TMP BY ≈ 1 POINT GE WHEN USED AT pH 5 TO 8, 80° C AND 80 PSIG.
- OXYGEN WITH PEROXIDE CAN BLEACH TMP BY 5 TO 8 POINTS GE.
- FOLLOW-UP BLEACHING WITH HYDROGEN PEROXIDE OR SODIUM HYDROSULFITE DOES NOT APPEAR TO BENEFIT SIGNIFICANTLY FROM THE OXYGEN PRETREATMENT.

TWO STAGE BLEACHING

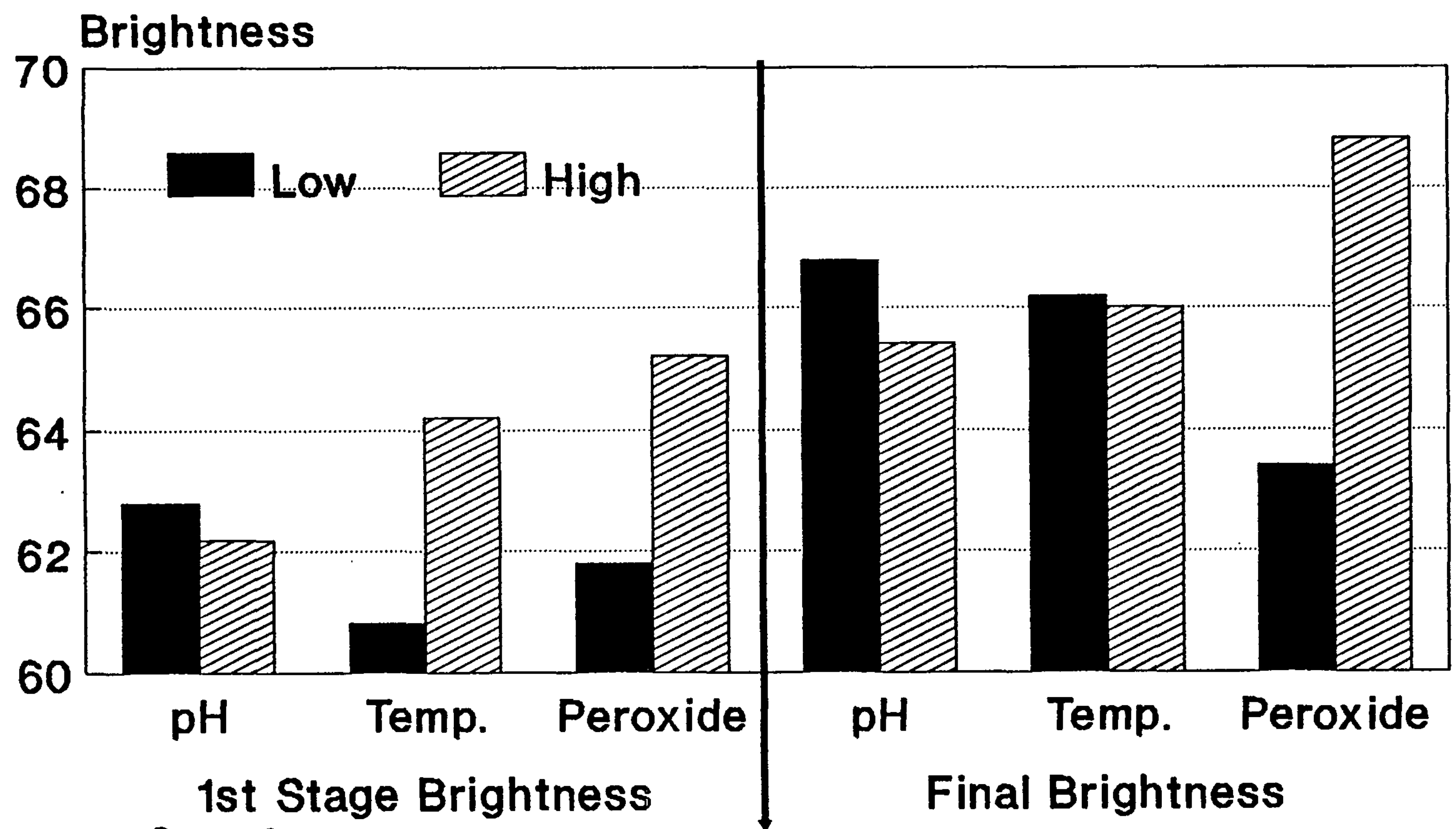
Oxygen and Peroxide



0.1% Anthraquinone at pH 8 and 80° C

OXYGEN and PEROXIDE

Factorial Design Data Averages
pH, Temperature and Peroxide



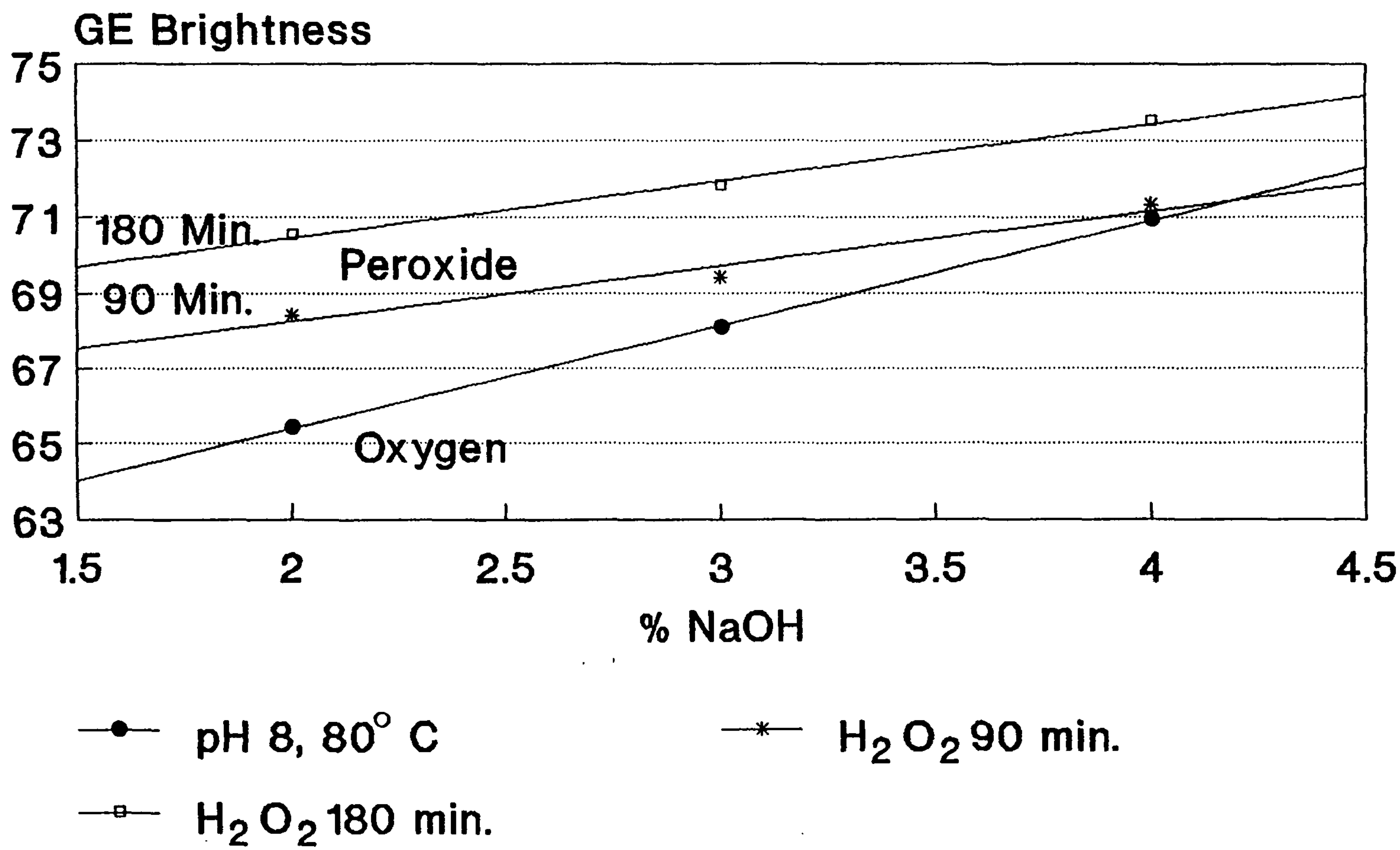
Temp. 60°/ 80° C, pH 8.0/9.5,
Peroxide 1%/4%

CONCLUSIONS:

FOLLOW-UP EXPERIMENTS

- PEROXIDE CHARGE HAS THE MOST SIGNIFICANT INFLUENCE ON INTERMEDIATE AND FINAL BRIGHTNESS.
- STARTING pH ALSO HAS A SIGNIFICANT EFFECT ON INTERMEDIATE AND FINAL BRIGHTNESS.
- POTENTIAL BRIGHTNESS ADVANTAGE FROM OPTIMIZATION IS NOT LIKELY TO EXCEED 1 TO 2 POINTS GE.

OXYGEN WITH PEROXIDE
Effect of 2nd Stage Alkali Charge



CONCLUSIONS:

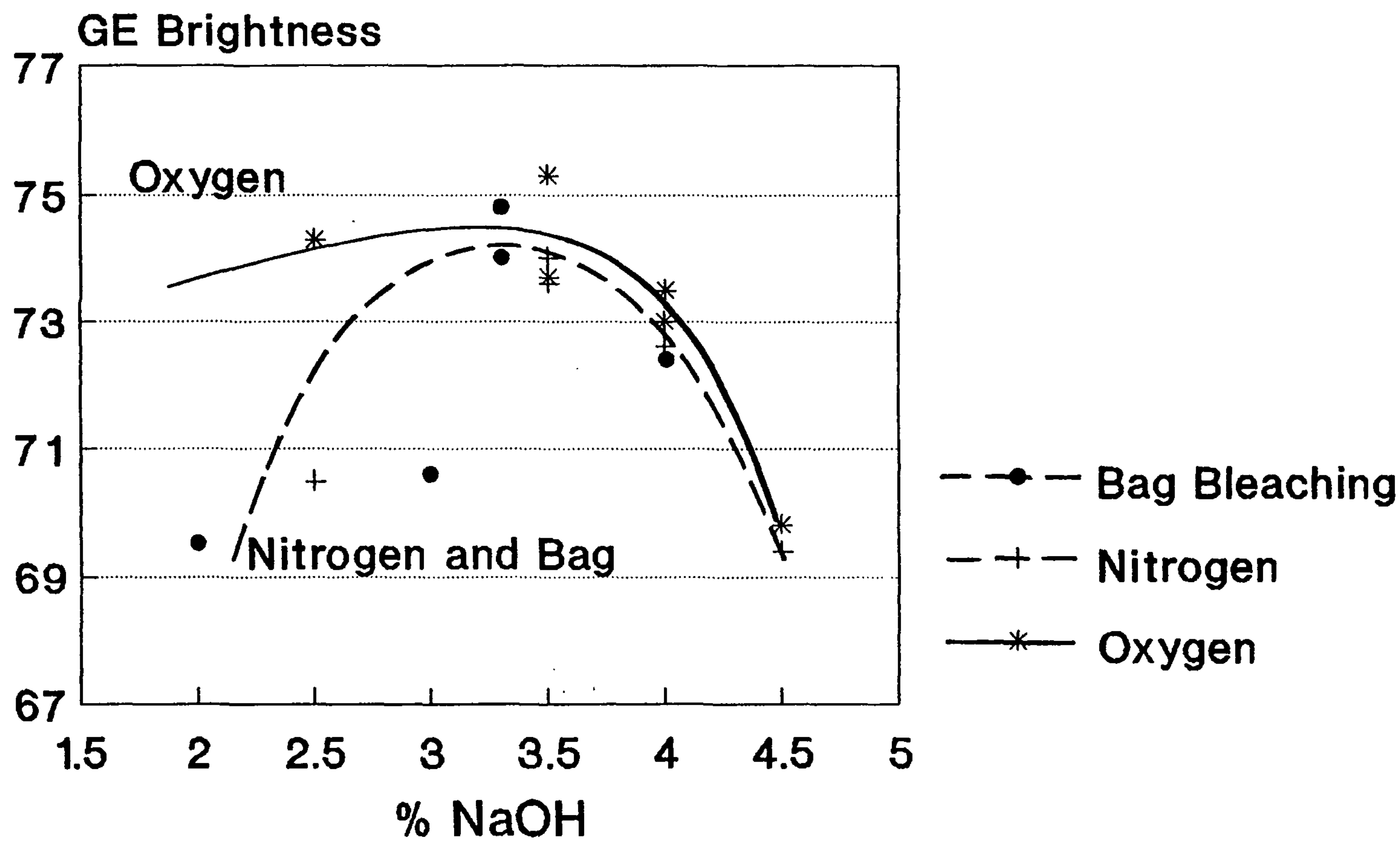
SECOND STAGE OPTIMIZATION EXPERIMENTS

- THE OXYGEN/PEROXIDE PRE-TREATMENT PROCESS DOES NOT OFFER A BENEFIT IN FINAL BRIGHTNESS.

- IN THE OXYGEN/PEROXIDE TREATMENT, THE BULK OF THE BLEACHING IS DUE TO THE PEROXIDE.

PEROXIDE BLEACHING

Effect of Methods and Atmosphere



Reactions conducted in a plastic bag or in a single shaft peg mixer under 60 psig of Nitrogen or Oxygen Gas

CONCLUSIONS:

OXYGEN WITH PEROXIDE

- THE PRESENCE OF OXYGEN IN A PEROXIDE BLEACH STAGE INCREASES PULP BRIGHTNESS BY 1 TO 3 POINTS GE, PARTICULARLY AT LOWER THAN OPTIMUM ALKALI CHARGE.

- THE USE OF OXYGEN WITH OR WITHOUT PEROXIDE AS A PRE-TREATMENT FOR PEROXIDE OR SODIUM HYDROSULFITE BLEACHING IS NOT EFFECTIVE.

91 GOALS: PROJECT 3694

- COMPLETE THE EXPERIMENTAL EVALUATION OF OXYGEN FOR USE IN BLEACHING HIGH YIELD PULPS.
- INITIATE A STUDY OF THE CAPABILITIES OF PERACETIC ACID FOR BLEACHING HIGH YIELD PULPS.

FUTURE ACTIVITIES:

- EVALUATE METAL CATALYSIS IN BLEACHING HIGH YIELD PULPS WITH OXYGEN.
- EVALUATE METAL CATALYSIS IN BLEACHING HIGH YIELD PULPS WITH HYDROGEN PEROXIDE
- EVALUATE HIGH YIELD PULP BLEACHING USING ORGANIC PEROXIDES GENERATED IN-SITU BY AUTOXIDATION OF ORGANIC COMPOUNDS.

PROJECT 3716

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

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:

<u>Spectroscopic</u>

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

<u>Other</u>

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

APPROACH (cont.)

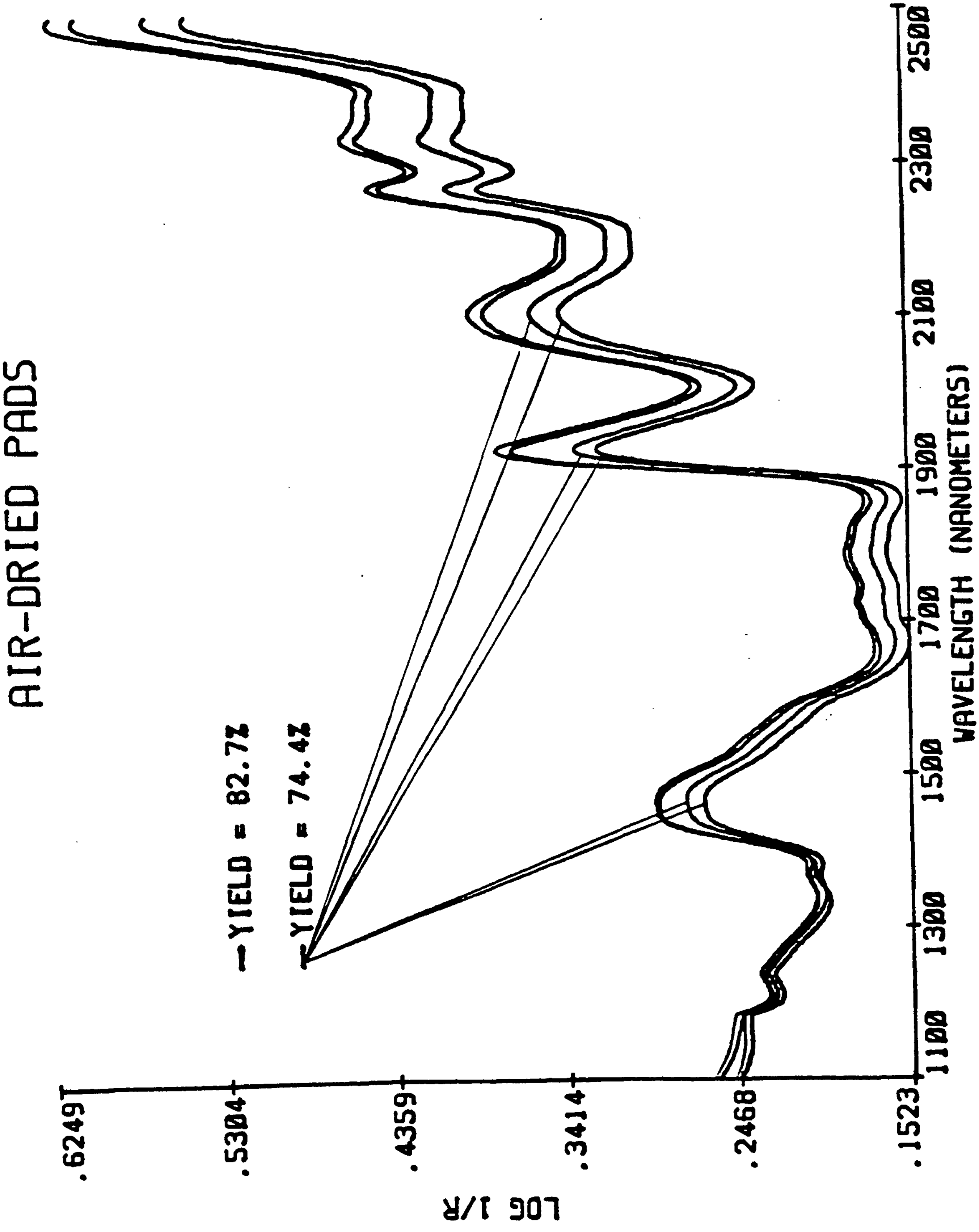
2. IDENTIFY THE METHOD(S) WITH THE HIGHEST POTENTIAL

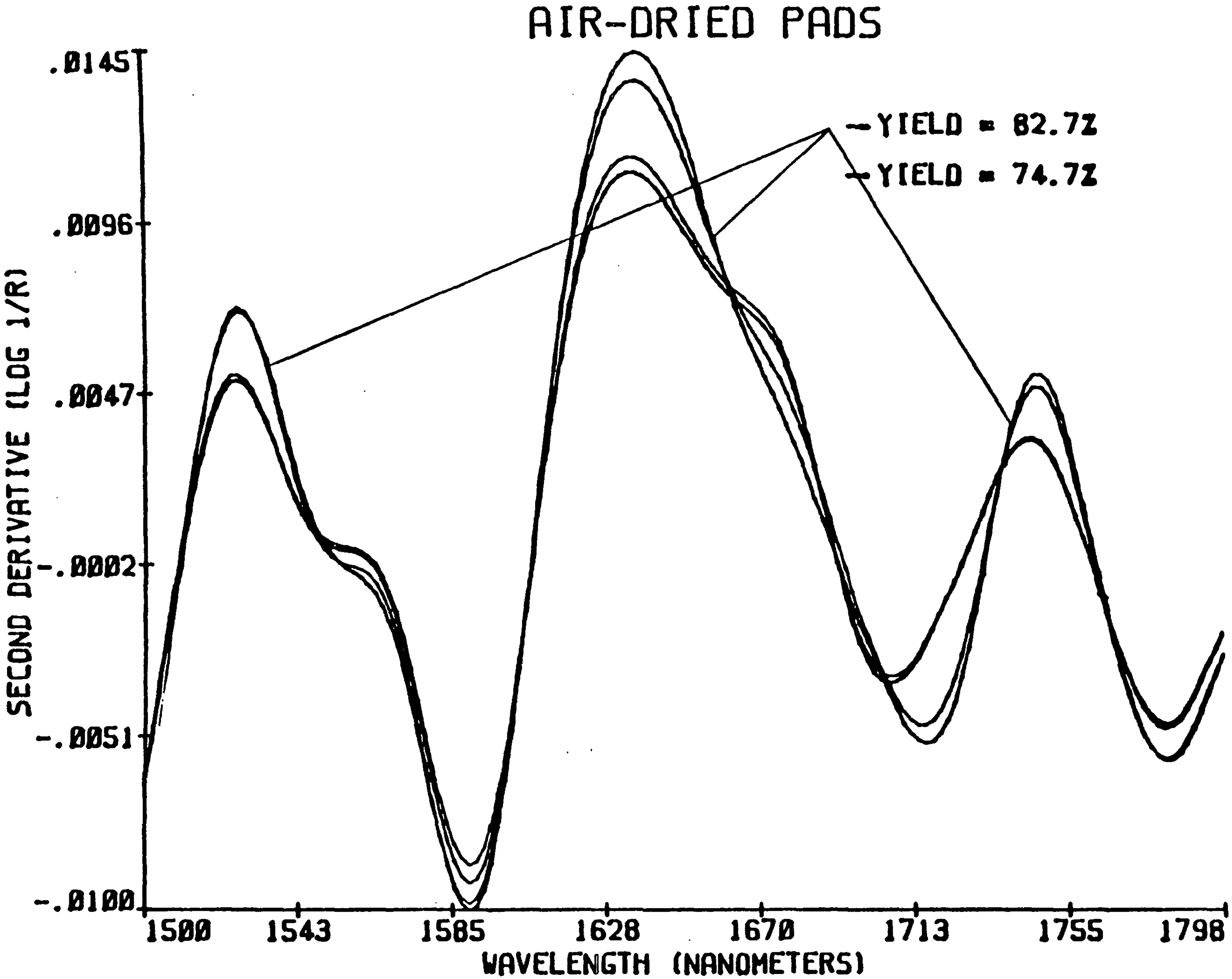
APPROACH (cont.)

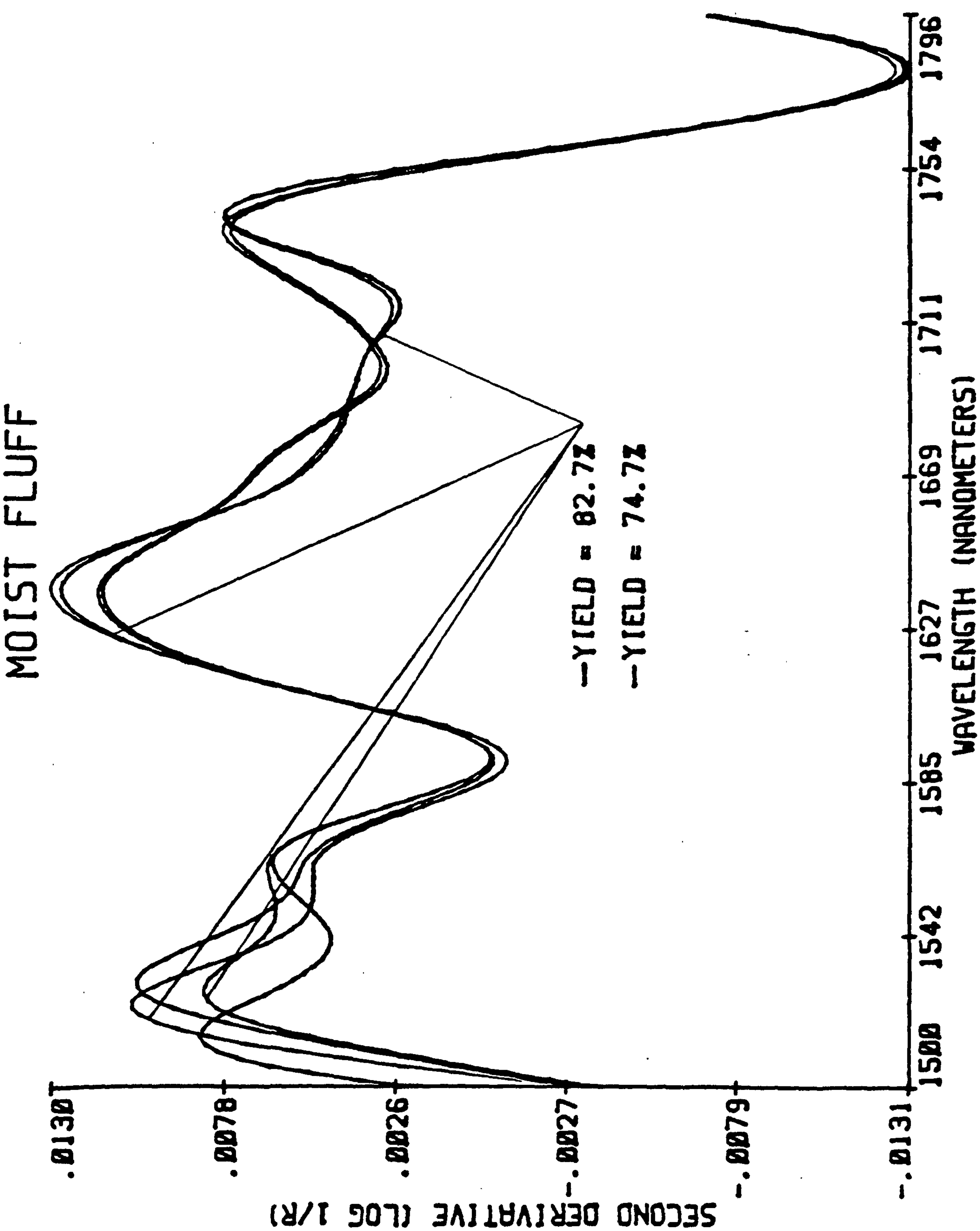
3. DEVELOP CORRELATIONS BETWEEN ANALYTICAL MEASUREMENTS, ESTIMATED YIELD, AND END-USE PROPERTIES

PRELIMINARY RESULTS

NEAR-INFRARED
REFLECTANCE SPECTROSCOPY

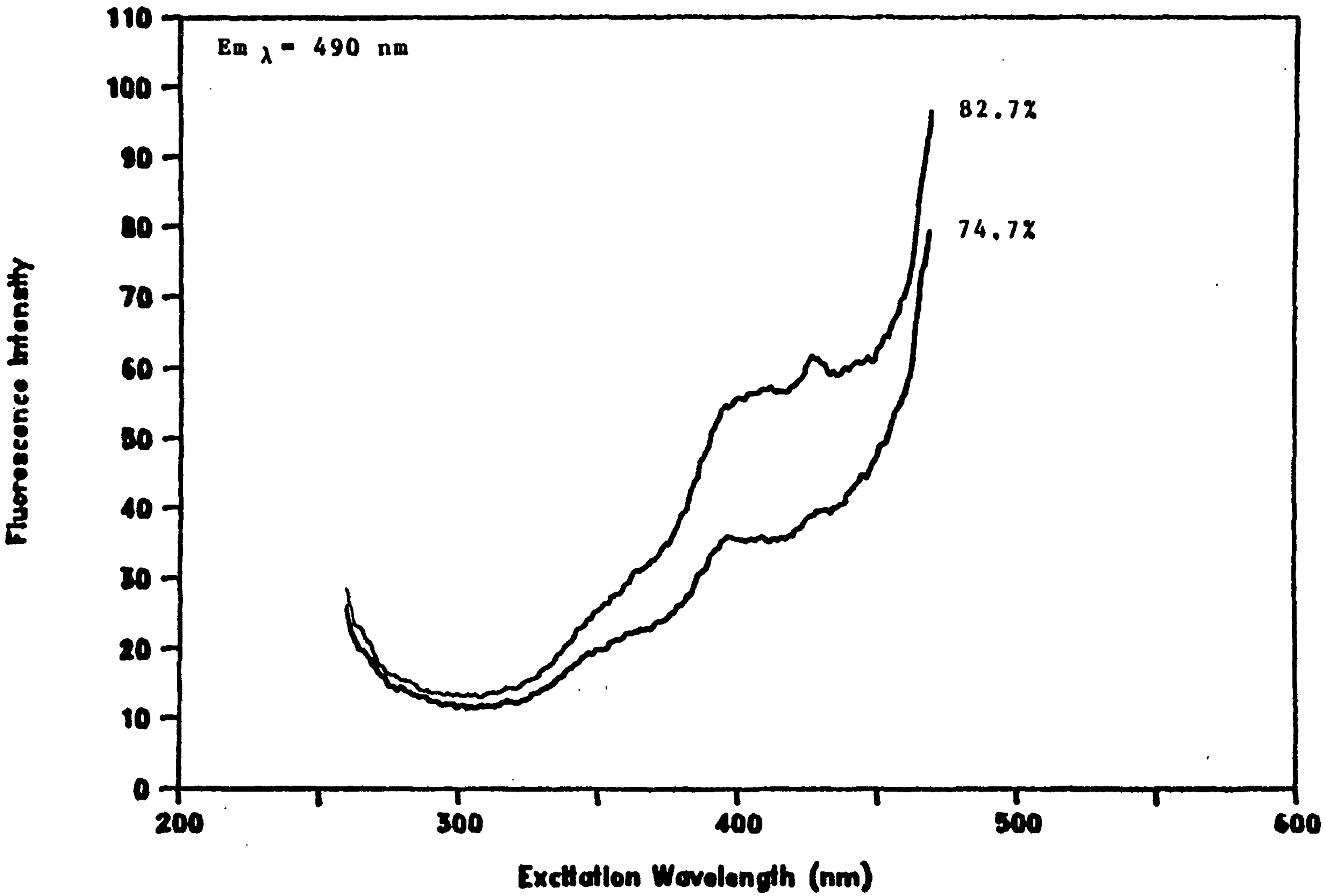

AIR-DRIED PADS
—YIELD = 82.7%
YIELD = 74.4%
LOG 1/R
.6249
.5304
.4359
.3414
.2468
.1523
1100
1300
1500
1700
1900
2100
2300
2500
WAVELENGTH (NANOMETERS)

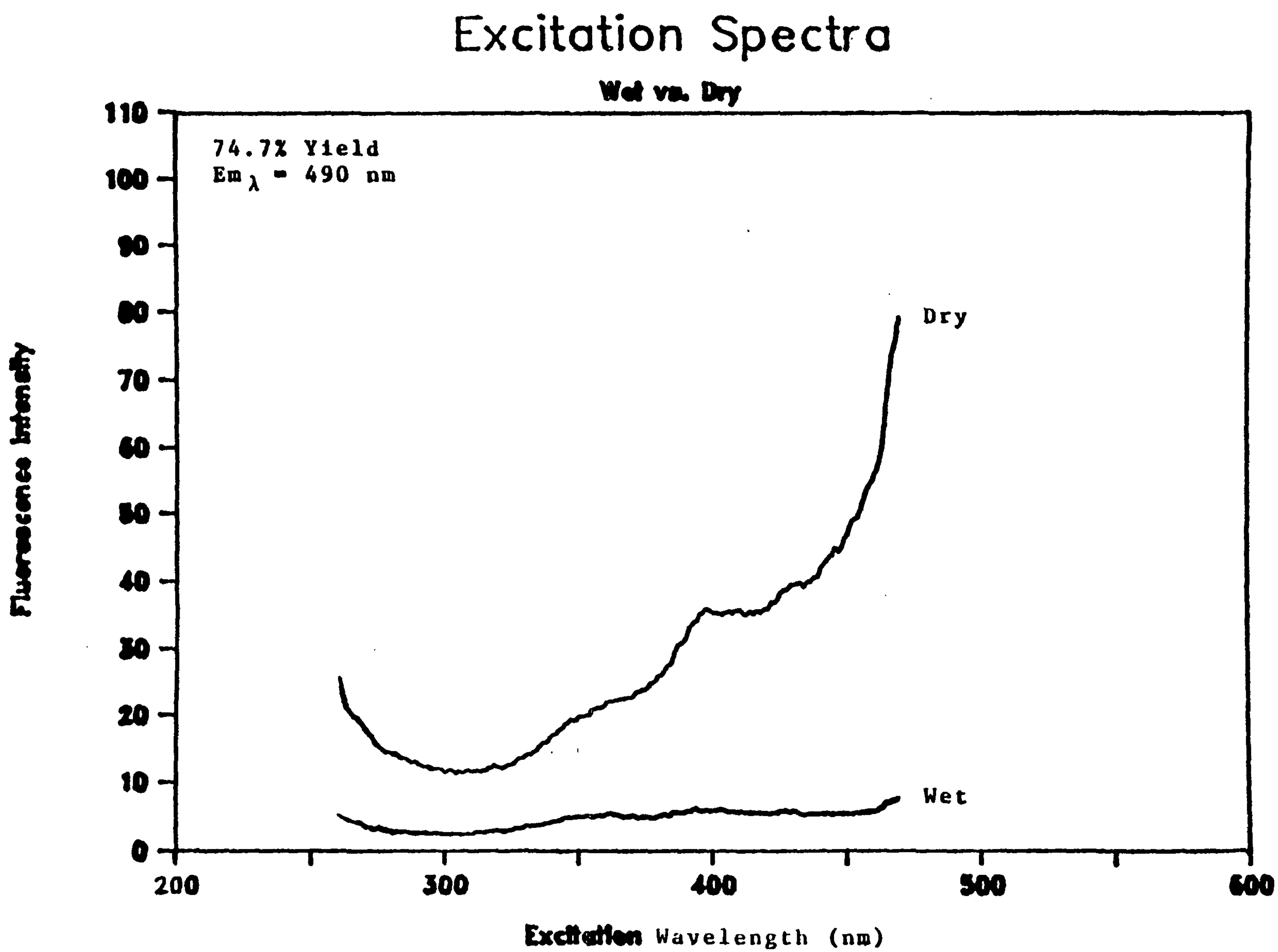

AIR-DRIED PADS
YIELD = 82.7%
YIELD = 74.7%
.0145
.0096
.0047
-.0002
-.0051
-.0100
SECOND DERIVATIVE (LOG 1/R)
1500
1543
1585
1628
1670
1713
1755
1798
WAVELENGTH (NANOMETERS)


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

ULTRAVIOLET-VISIBLE LUMINESCENCE SPECTROSCOPY

Excitation Spectra




Excitation Spectra
Wet vs. Dry
74.7% Yield
Em$_\lambda$ = 490 nm
Dry
Wet
Fluorescence Intensity
Excitation Wavelength (nm)
0
10
20
30
40
50
60
70
80
90
100
110
200
300
400
500
600

CONCLUSION

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

PROJECT 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

INTRODUCTION

Bleached and/or Unbleached Mechanical Pulp

$$\Delta \quad \Big\downarrow \quad h\nu$$

Yellowed Mechanical Pulp

Yellowing
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

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

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.

<u>Research Directions</u>

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

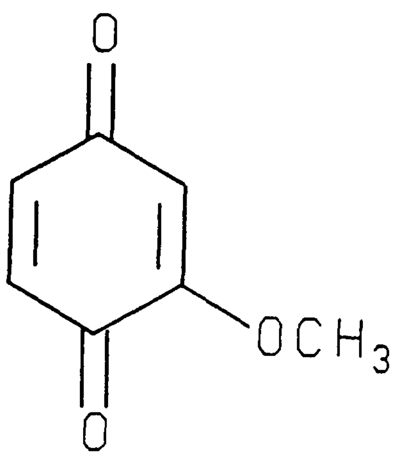
(ii) the photo-reactivity of chromophoric structures employing model compounds and TMP

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

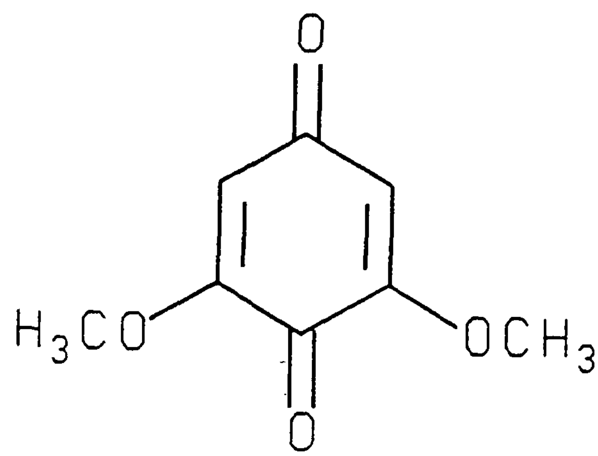
STUDIES DIRECTED AT INVESTIGATING THE PHOTO-REACTIVITY OF QUINONES UNDER THE BRIGHTNESS REVERSION CONDITIONS

Compounds of Interest

Para Quinones



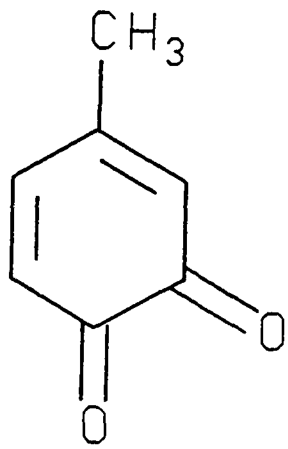
MMBQ

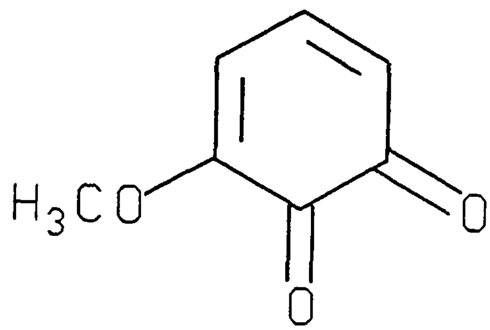


DMBQ

- 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

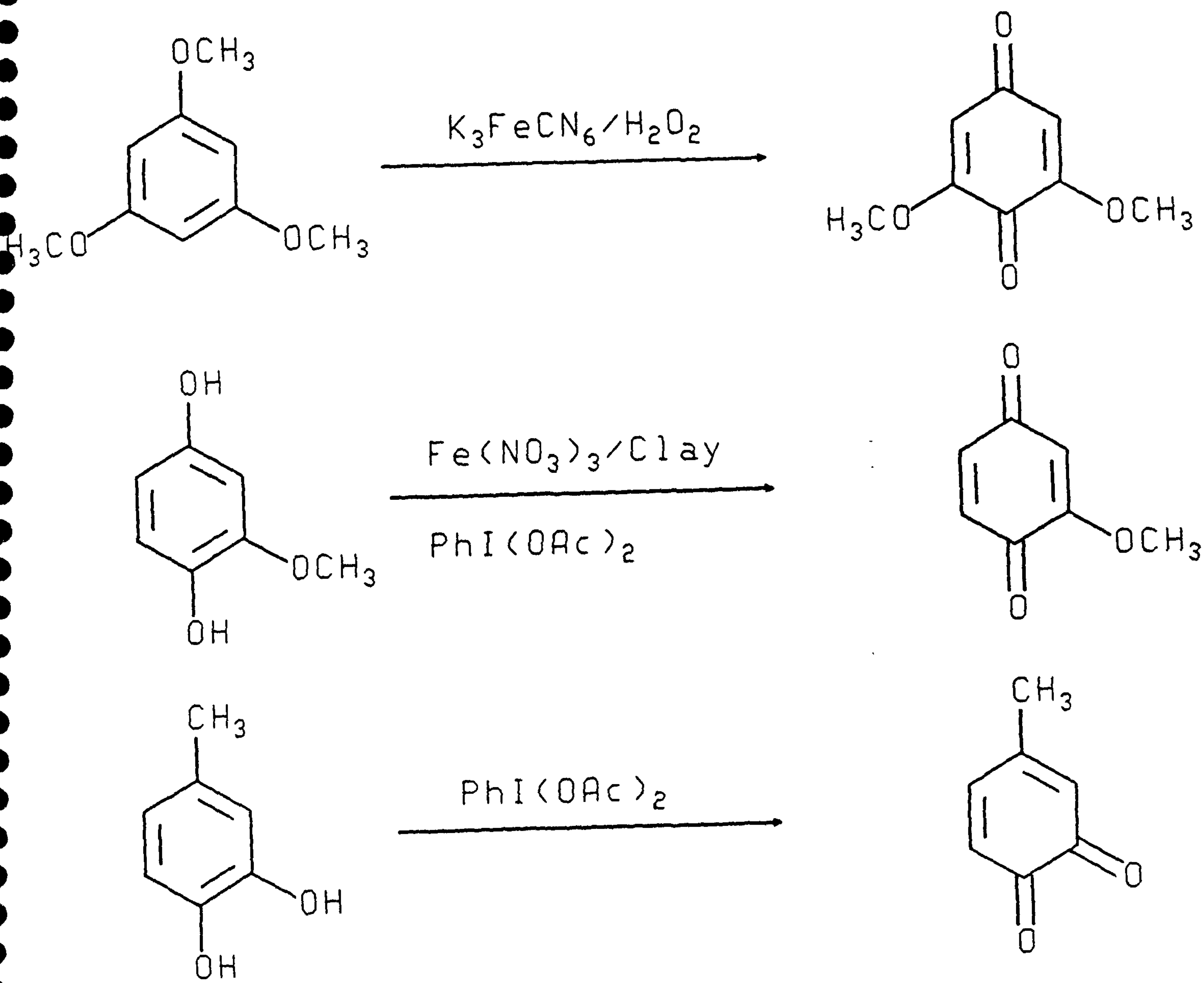
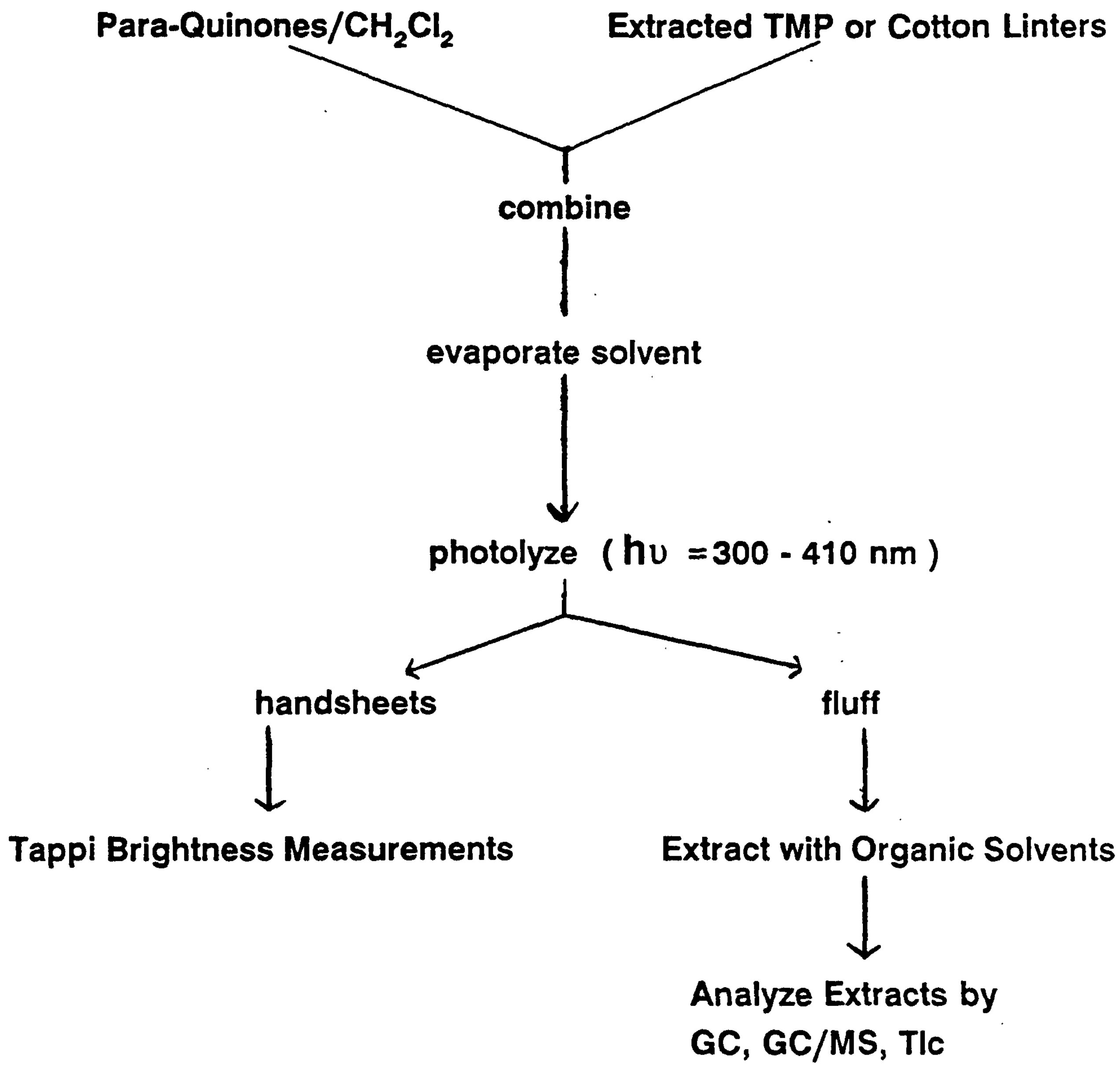


PHOTO-CHEMICAL STUDIES OF PARA-QUINONES

<u>Experimental Procedures</u>



-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

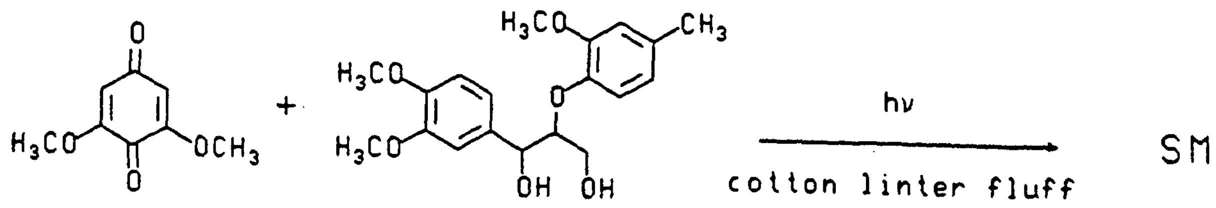
DMBQ/TMP Fluff

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

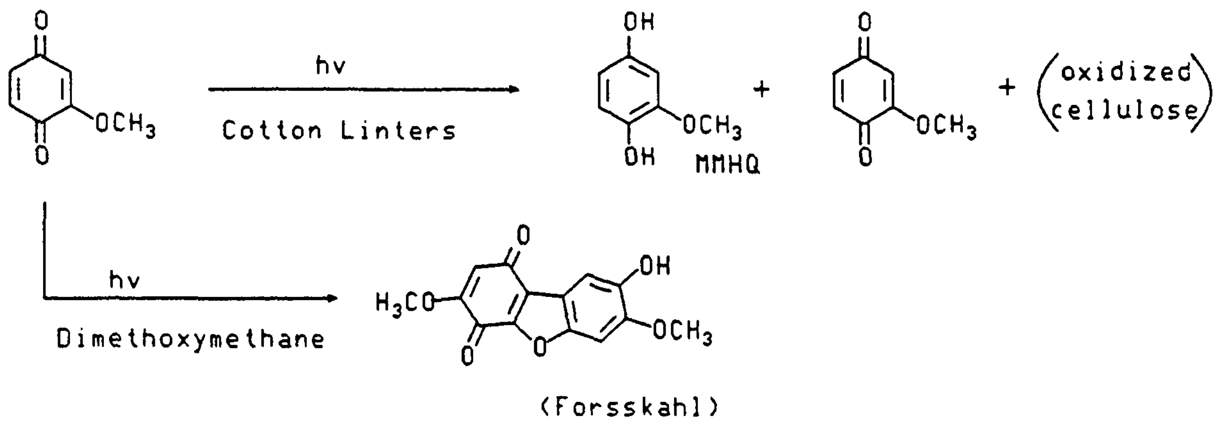
Period of Irradiation (h)	% MMBQ Recovered[a]	% MMHQ[a]
0	82	
1/2	65	6
1	58	5
2	65	5
4	70	8

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



MMBQ/Cotton Linter Handsheets

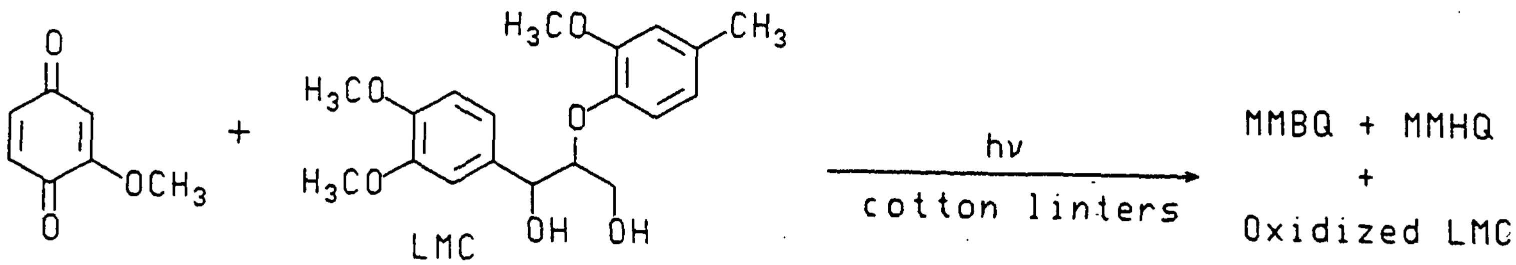
Period Irradiation (h)	TAPPI Brightness
0	44
1	35
2	32
4	33

-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.

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