



THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

ATLANTA, GEORGIA

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

MARCH 20-21, 1990

HANDOUT

PULPING PROCESSES
PROJECT ADVISORY COMMITTEE MEETING

MARCH 20, 1990

RESEARCH OVERVIEW

E. W. Malcolm

WELCOME

PULPING, BLEACHING AND RECOVERY STAFF March, 1990

Ph.D. (Faculty) 10 + 2

M.S./B.S. 9

Postdoctoral Fellows 1

CURRENT SENIOR STAFF

Malcolm
McDonough
Rudie
Courchene
Woitkovick
Dimmel
Sonnenberg
Ragauskas
Banerjee
Empie
Nichols
Horton
Adams (pt.)
Grace (pt.)
Lien

RESEARCH AREAS

Chemical Pulp

Chemical Recovery

High Yield Pulp

SCIENCE AREAS

Wood Chemistry (Organic/Physical)

Chemical Engineering

Analytical Chemistry

RESEARCH TYPE

IPST Funded

Contract (Company - Organization)

Student (M.S./Ph.D.)

IPST RESEARCH BUDGET (1989-1990) - CHEMICAL SCIENCES DIVISION

(REVISED - March, 1990)

MEMBER FUNDED

Chemical Pulping and Bleaching

Fundamentals of Selectivity in Pulping and Bleaching (3475)	- 120
Environmentally Compatible Production of Bleached Pulp (3474)	- <u>250</u>
	370

Recovery

Fundamental Processes in Alkali Recovery (3473-1)	- 280
Computer Model of Recovery Furnace (3605)	- <u>80</u>
	360

High Yield Pulps

Strong, Intact High Yield Fibers (3566)	- 50
Fundamentals of Brightness Stability (3524)	- 155
High Brightness, High Yield Pulps (NEW)	- <u>120*</u>
	325

Other

Exploratory Research (3534)	- 60
Analytical (3477)	- <u>15</u>
	75

TOTAL MEMBER FUNDED 1130

*moved from fiber structure project

CONTRACT RESEARCH

GOVERNMENT FUNDED

Black Liquor Combustion (Project 3473-6) ³	IPST	100	
	OSU	20	
New Pulping Process (DOE/SERI) (Project 3661)		160	(487) ¹
Black Liquor Delivery Systems (Project 3657-2)		<u>350</u>	(1510) ²
		630	

NONGOVERNMENT FUNDED

Pulping/Bleaching		200	
API/NCASI (Dioxin)		425	
NCASI (Combustion)		75	
Other		<u>50</u>	
		750	

TOTAL CONTRACT RESEARCH 1380

- 1 - 3-year budget
- 2 - 4-year budget
- 3 - completed 31 Dec 1989

FUNDED AND CONTRACT

Total \$2,560,000

(45% member funded
55% contract)

STUDENT RESEARCH (March, 1990)

	Ph.D.	M.S.	Postdoc
Chemical Pulping	3	5	1
Chemical Recovery	4	5	-
Mechanical Pulping	$\frac{0}{7}$	$\frac{3}{13}$	$\frac{-}{1}$

APPROXIMATE BUDGETS FOR SELECTED RESEARCH GROUPS
(March, 1990)
(not including students)

Chemical Pulping	\$1,155,000
Kraft Recovery Furnace	\$ 905,000
High Yield	\$ 325,000

MEMBER FUNDED

DOE FUNDED
API/NCASI FUNDED

PROJECT HIGHLIGHTS

Chemical Pulping

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP
(Project 3474) McDonough

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING
(Project 3475) Dimmel

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION
PART I: PRECURSOR FORMATION AND REACTIVITY
PART II: CHLORINATION AND DIOXIN REACTIONS
(Projects 3684 & 3685) Sonnenberg
Dimmel

SULFUR-FREE SELECTIVE PULPING PROCESS
(Project 3661) Dimmel
SERI

Kraft Chemical Recovery Furnace

FUNDAMENTAL PROCESS IN ALKALI RECOVERY
(Project 3473-1)

Empie
Lien
Nichols

COMPUTER MODEL OF RECOVERY FURNACE
(Project 3605)

Horton

High Yield Pulping

FUNDAMENTALS OF BRIGHTNESS STABILITY
(Project 3524)

Ragauskas

STRONG, INTACT HIGH YIELD FIBERS
(Project 3566)

Rudie

Research Presentations

Kraft Recovery Furnace

Chemical Pulping

High Yield Pulping

PROJECT 3661 OBJECTIVE

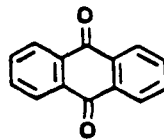
DEVELOP A SELECTIVE/ECONOMICAL PULPING SYSTEM BASED ON THE USE OF PULPING CATALYSTS GENERATED FROM LIGNIN

POTENTIAL BENEFITS

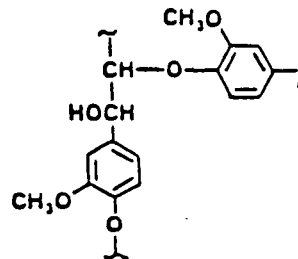
- GREATER PRODUCTIVITY
- LOWER ENERGY INPUTS
- LOWER BLEACHING COSTS/BY-PRODUCTS
- SIMPLIFIED RECOVERY SYSTEM
- CONSERVATION OF RAW MATERIALS

CATALYSTS FROM LIGNIN

JOHN WOZNIAK, Ph.D. THESIS

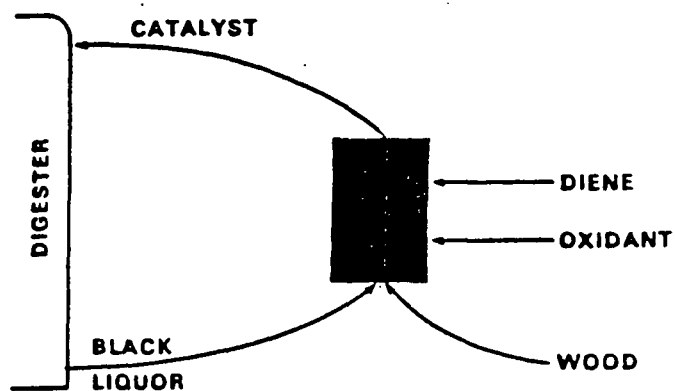


ANTHRAQUINONE

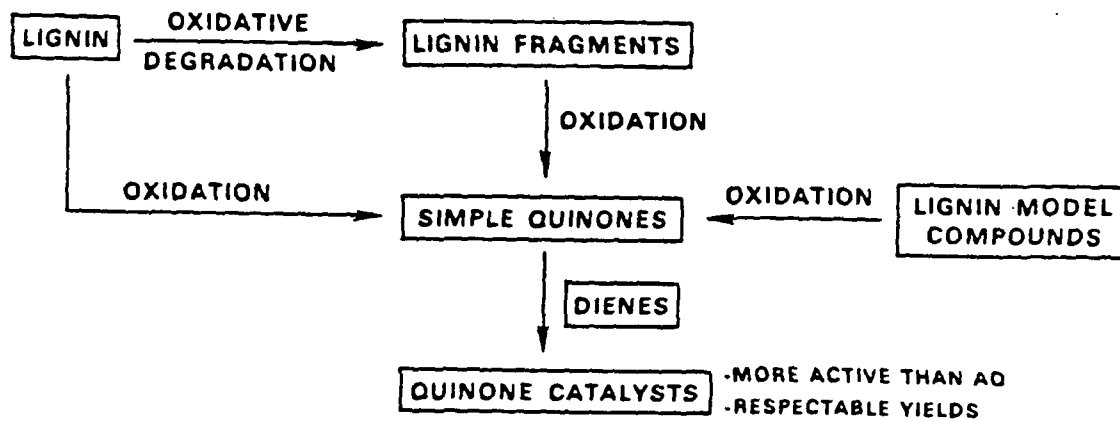


LIGNIN UNIT

CATALYSTS FROM LIGNIN APPROACHES



CATALYSTS FROM LIGNIN RESULTS



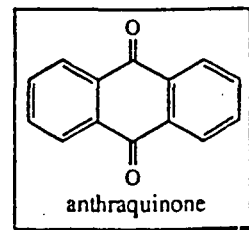
OIP Sulfur-Free Selective Pulping Process

A joint project between the Institute of Paper Science and Technology
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

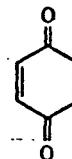


1) Lignin Processing

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

2) Chemical Processing

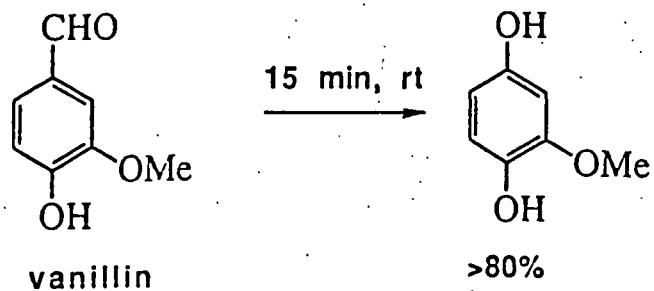
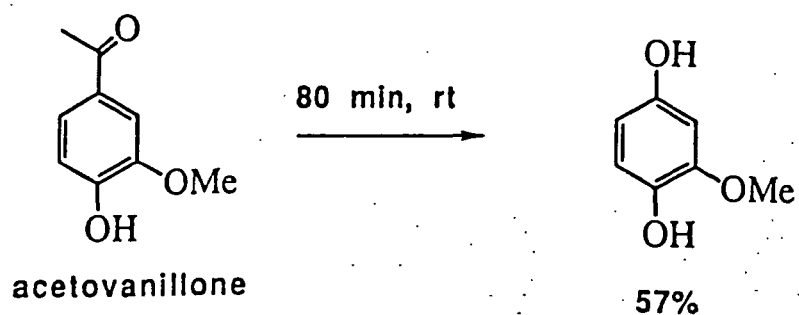
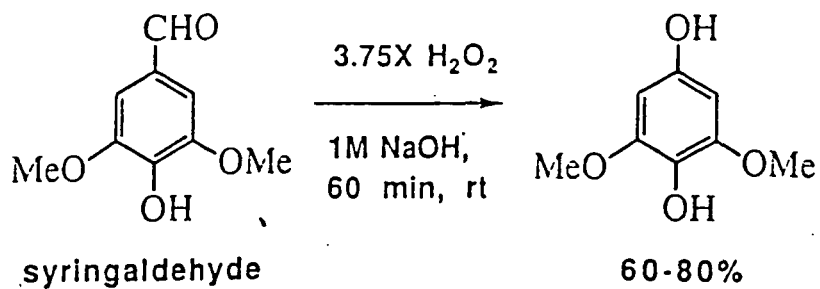
a) low molecular weight fraction $\xrightarrow{\text{oxidation}}$ benzoquinone mixture e. g.,



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

c) anthraquinone precursor $\xrightarrow{\text{dhydrogenation catalyst}}$ anthraquinone

Peroxide oxidation of lignin model compounds



P. VanVreede, IPST

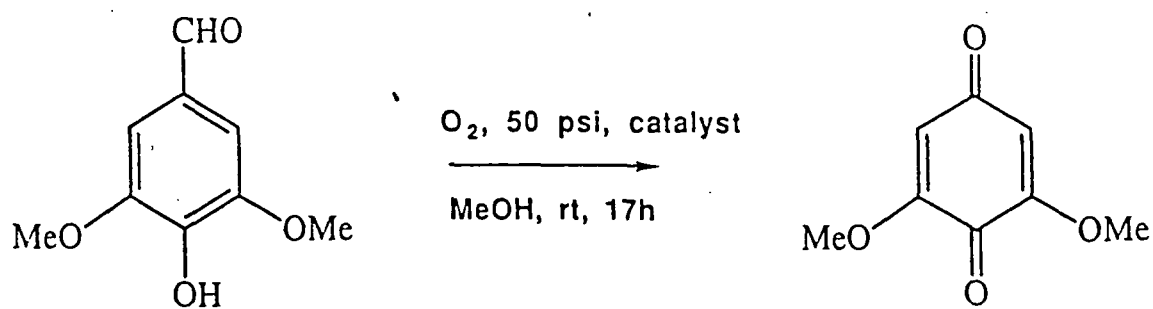
RECENT PEROXIDE STUDIES

- INITIAL HYDROQUINONE APPEARS STABLE
- QUINONE YIELDS FROM HYDROQUINONE OXIDATION
- QUINONE YIELD INCREASES WITH H₂O₂ CONC.
- LC QUANTIFICATION OF QUINONE YIELDS

FUTURE PEROXIDE STUDIES

- COMPLETE QUANTIFICATION STUDIES BY LC
- DEFINE BEST CONDITIONS FOR A SYN. MIXTURE
- OXIDIZE LMW LIGNIN SAMPLES
- PEROXYSULFURIC ACID, PEROXYFORMIC ACID, - - - -

Metal Catalyzed Oxidation of Lignin Models



syringaldehyde

97% selectivity at
84% conversion

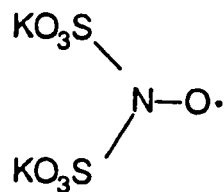
- reaction proceeds with 10% catalyst
- 1% catalyst level works, although to lower conversions
- other models under study

Oxidation of Lignin Model Compounds

<u>Lignin Model</u>	<u>Oxidizing agent, yield (%)¹</u>		
	<u>Fremy's salt²</u>	<u>hydrogen peroxide³</u>	<u>peracetic acid⁴</u>
α -methylvanillyl alcohol	79	4	1
vanillic acid	77	NR	NR
acetovanillone	0	77	89
vanillin	0	95	21
α -methylsyringyl alcohol	79	12	30
syringic acid	77	0	3
syringaldehyde	65	96	17
acetosyringone	3	43	32
lignin samples	16 (lmw ethanol) 15-25 (SCE)	none	traces

Notes:

- 1-yields calculated from GC by internal standard method
- 2-products almost exclusively the corresponding benzoquinone
- 3-products almost exclusively the corresponding hydroquinone
- 4-products a mixture of hydroquinone and acetylated hydroquinone

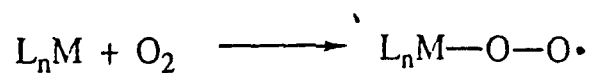


Expensive
Consumed
Requires >2 equivalents
Sometime explosive
Requires low reaction temperature
Reaction time is usually 2-5 hours

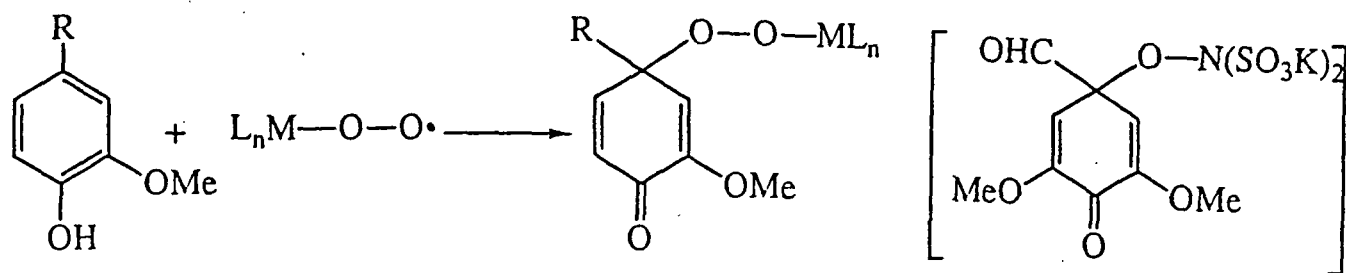
Alternatives to Fremy's Salt

Fremy's Salt: $(\text{KSO}_3)_2\text{N}-\text{O}\cdot$

Compare:



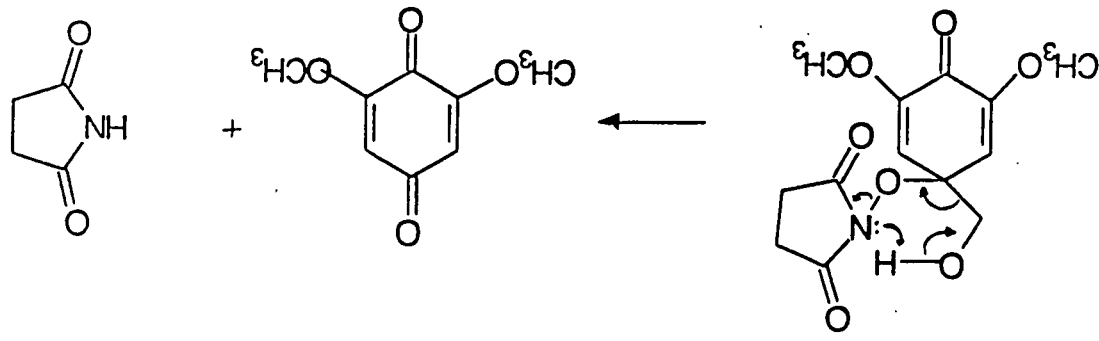
Known:



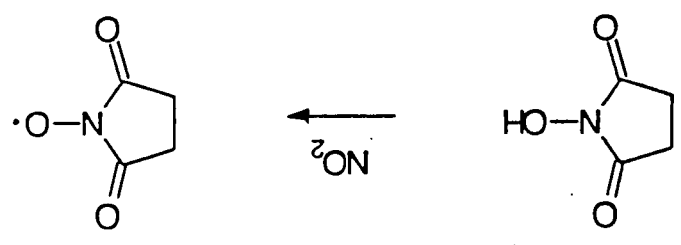
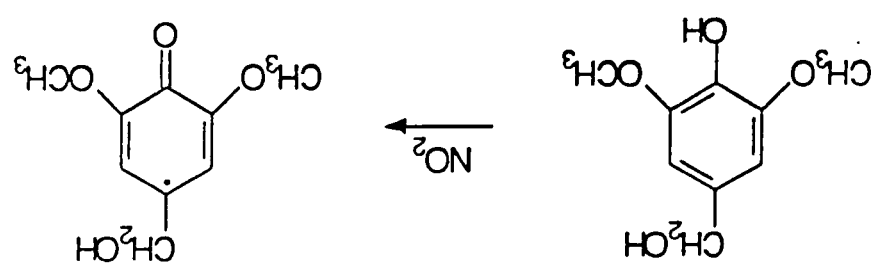
-reaction catalytic in metal complex

-often proceeds in high yields

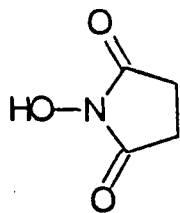
-uses oxygen as the oxidizing agent



Suggested Key Step:



Use of NO_2 to Generate Radicals:



A POTENTIAL OXIDIZING AGENT

Less expensive

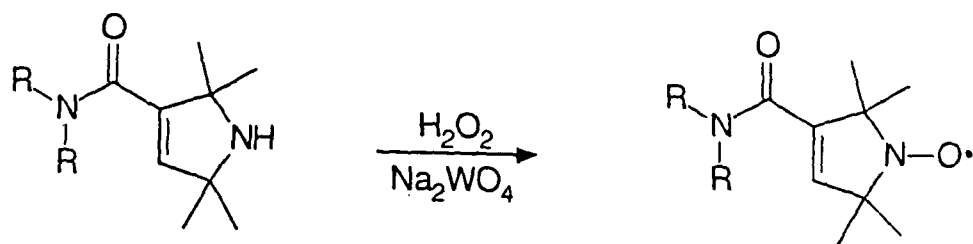
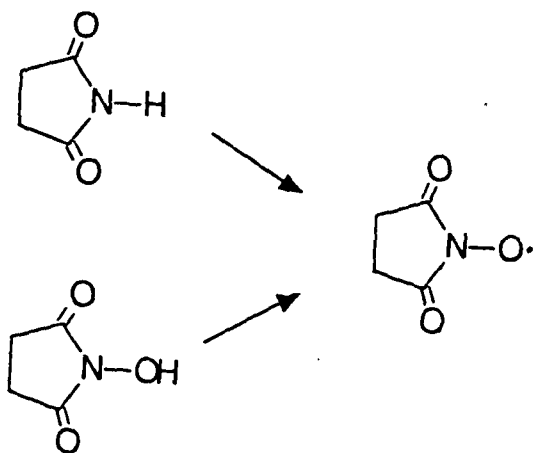
Not explosive

Easy to handle

Does not require low reaction temperature

Reaction time is very short

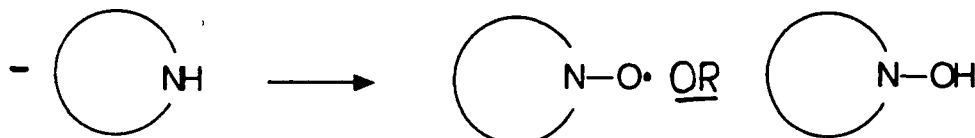
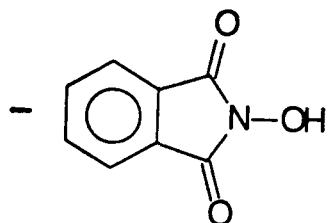
Can We Generate ?



Chen, K.; Swartz, H. *Biochem. Biophys. Acta*
1988, 970, 270

FUTURE PLANS:

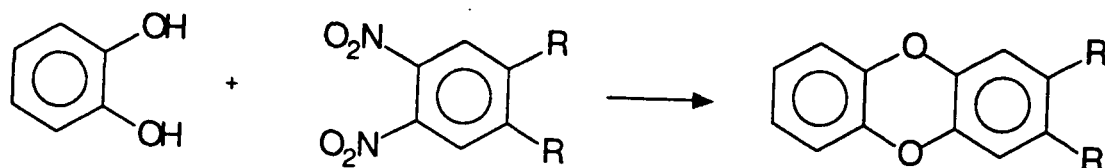
- Complete Evaluation of N-Hydroxysuccinimide as an Oxidizing Agent on Model Systems.

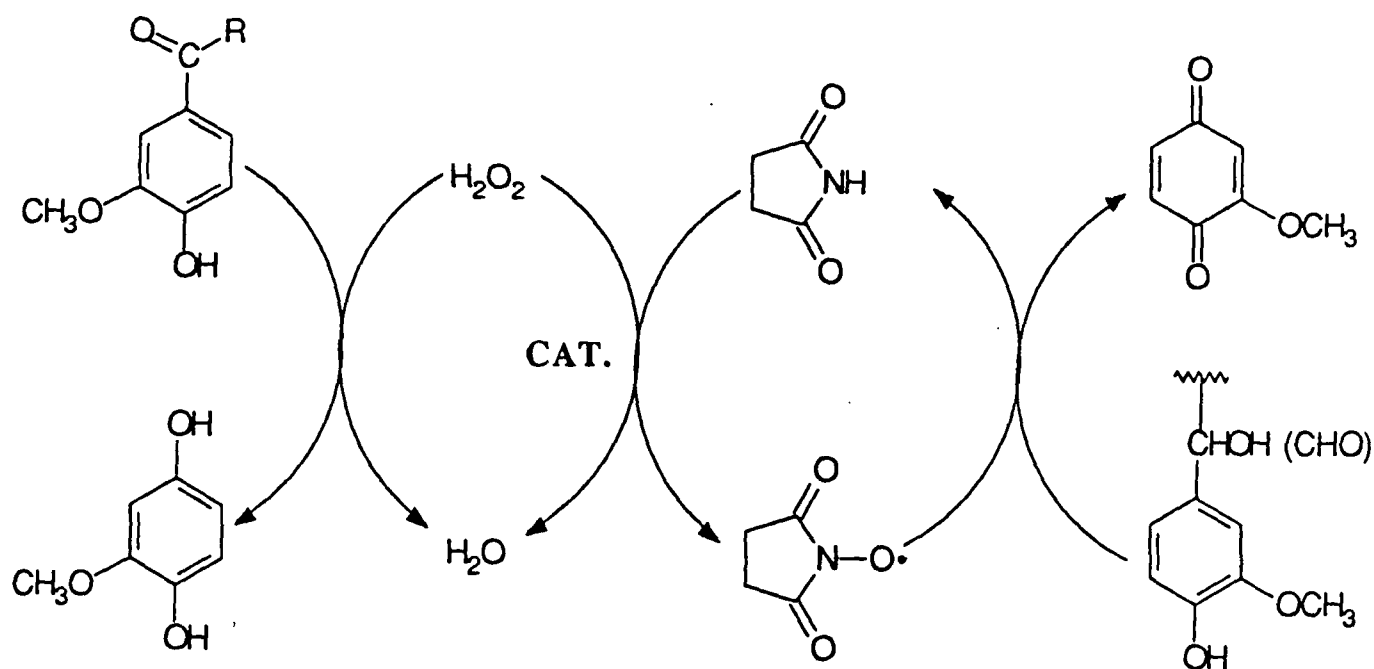


- Apply to Lignin

- Carry out Diels-Alder Reaction in Presence of a Base

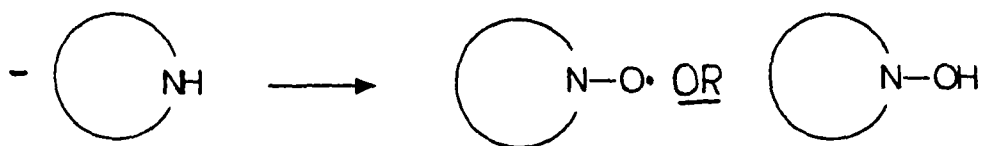
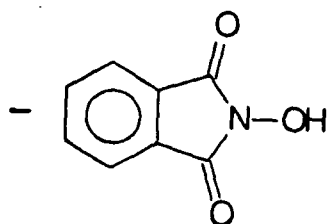
- Synthesis of Dibenzodioxin





FUTURE PLANS:

-Complete Evaluation of N-Hydroxysuccinimide as an Oxidizing Agent on Model Systems.



-Apply to Lignin

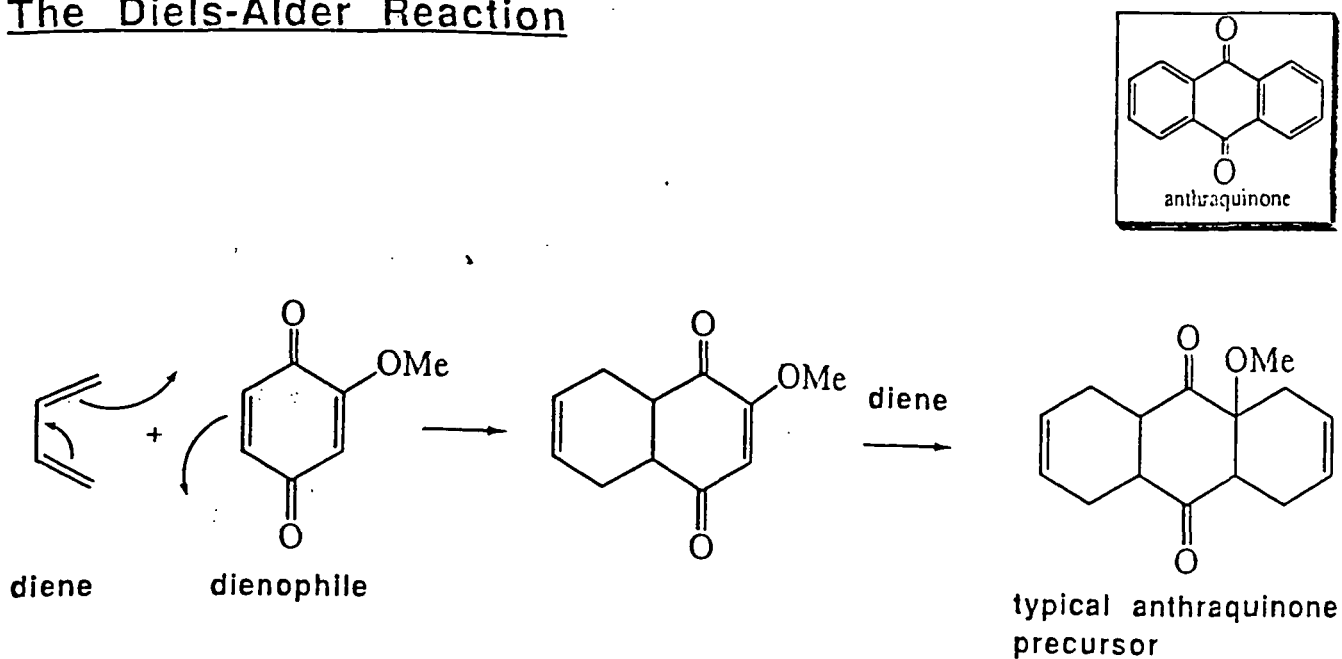
Metal Oxides as Oxidizing Agents



Table I: Oxidation of lignin model compounds with CuO

Entry	Starting Material	Reaction Conditions	% Quinone	%SM	% Unidentified
1	Vanillyl Alcohol (R ₁ = CH ₂ OH, R ₂ = H)	CuO/KOH 6 hrs.	0	60	40
2	Syringaldehyde (R ₁ = CHO, R ₂ = OCH ₃)	CuO/KOH 6 hrs.	0	45	55
3	Syringyl alcohol (R ₁ = CH ₂ OH, R ₂ = OCH ₃)	CuO/KOH 4 hrs.	0	55	45

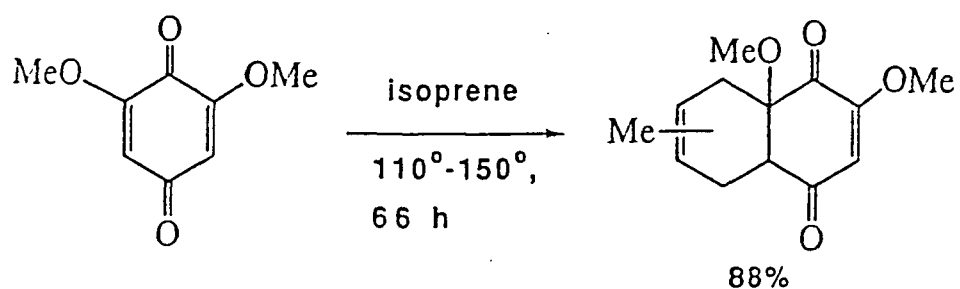
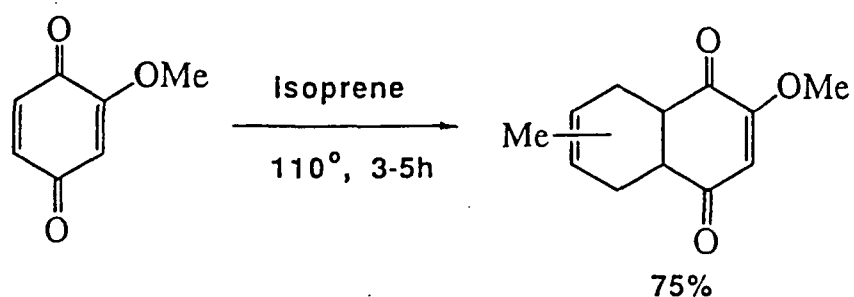
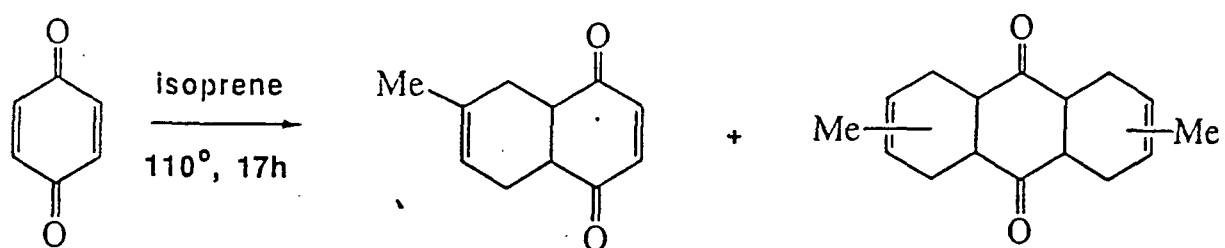
The Diels-Alder Reaction



-for anthraquinone synthesis, two moles of diene must add

-methoxyl groups tend to slow the reaction

Diels-Alder Reaction of Benzoquinones



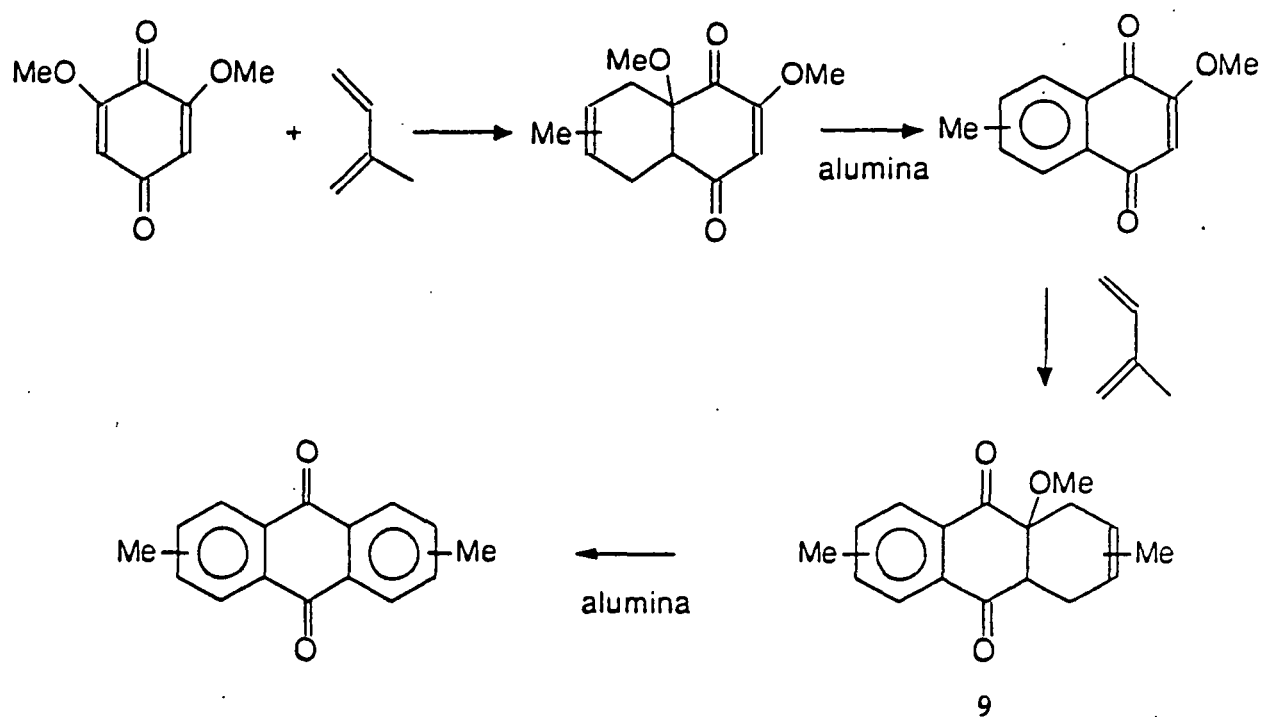


Figure 4. One pot reaction of DMBQ and isoprene with alumina added.

Table 5. MMNQ, DMAQ, and Diels-Alder adduct yields from the reaction of DMBQ and isoprene in toluene with alumina (3.4 eq. per DMBQ) at 180°C.

Time, hr	Diene/dieophile ratio, eq.	Alumina type	MMNQ, %	DMAQ, %	Diels-Alder Adduct, %
2	3.4	Woehm/O ^a	32.0	1.6	-
5	3.4	Woehm/O	31.4	2.2	-
12	3.4	Woehm/O	21.5	9.6	-
24	3.4	Woehm/O	11.3	17.9	-
24	3.4	EM Reagents/O	9.1	17.4	-
24	3.4	Camag/O	8.3	20.7	-
24	3.4	Woehm/N ^b	19.0	10.2	-
24	3.4	EM Reagents/N	10.3	15.6	-
24	3.4	Camag/N	7.9	18.8	-
24	3.4	-	12.9	0.9	-
24	3.4	-	11.0	0.5	68.6
24	5.0	-	17.1	1.6	63.7
24	3.4	EM Reagents/O	2.5	21.9	-
24	3.4	Camag/O	8.5	18.3	-
24	3.4	Camag/I ^c	5.6	20.7	-
24	4.4	Camag/O	4.3	24.0	-
24	2.4	Camag/O	11.6	15.9	-
24	3.4	Camag/O ^d	0.7	21.8	-

^a The O represents activated alumina stored under O₂.

^b The N represents activated alumina stored under N₂.

^c The I represents alumina obtained from the manufacturer.

^d This sample had double the alumina loading.

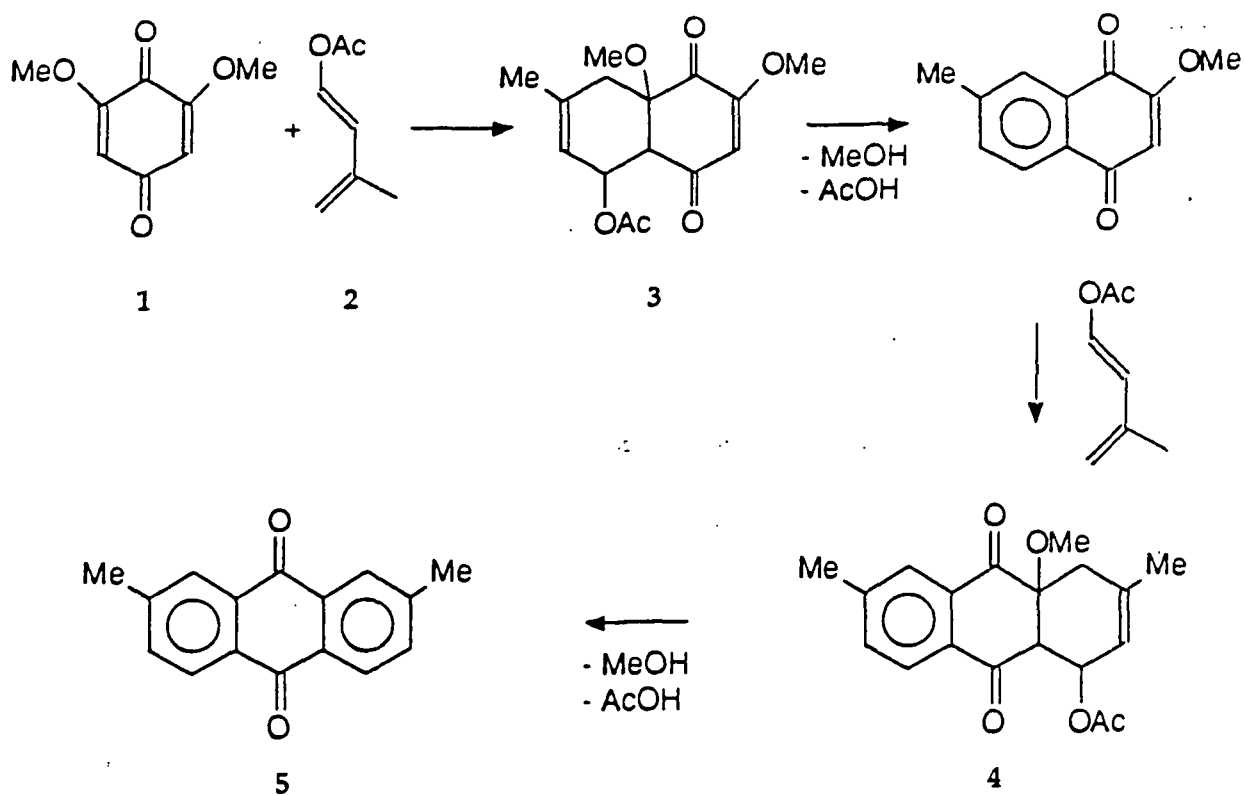
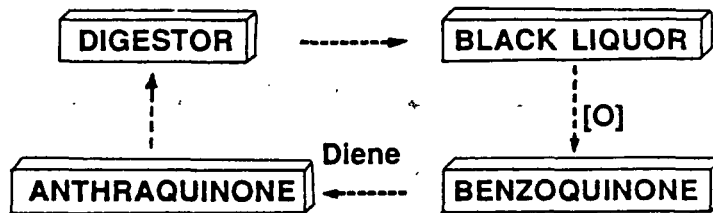


Figure 1. Diels-Alder reactions of DMBQ with 1-acetoxy-3-methyl-1,3-butadiene.

Table 3. DMAQ yields from the reaction of DMBQ and AMB in toluene at 180°C.

Time, hr.	Diene/dieneophile ratio, eq.	DMAQ yield, %
2	2.4	1.9
4	2.4	4.7
6	2.4	11.2
24	2.4	32.4
48	2.4	41.0
48	2.9	53.3
48	4.0	61.5
48	4.9	70.5



Bleaching Liquors as a Source of Quinones

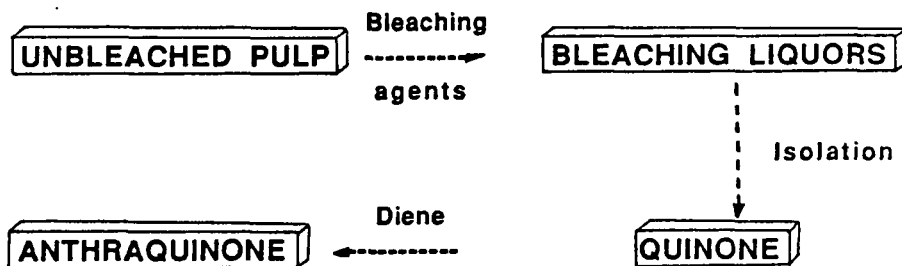
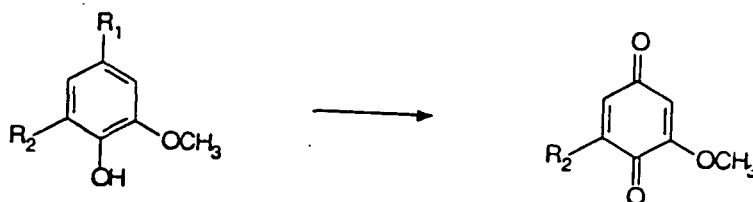


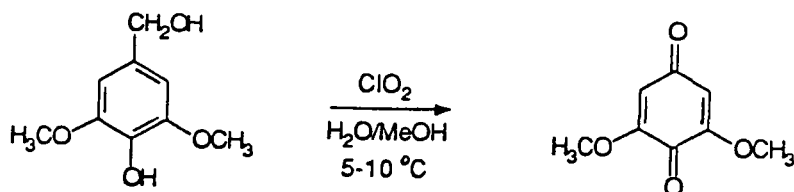
Fig. 2: Generation of catalyst from bleaching liquors

Sodium Chlorite as the Oxidizing Agent:



Entry	Starting Material	Reaction Conditions	% SM	% Quinone	% Unknown
1	Syringaldehyde R ₁ = CHO, R ₂ = OCH ₃	H ₂ SO ₄ /RT	63	0	37
2	Syringyl Alcohol R ₁ = CH ₂ OH, R ₂ = OCH ₃	H ₂ SO ₄ /RT	15	13	72
3	guaicol R ₁ = R ₂ = H	H ₂ SO ₄ /RT	-	13	81
4	Syringol R ₁ = H, R ₂ = OCH ₃	H ₂ SO ₄ /RT	40	14	42
5	Vanillyl alcohol R ₁ = CH ₂ OH, R ₂ = H	H ₂ SO ₄ /RT	33	21	46
6	Vanillin R ₁ = CHO, R ₂ = H	H ₂ SO ₄ /RT	8	17	75

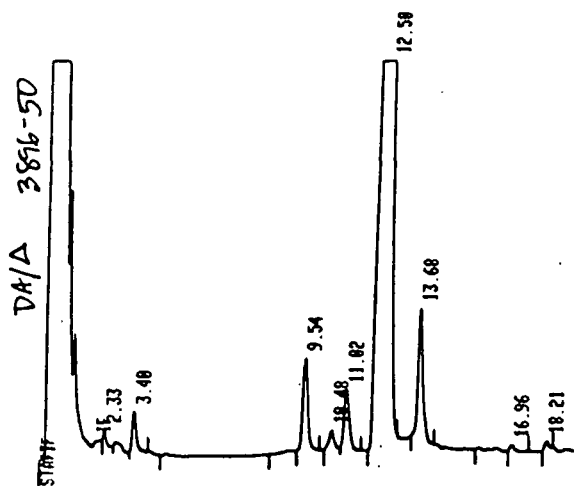
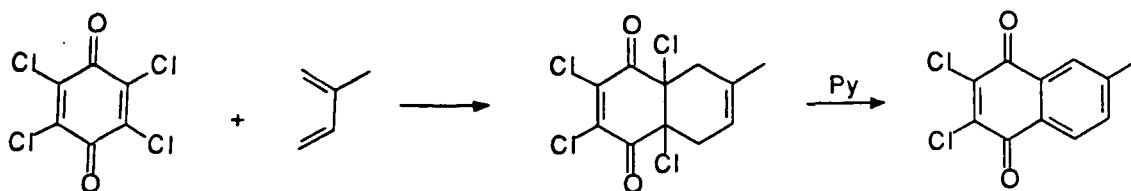
Table III: Oxidation of syringyl alcohol with chlorine dioxide



Starting Material	Reaction conditions	Reaction Time	GC Results	
Syringyl Alcohol	ClO ₂ /MeOH H ₂ O/5-10 C	5 min.	A	11.76%
			B	33.06%
			C	34.25%
			D	10.86%
		1 hr.	A	14.29%
			B	35.46%
			C	27.93%
			D	10.71%
		5 hrs.	A	8.13%
			B	27.81%
			C	41.96%
			D	16.20%
22 hrs.	A	7.35%		
	B	15.04%		
	C	54.10%		
	D	15.73%		

A = 2,6-Dimethoxy-1,4-benzoquinone
 B = Unidentified
 C = Syringyl Alcohol
 D = Unidentified

Diels-Alder Reaction of Chlorinated Quinones:

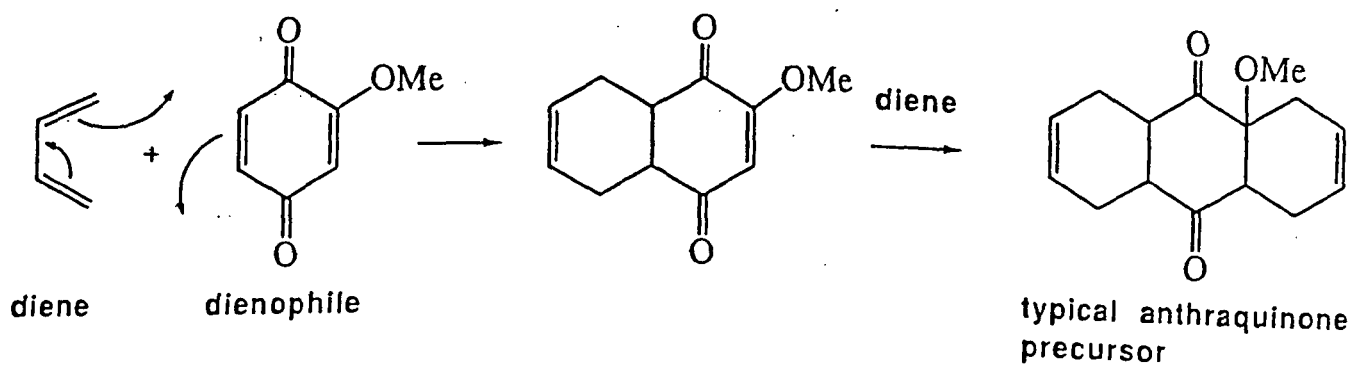
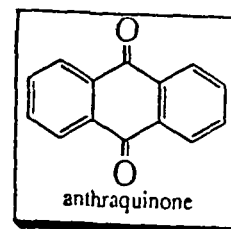


RUN # 579
 WORKFILE ID: C
 WORKFILE NAME:

FEB/02/98 10:41:29

RT	AREA	TYPE	AR/HT	AREA%
2.33	3201	BP	0.102	0.158
3.40	17880	PB	0.177	0.885
9.54	43186	BB	0.196	2.137
10.48	11233	BY	0.235	0.556
11.02	32940	VB	0.222	1.630
12.50	1844500	PB	0.325	91.281
13.68	61719	BB	0.197	3.054
16.96	2825	BB	0.162	0.140
18.21	3197	PB	0.151	0.158

The Diels-Alder Reaction



-for anthraquinone synthesis, two moles of diene must add

-methoxyl groups tend to slow the reaction

IMMEDIATE FUTURE STUDIES

- Repeat organosolv lignin extraction studies to determine the reproducibility of the results and to more completely characterize the extracted lignin.
- Optimize oxidation yields in the reactions of simple lignin model substrates with peroxide, oxygen, and hydroxysuccimide.
- Expand Diels-Alder reactions in water, in supercritical solvents, and with chlorinated quinones.
- Develop analytical methods for determining quinone yields from the oxidation of lignin substrates.

LONG-TERM RESEARCH AREAS

- 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.

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

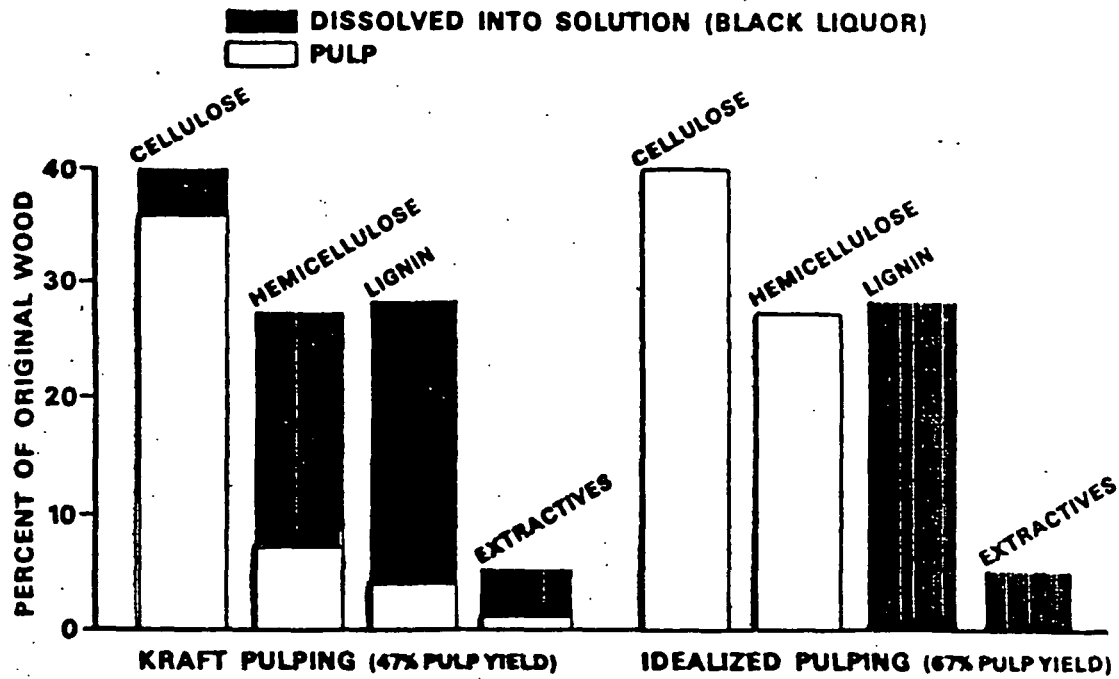
**A FUNDAMENTAL KNOWLEDGE OF CARBOHYDRATE CHAIN
CLEAVAGE REACTIONS WILL LEAD TO BETTER PULPING AND
BLEACHING STRATEGIES FOR PRODUCING HIGH QUALITY FIBERS**

Physical Structural Effects During Carbohydrate Pulping And Bleaching Reactions

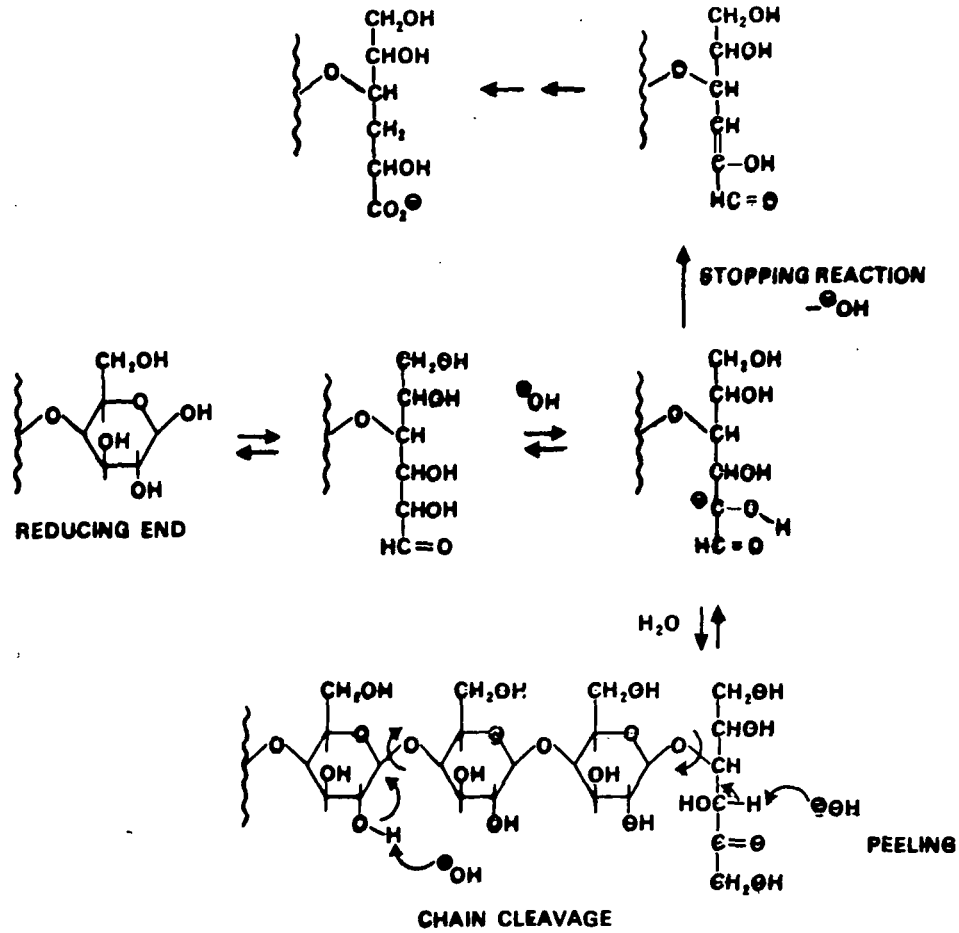
D. R. Dimmel
L. R. Schroeder
E. W. Malcolm
H. J. Willenbrink

Institute of Paper Science And Technology
Atlanta, Georgia

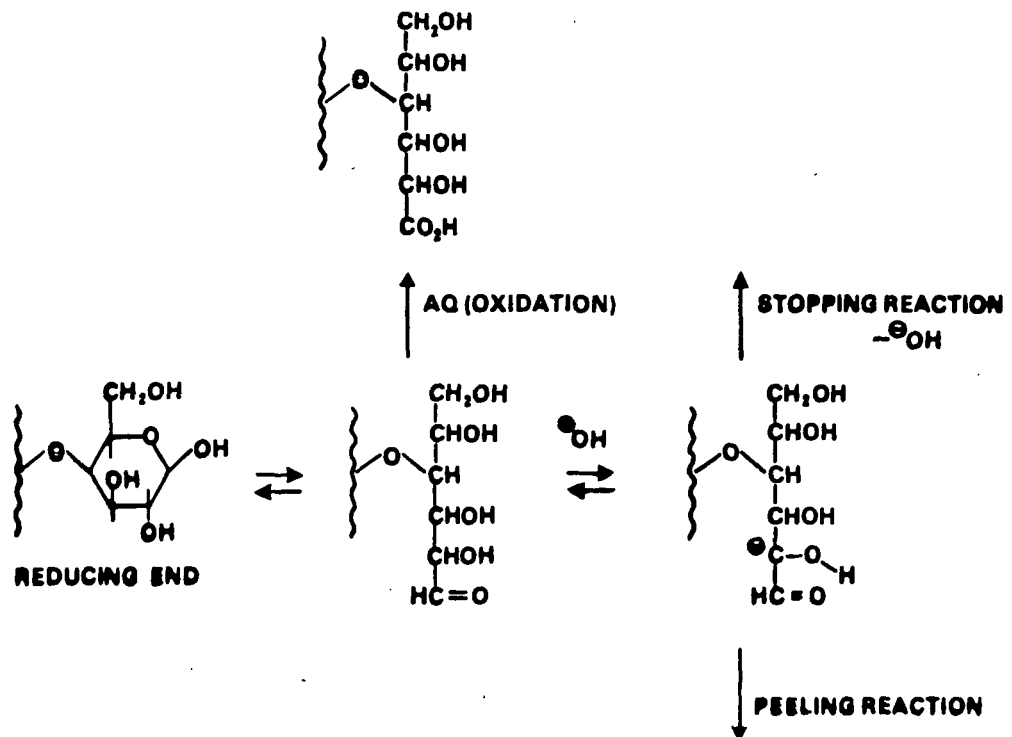
COMPONENT CHANGES WITH PULPING



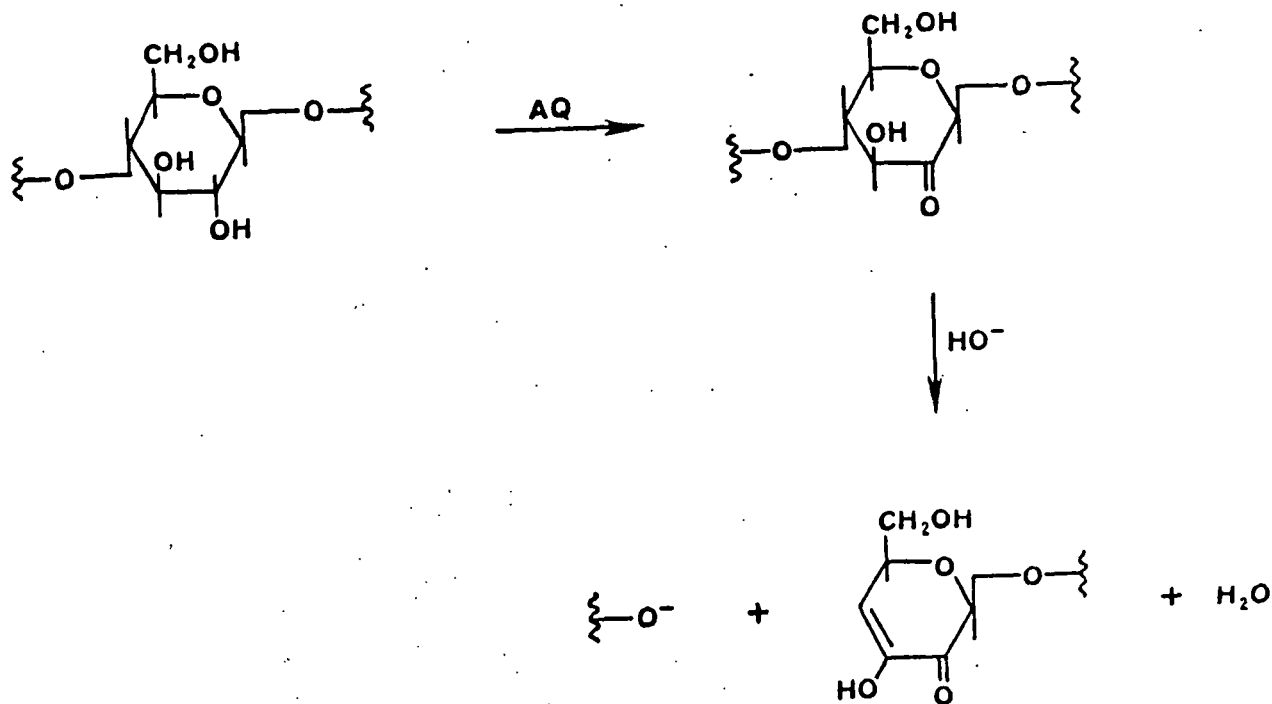
ALKALINE CARBOHYDRATE REACTIONS



ALKALINE CARBOHYDRATE REACTIONS



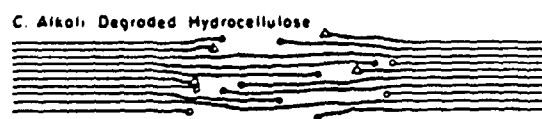
AQ-PROMOTED CHAIN CLEAVAGE



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

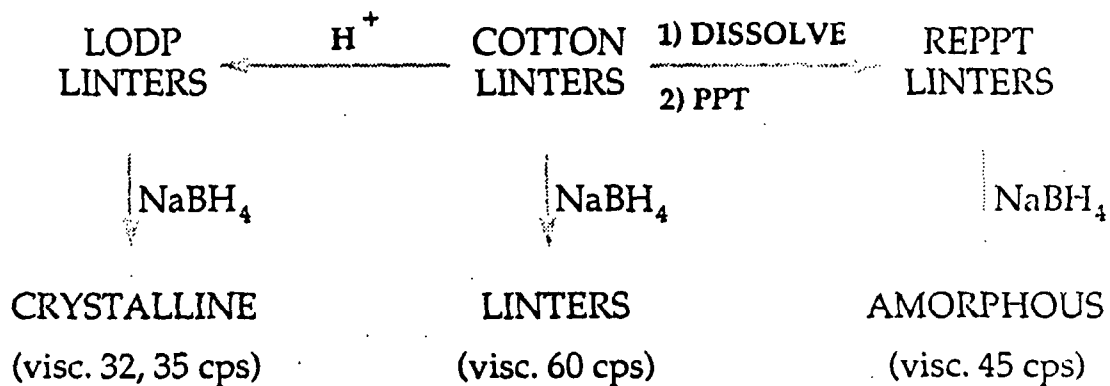
PHYSICAL EFFECTS IN CARBOHYDRATE REACTIONS



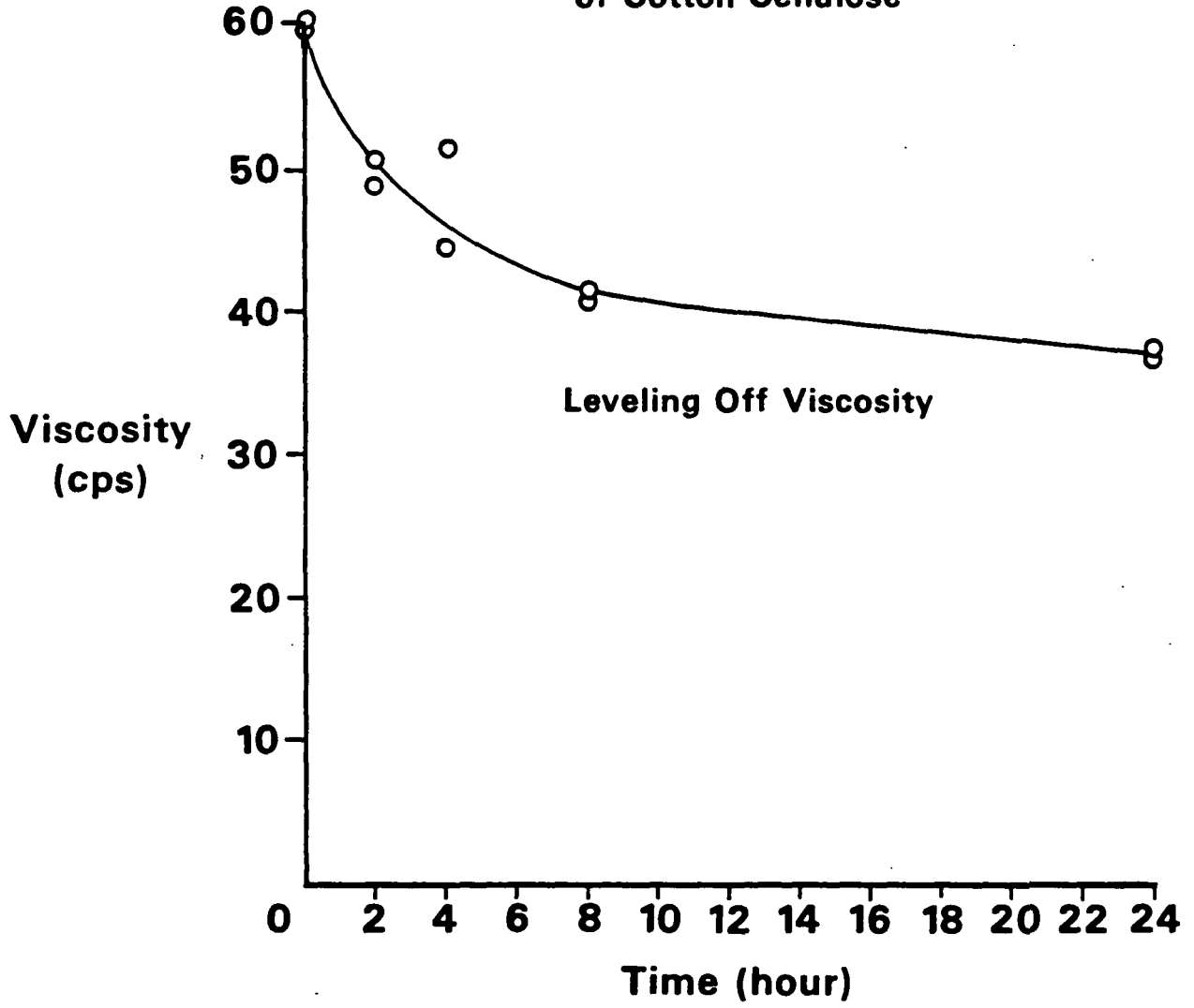
- Nonreducing end group
- Reducing end group
- △ Methylsaccharinic acid end group

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

Cellulose Sample Preparations



**Mild Acid Treatment (0.25N HCl/Room Temperature)
of Cotton Cellulose**

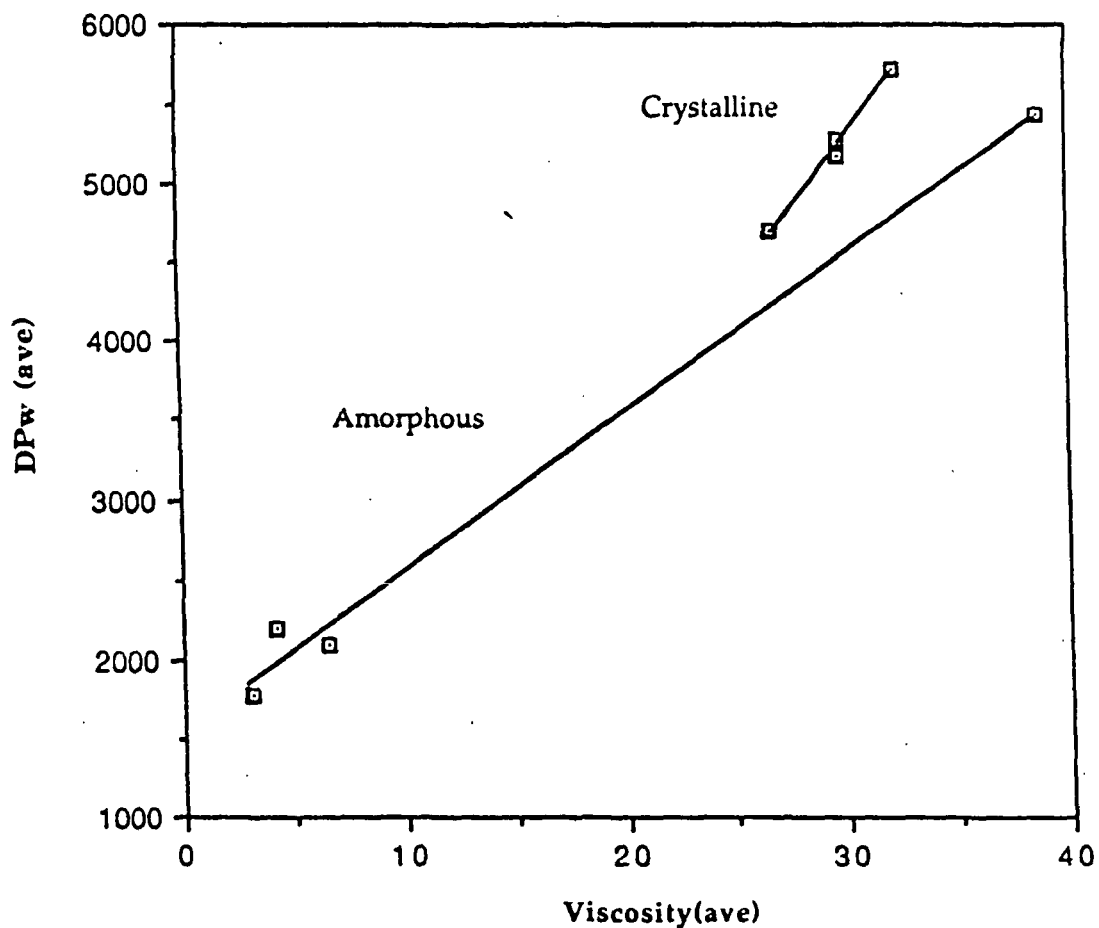


Estimating Chain Cleavage

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

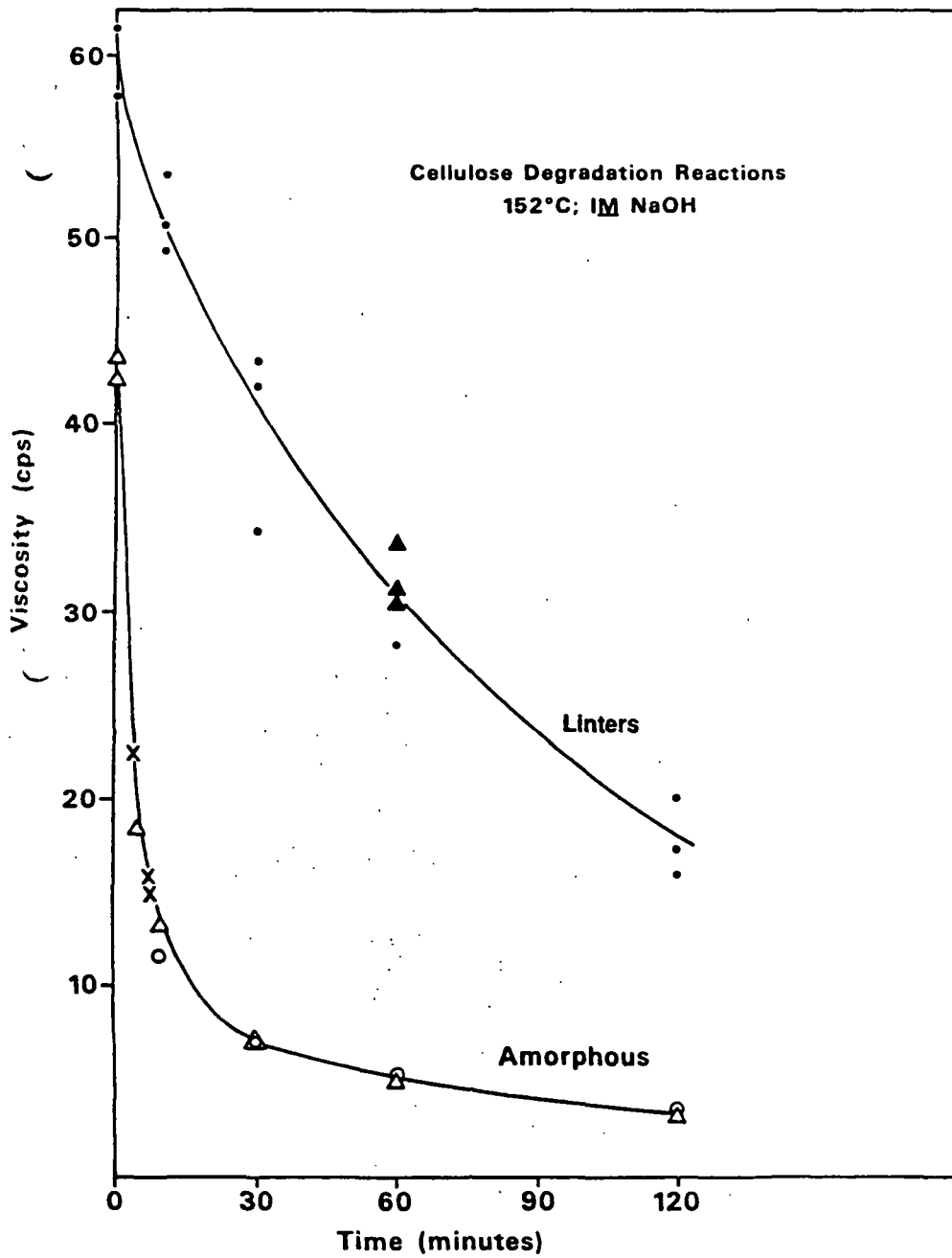
Correlation of DPw and Viscosity

Cellulose Samples in The Presence of Oxygen/Alkali/Cobalt

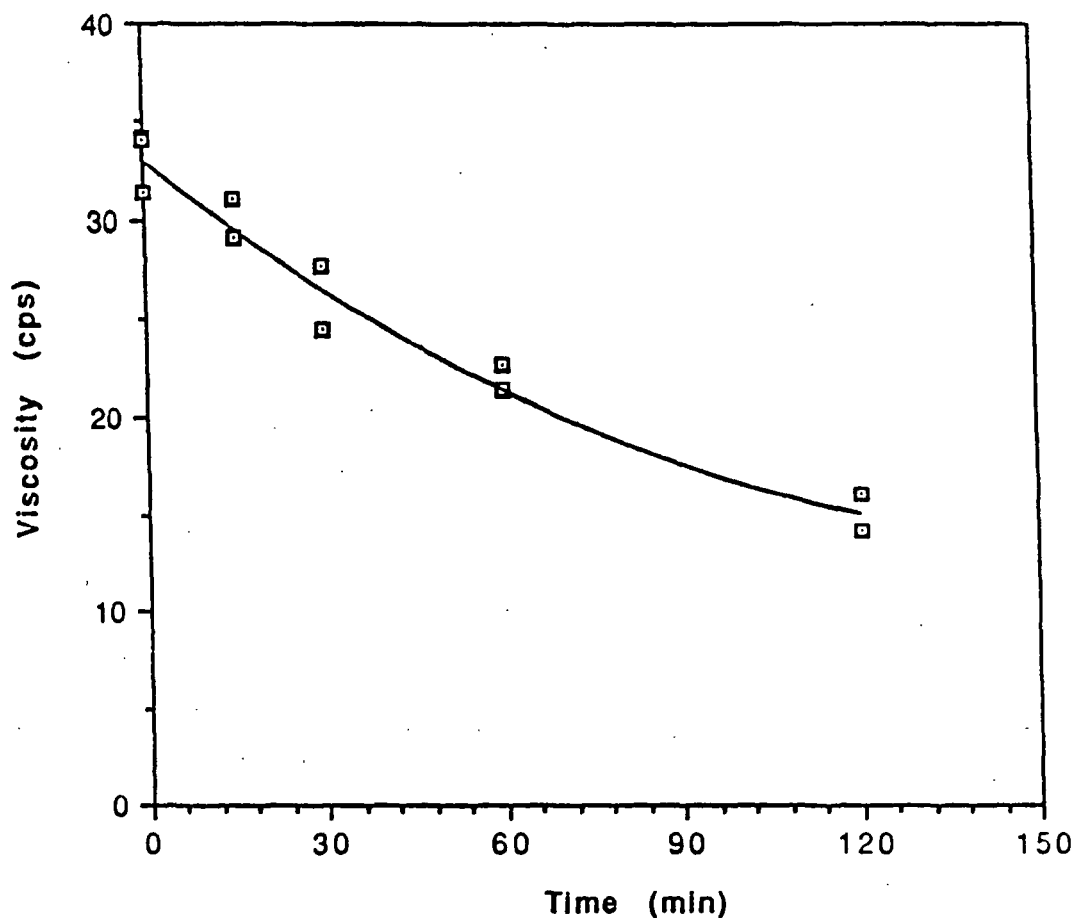


AMORPHOUS vs. CRYSTALLINE CELLULOSE REACTIONS

- PULPING
 - SODA
 - SODA/AQ
- BLEACHING
 - OXYGEN-ALKALI
 - PEROXIDE



Crystalline (LODP-NaBH₄) Cellulose Degradation Reactions
150°C; 1M NaOH



Cellulose viscosities (cps) after heating in 1M NaOH.

Crystalline, ^a 148°C, 60 minutes		Amorphous, ^a 135°C, 10 minutes	
No AQ	AQ ^b	No AQ	AQ ^b
27.5 (27.1-28.0) ^c	29.3 (28.2-30.5) ^c	16.2 (14.0-18.0) ^c	14.6 (13.9-15.5) ^c
35.8 (32.5-38.4) ^d	32.4 (31.3-33.4) ^d	24.9 (21.7-26.8) ^d	22.1 (18.0-24.1) ^d

^aThe two samples had different starting viscosities.

^bOne equiv./glucose equivalent.

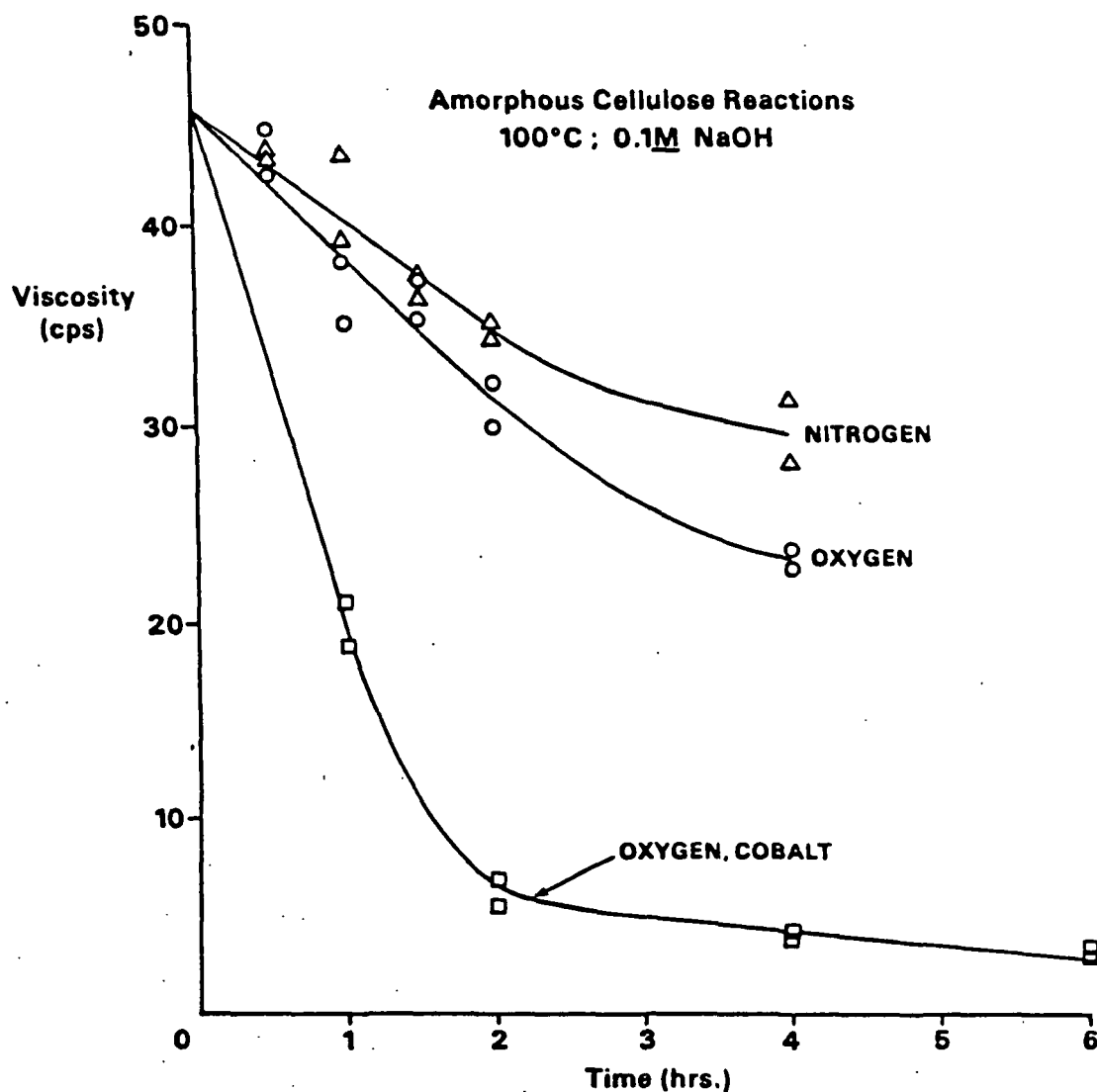
^cTriplicate average (range).

^dSix sample average (range).

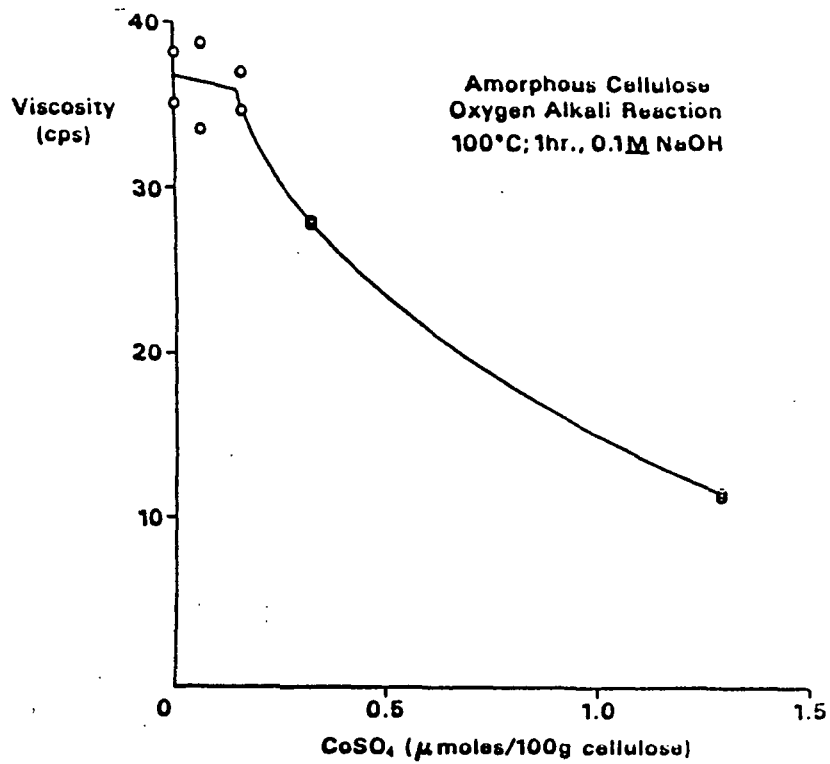
AQ Chain Cleavage Effects

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

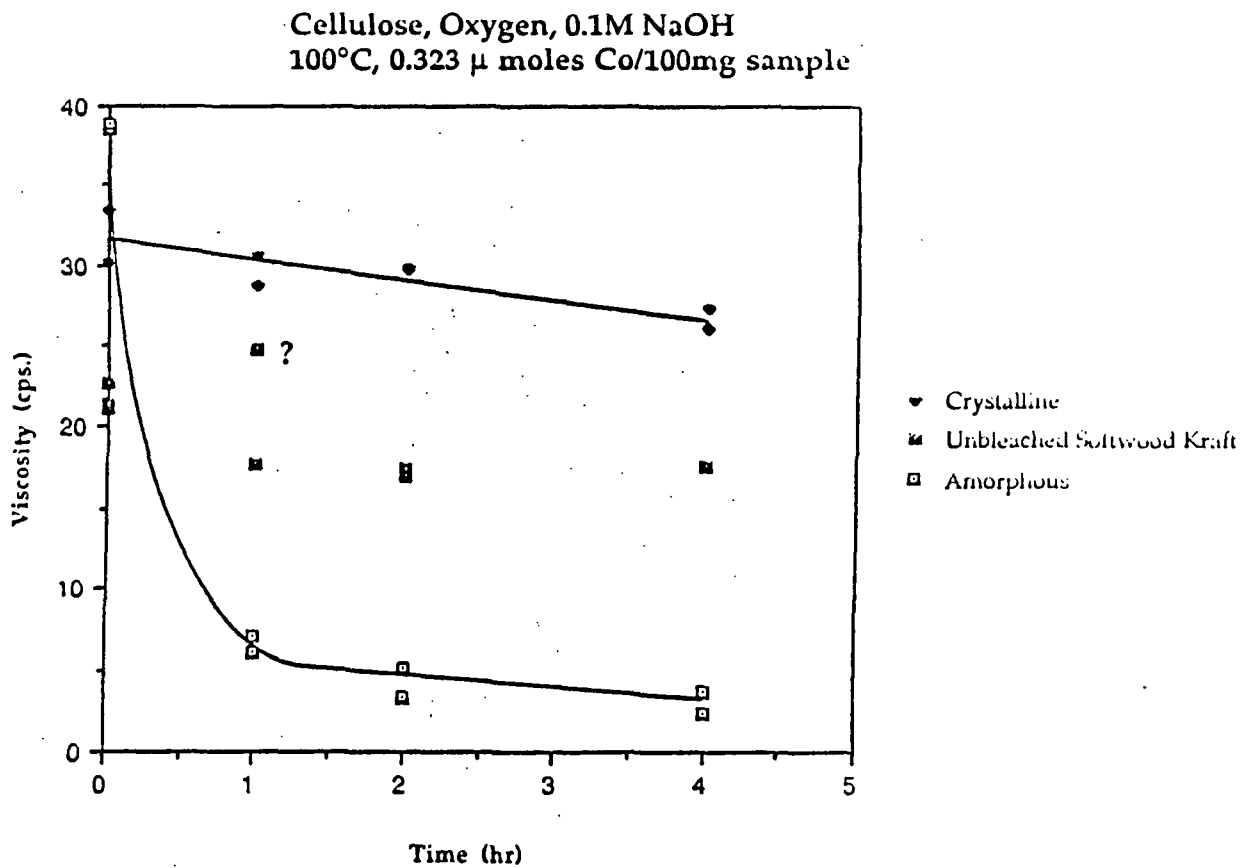
Low tear strength of AQ pulps probably reflects greater Hemicellulose content more than shorter Cellulose fiber length.



Variations in amorphous cellulose viscosities as a function of time following treatment at 100°C in 0.1M NaOH with the indicated chemicals.

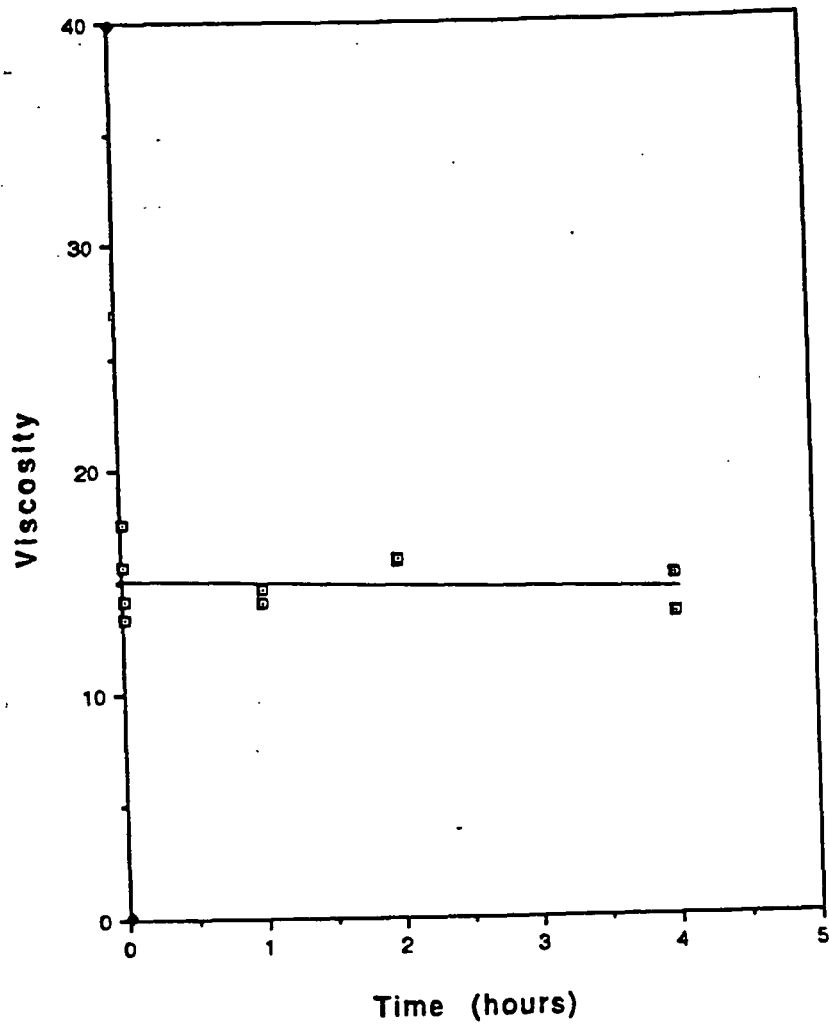


Variations in amorphous cellulose viscosities with different levels of cobalt for samples heated at 100°C for 1 hr in 0.1M NaOH; duplicates were done at each cobalt level.

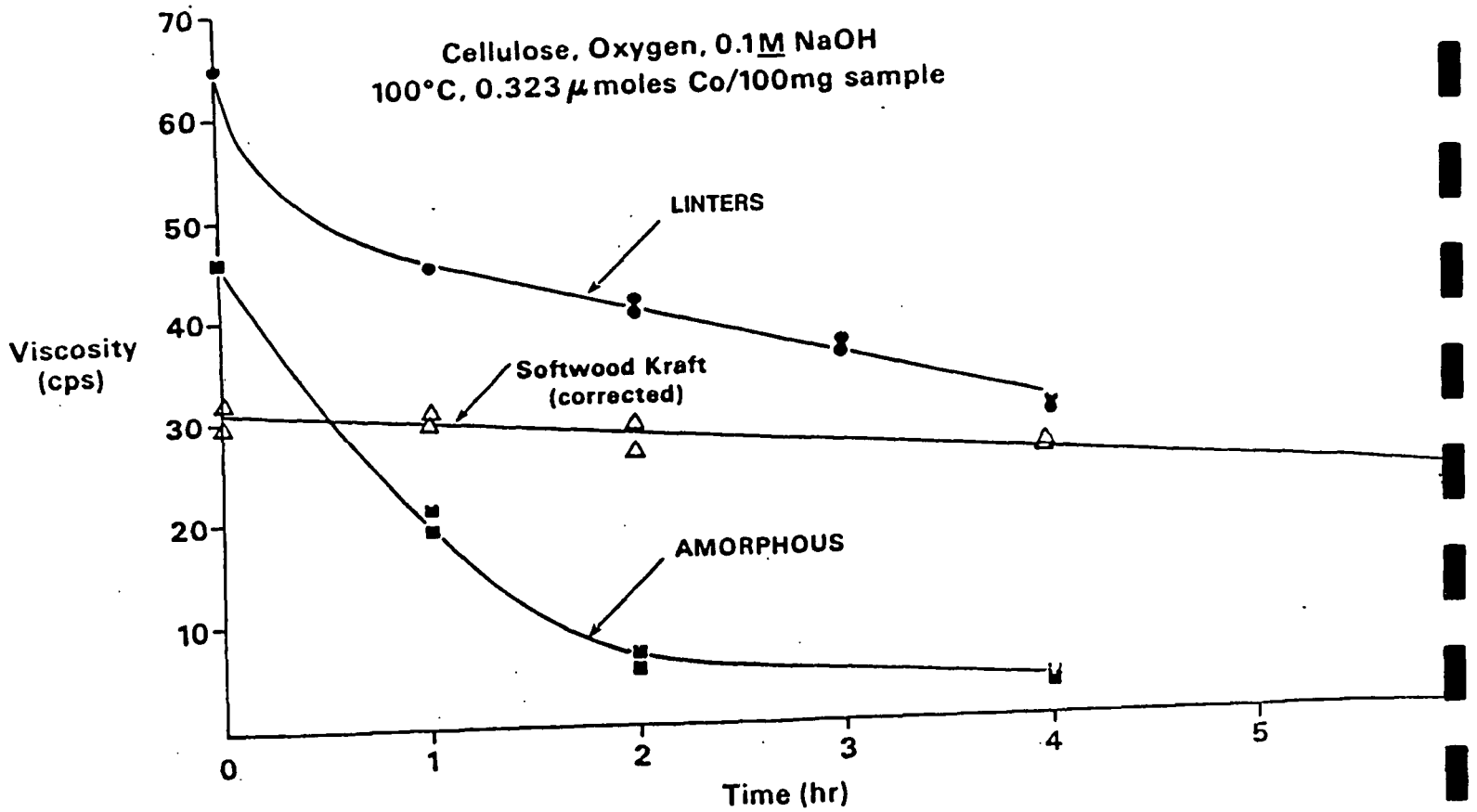


Viscosity vs. Time

Oxygen Alkali Cook of Unbleached Kraft Pulp (w/ Cobalt)

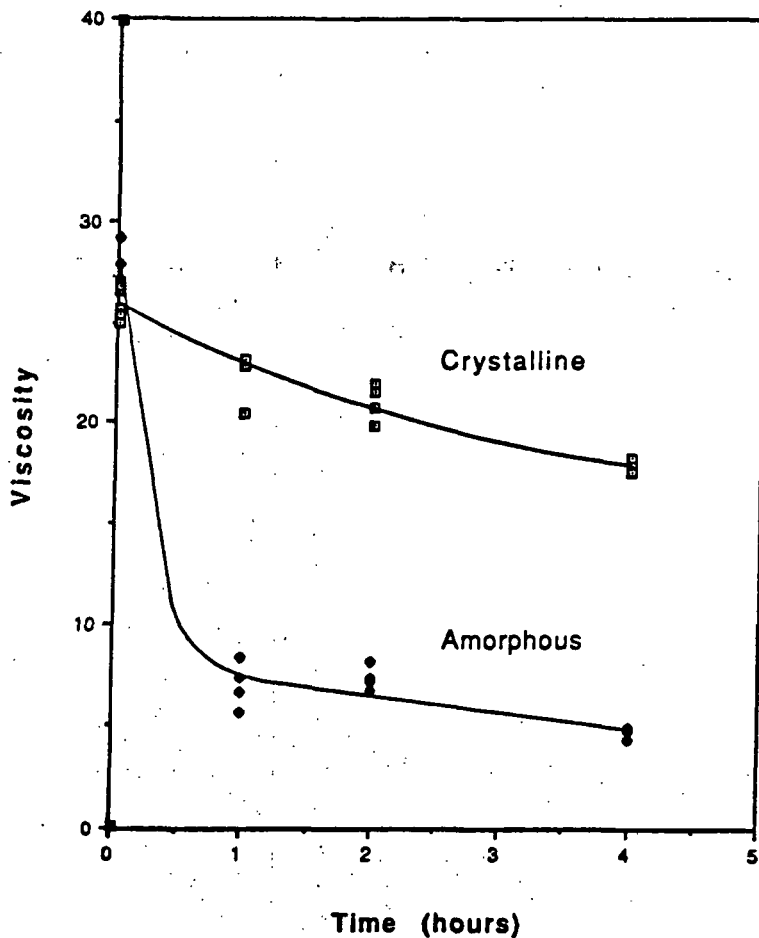


Cellulose, Oxygen, 0.1M NaOH
100°C, 0.323 μ moles Co/100mg sample



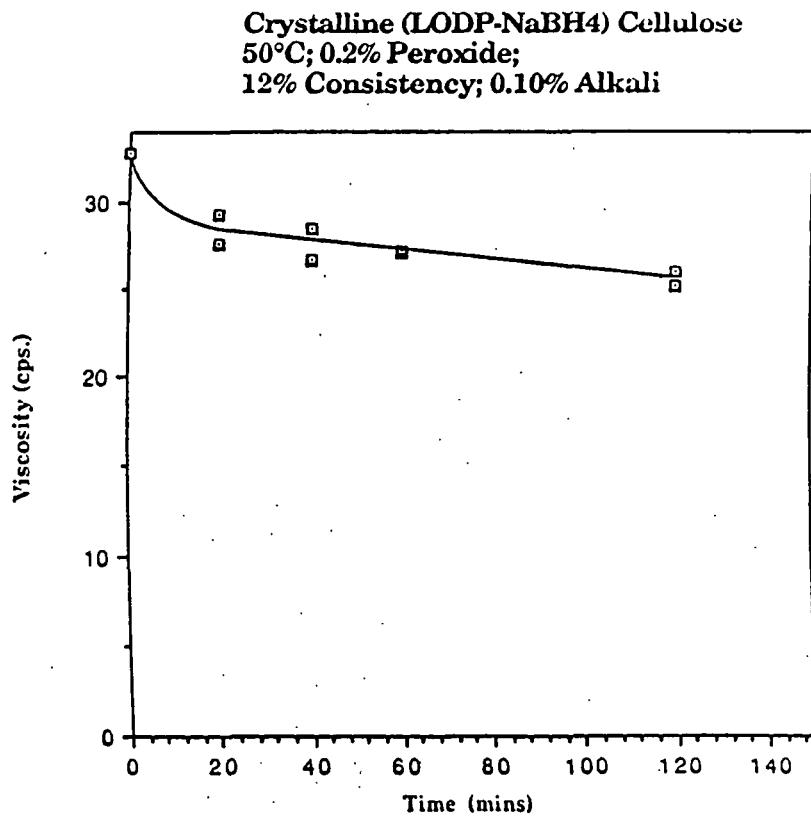
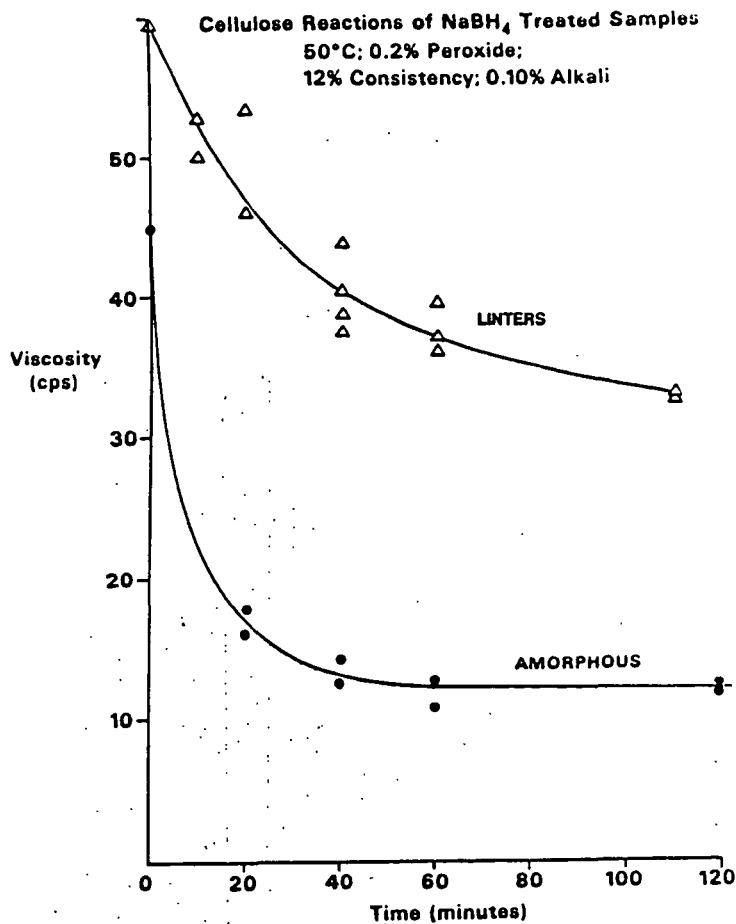
Viscosity vs. Time

Oxygen Alkali Cook (w/ Cobalt)



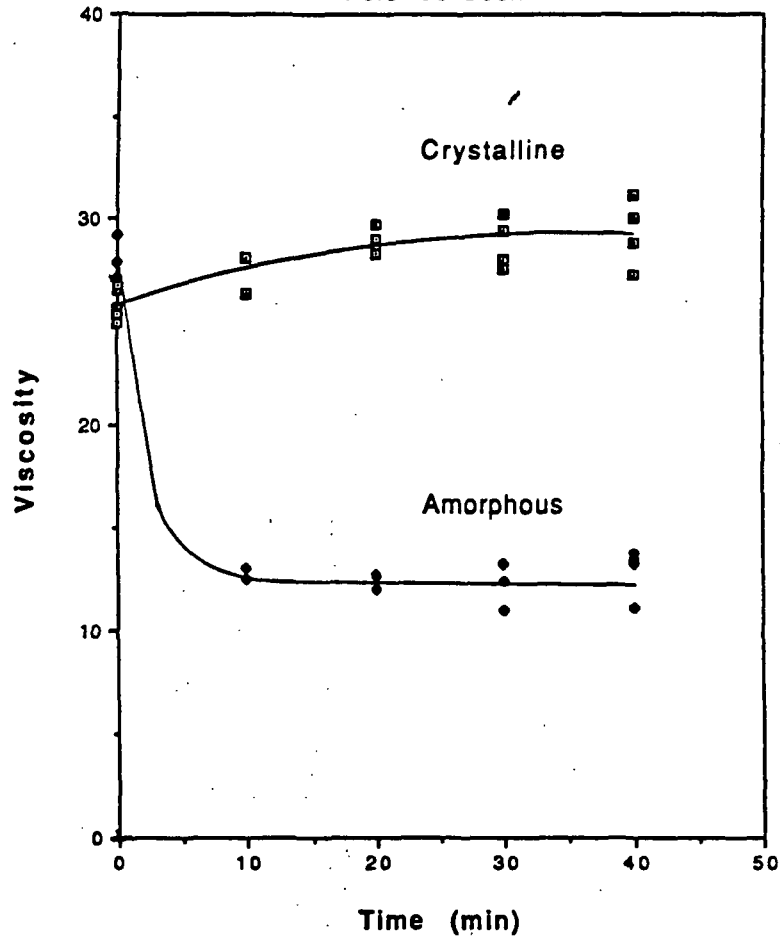
Viscosity values after heating amorphous cellulose at 60°C for 1 hour at 12% consistency with different levels of peroxide and metal salts.

Peroxide (%)	Alkali (%)	Additives	Viscosity (cps) - Duplicates
--	0.033	--	44.5, 43.2
0.2	0.10	--	12.3, 10.7
0.4	0.15	--	7.1, 7.8
1.0	0.39	--	4.4, 4.5
0.4	0.14	0.37 μ M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	13.8, 10.1
0.4	0.13	0.2% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	39.8, 35.1
		4.5% Na_2SiO_3	



Viscosity vs. Time

Peroxide Cook



Summary

- Physical Effects Have Pronounced Effects on Reactivity:

Soluble > Amorphous > Crystalline

- Amorphous Cellulose Reactions Are Sensitive Indicators of Pulp Degradation Reactions

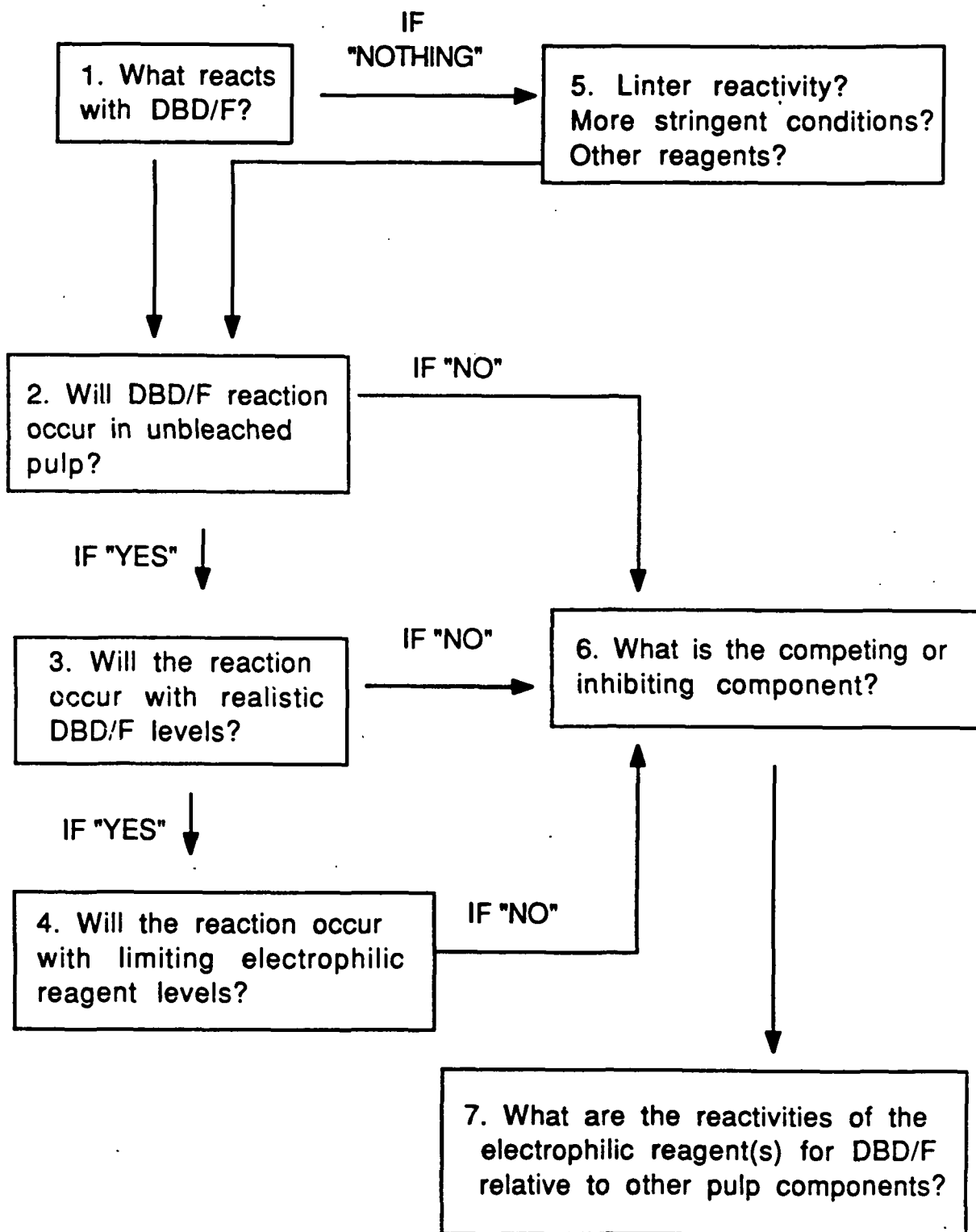
PROJECT 3475 FUTURE ACTIVITIES

- **ORGANIZE AND PUBLISH PAST RESEARCH**
- **AMORPHOUS REACTIONS WITH**
 - OZONE**
 - Cl₂O**
 - O₂/ALKALI AND SELECTED METALS AND SALTS**
(DEAD LOAD EFFECTS)
 - CHANGES IN PROCESS VARIABLES**
- **MOL. WEIGHT DISTRIBUTIONS FOR CELLULOSE RXS**

Electrophilic Reagents

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

CHART 1



Significance

- Determination of DBD/F reactivities will
 - promote understanding of the chemistry of the formation of chlorinated dioxins and furans during bleaching.
 - elucidate potential methods of destruction of precursors.
 - allow development of rational, scientific methods for eliminating chlorinated dioxins and furans in bleached pulp.

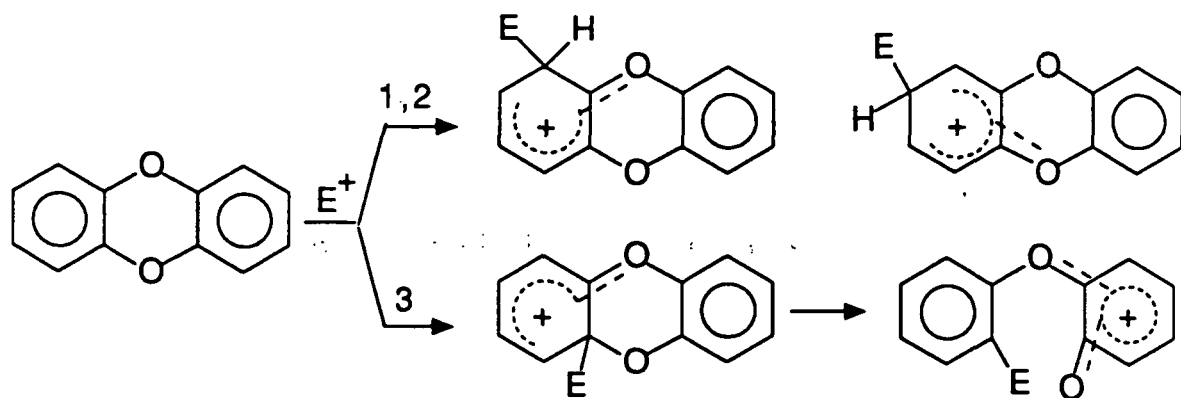
PROJECT 3684

PART I

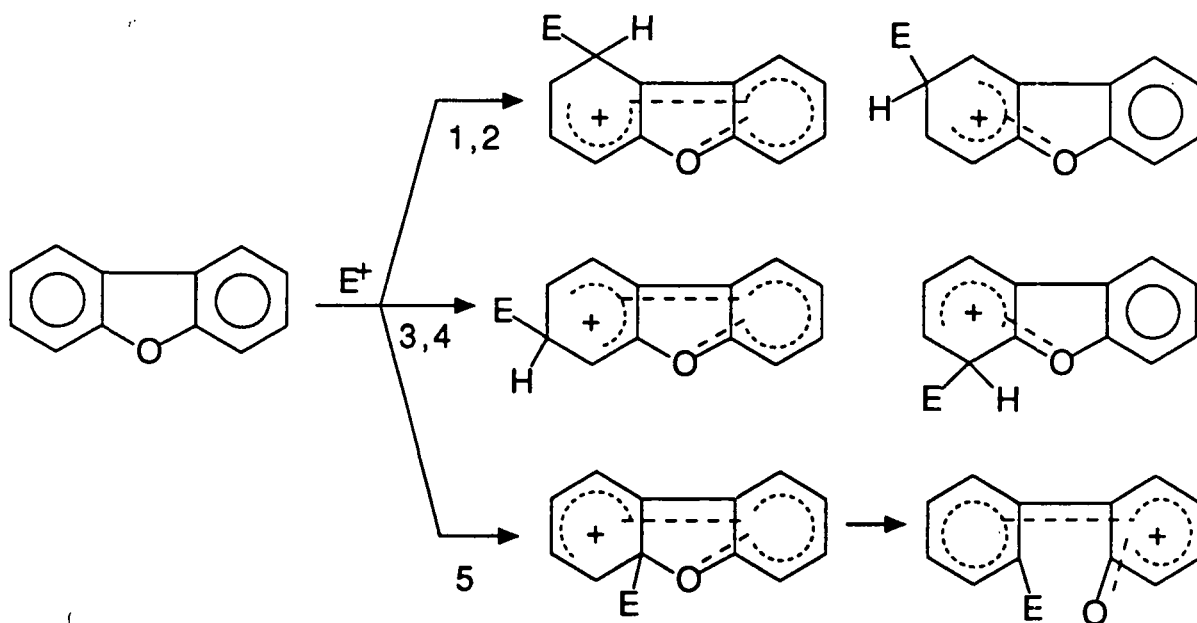
OBJECTIVES

1. Find reagents which will selectively react with precursors in pulp.
2. Determine which wood component(s) are responsible for precursors.

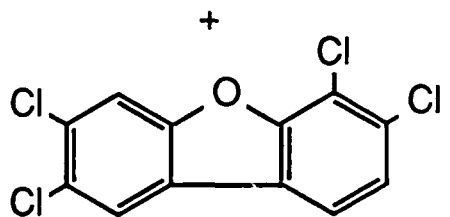
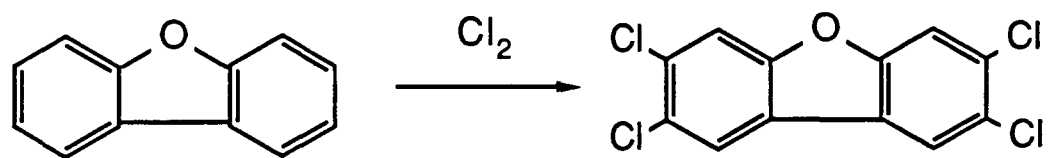
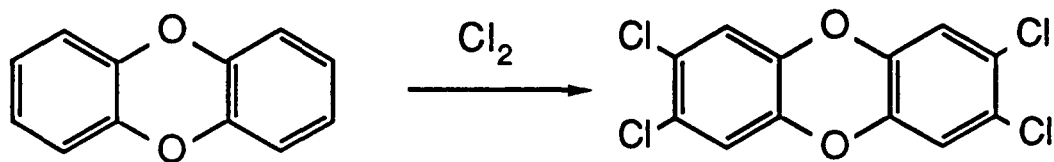
Electrophile Addition to DBD

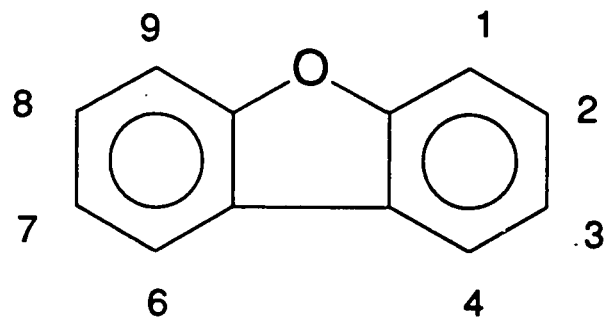


Electrophile Addition to DBF

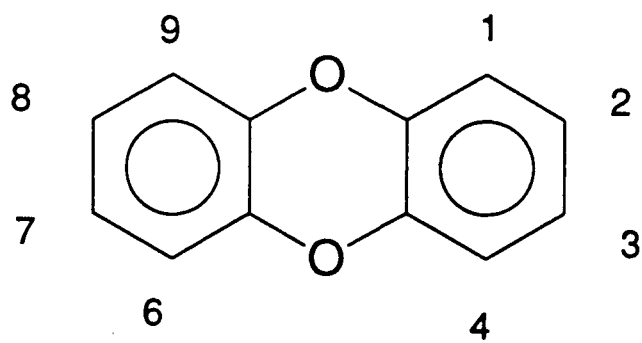


Chlorinated Dioxin and Furan Formation





DIBENZOFURAN



DIBENZODIOXIN

Project 3684

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

Lucinda B. Sonnenberg

Sponsored by API / NCASI

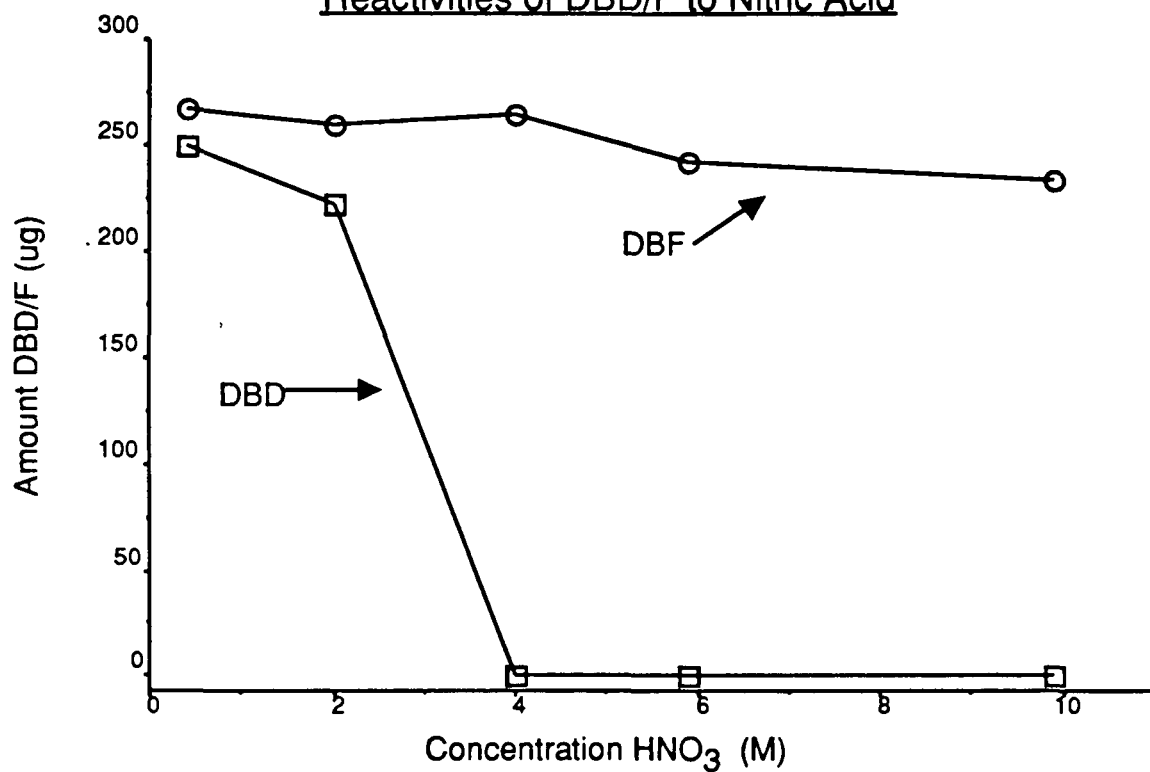
Methods

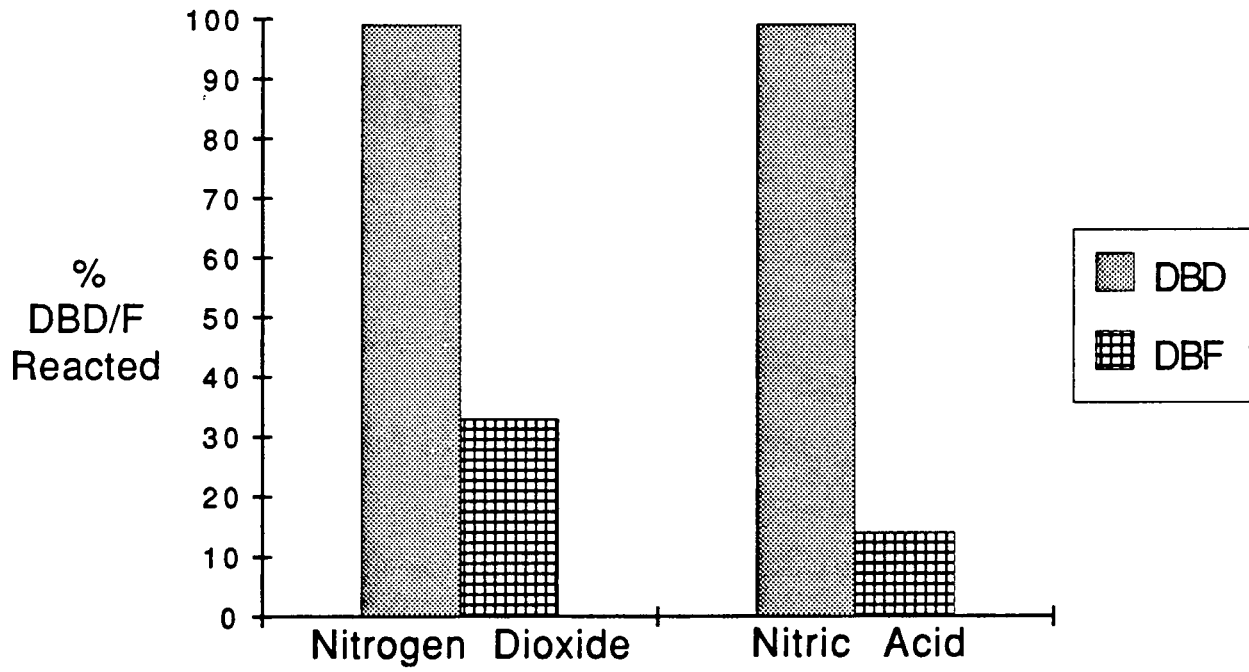
- DBD/F Reactions with Electrophilic Reagents
 - spiked cotton linters
 - ppm levels of DBD/F
 - excess reagent
- Sample Preparation
 - soxhlet extract linters
 - liquid-liquid extract aqueous solutions
 - rotoevaporate extracts
- Analyses
 - GC/FID quantitation
 - GC/MS identification of major products

Reactions of DBD/F with NO₂

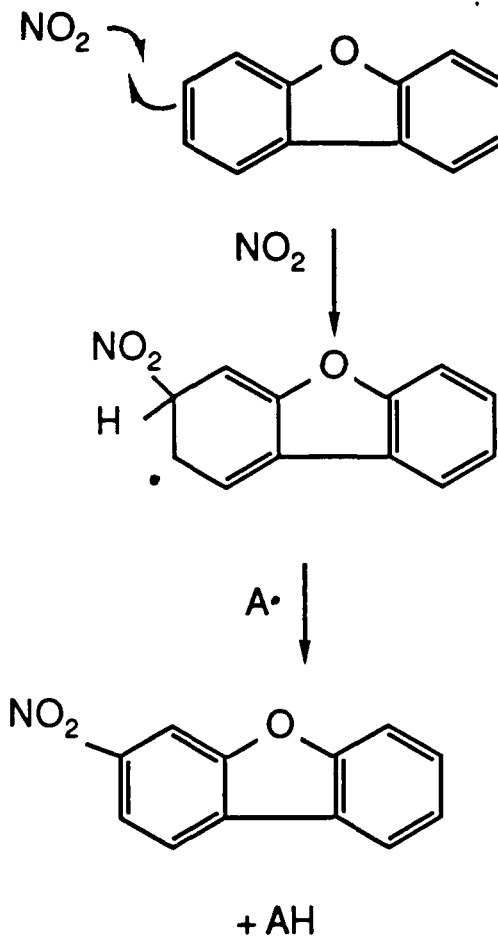
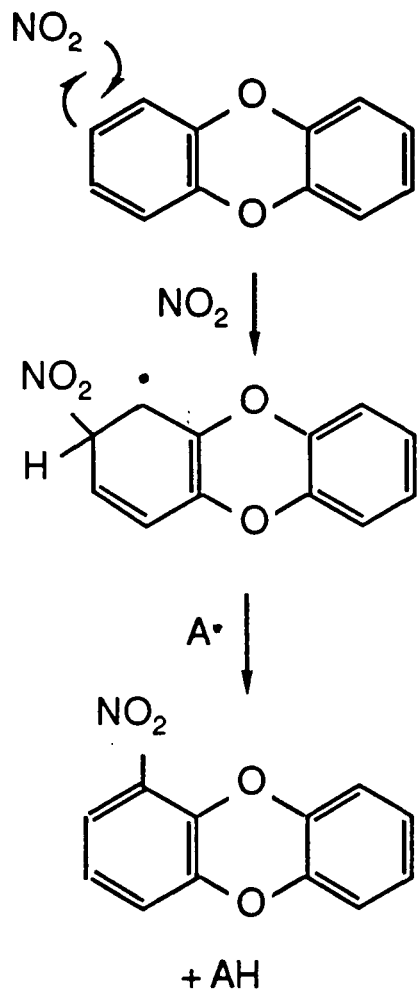
	DBD/F Remaining (umole)	% Reacted
10 minutes		
DBD	≤0.02	≥99
DBF	1.5	33
40 minutes		
DBD	≤0.02	≥99
DBF	1.9	13-47

Reactivities of DBD/F to Nitric Acid

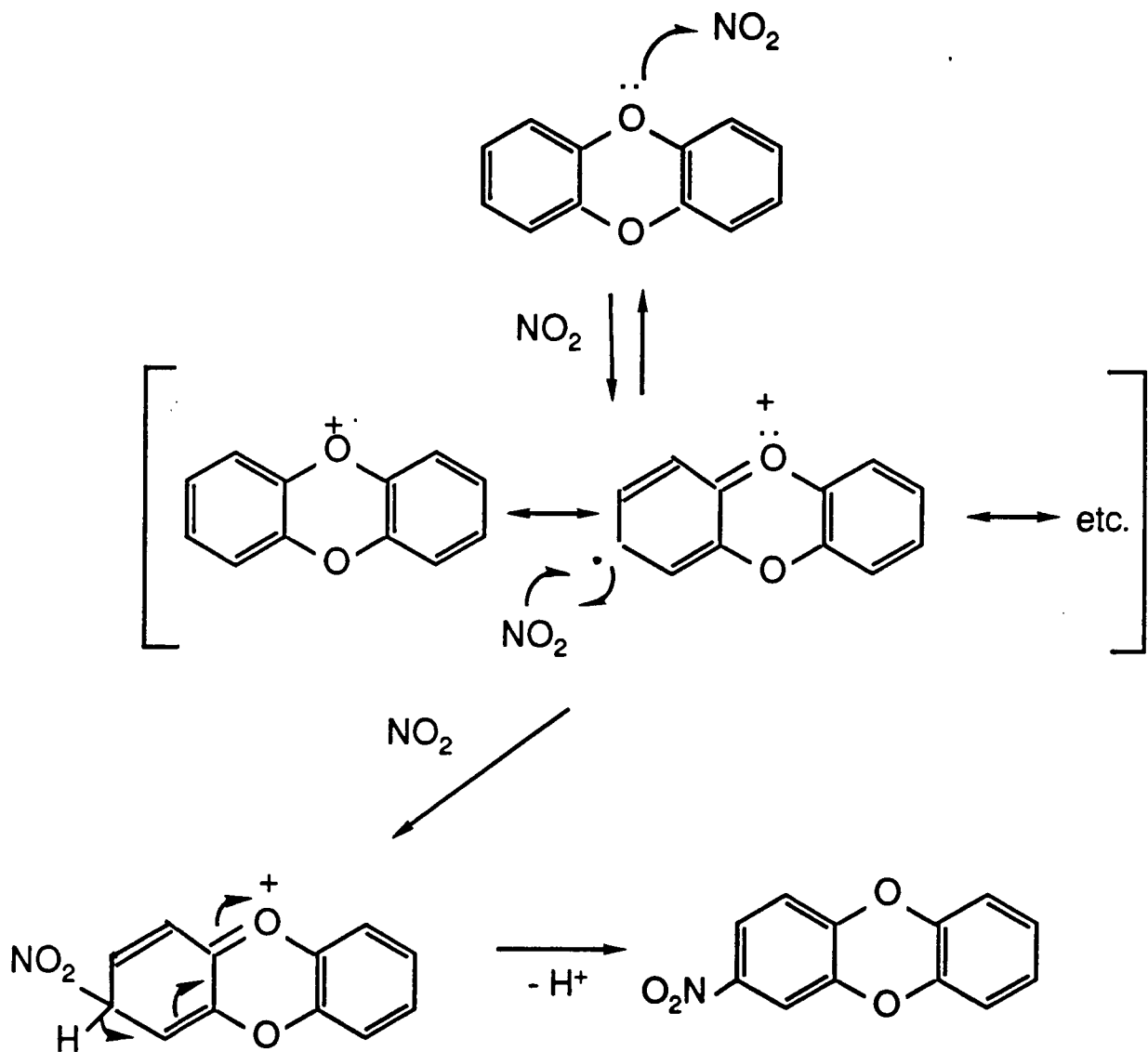




Possible Mechanism of Nitration of DBD/F
with Nitrogen Dioxide



Possible Mechanisms of DBD Nitration with NO_2



Conclusions

- NO_2 and HNO_3 effectively react with DBD
- NO_2 and HNO_3 do not effectively react with DBF
- NO_2 and HNO_3 are similar in their reactivities toward DBD/F

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

PROJECT 3685 BUDGET

	<u>Dollars</u>
Dr. Donald Dimmel, Project coordinator	\$20,000
IPST personnel	5,000
Equipment and Supplies	10,000
Travel	8,000
Battelle	137,000
	<hr/>
TOTAL	\$180,000

PROJECT 3685 TIME SCHEDULE

SIGNED CONTRACTS	MID-MARCH 1990
PROJECT START UP	APRIL 1, 1990
COMPLETION OF LAB WORK	FEBRUARY 1, 1991
WRITTEN REPORT	APRIL 1, 1991

PULPING AND BLEACHING GROUP

**PEOPLE
FUNCTION
CURRENT ACTIVITIES**

PULPING AND BLEACHING GROUP

STAFF

Group Leader	Tom McDonough
Senior Research Scientist	Alan Rudie
Senior Associate Scientist	Charles Courchene
Assistant Scientist	Clark Woitkovich
Senior Technician	Amy Malcolm
Technicians	Randy Cordle Jim Kramer Elizabeth Martin Tanya Kubicar* Jon McCabe*

*Ga Tech Co-op Students

PULPING AND BLEACHING GROUP

STUDENTS

Barbara Burns (Ph.D., TJM)
Deborah Mallat (M.S., TJM)
Mike Rice (M.S., AWR)
Laura Thompson (M.S., EWM)
Rick Waren (M.S., EWM)

PULPING AND BLEACHING GROUP

FUNCTIONS

**IPST Funded Projects
Group Funded Projects
Contract Projects
Routine Testing
Student Research
Service, Internal and External**

PULPING AND BLEACHING GROUP

RECENT ACTIVITIES

Reestablishing Laboratory Facilities

Recruiting and Training

Project 3664: API/NCASI Funded Dioxins Research

Project 3474: Environmentally Compatible Production

CTMP Pilot Plant Startup

Project 3662: Process Effects on AOX, Dioxins (Contract)

Project 3675: Process Effects on AOX, Dioxins (Contract)

Contract Research Proposals:

CTMP Pulping and Bleaching

Evaluation of Conductivity Sensors

Evaluation of Pulping Additives

Repulpability Study

Collaborative Proposal with GT on AOX Biodegradability

Student Research

Teaching (2 1/2 Courses)

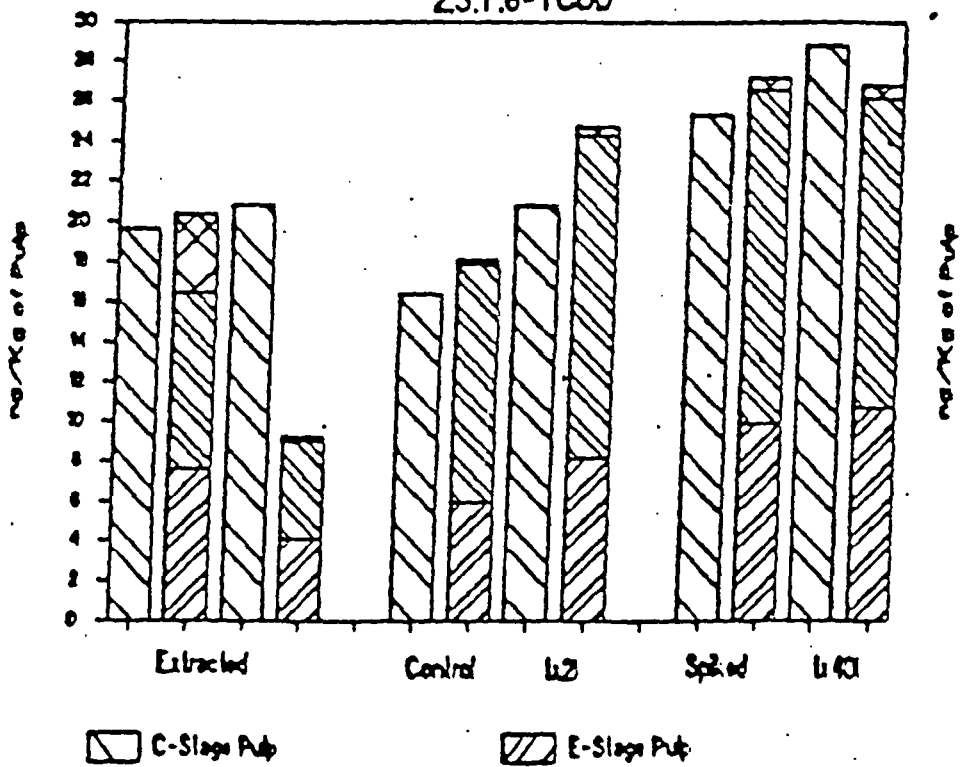
PROJECT 3664

PRECURSORS AND VARIABLES IN DIOXINS FORMATION

(API/NCASI FUNDED)

- (1) PRECURSOR SOURCE
- (2) PRECURSOR SIGNIFICANCE
- (3) PRECURSOR DESTRUCTION BY CLO₂
- (4) EFFECTS OF C-STAGE VARIABLES

2,3,7,8-TCDD



2.3.7.8-TCDF

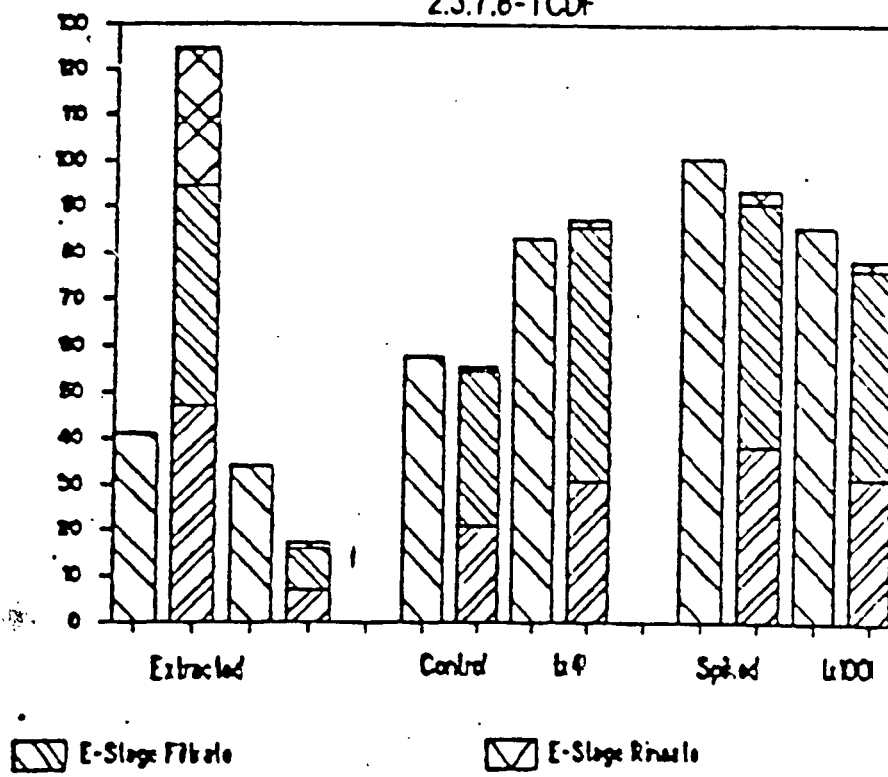


Table 1. Summary of Brownstock and C Stage Pulp Analysis Results

<u>Sample</u>	Concentration (ng/kg)				
	<u>DBD in</u> <u>Brownstock</u>	<u>2378-</u> <u>TCDD</u>	<u>DBF in</u> <u>Brownstock</u>	<u>2378-</u> <u>TCDF</u>	<u>1278-</u> <u>TCDF</u>
Extracted Brownstock	ND (0.6) ND (0.6)	19.7 20.8	49 NQ (26)	41.2 33.9	26.1 20.8
Control Brownstock	34.0	32.8 41.5	2030	231 333	113 162
Spiked Brownstock	1740 1750	1011 1150	61700 60100	10000 8540	4570 4080

TABLE 1 THREE STAGE CHLORINATION DATA

Chemical Charges as Multiples of Unbleached Kappa Number			Total Cl ₂	Total Active Cl	Concentration (ppt)		
Stg 1 (Cl ₂)	Stg 2 (ClO ₂)*	Stg 3 (Cl ₂)			2378- TCDD	2378- TCDF	1278- TCDF
0.12	0.08	0.00	0.12	0.20	ND (0.3)	0.6	0.5
0.12	0.08	0.06	0.18	0.26	0.6	3.1	2.9
0.12	0.08	0.08	0.20	0.28	13.9	50.3	24.6
0.12	0.08	0.12	0.24	0.32	21.3	105.5	49.9
0.12	0.08	0.16	0.28	0.36	40.4	331.9	152.2
0.12	0.00	0.00	0.12	0.12	ND (0.3)	1.7	1.5
0.12	0.00	0.06	0.18	0.18	0.8	3.5	2.8
0.12	0.00	0.08	0.20	0.20	1	8.7	6.8
0.12	0.00	0.12	0.24	0.24	10.1	30.3	14.5
0.12	0.00	0.16	0.28	0.28	15.1	64.2	28.0
0.25	0.00	0.00	0.25	0.25	32.8	231.4	112.7
0.25	0.00	0.00	0.25	0.25	41.5	333.3	161.5

*As active chlorine

Chemical Charges as Multiples
of Unbleached Kappa Number

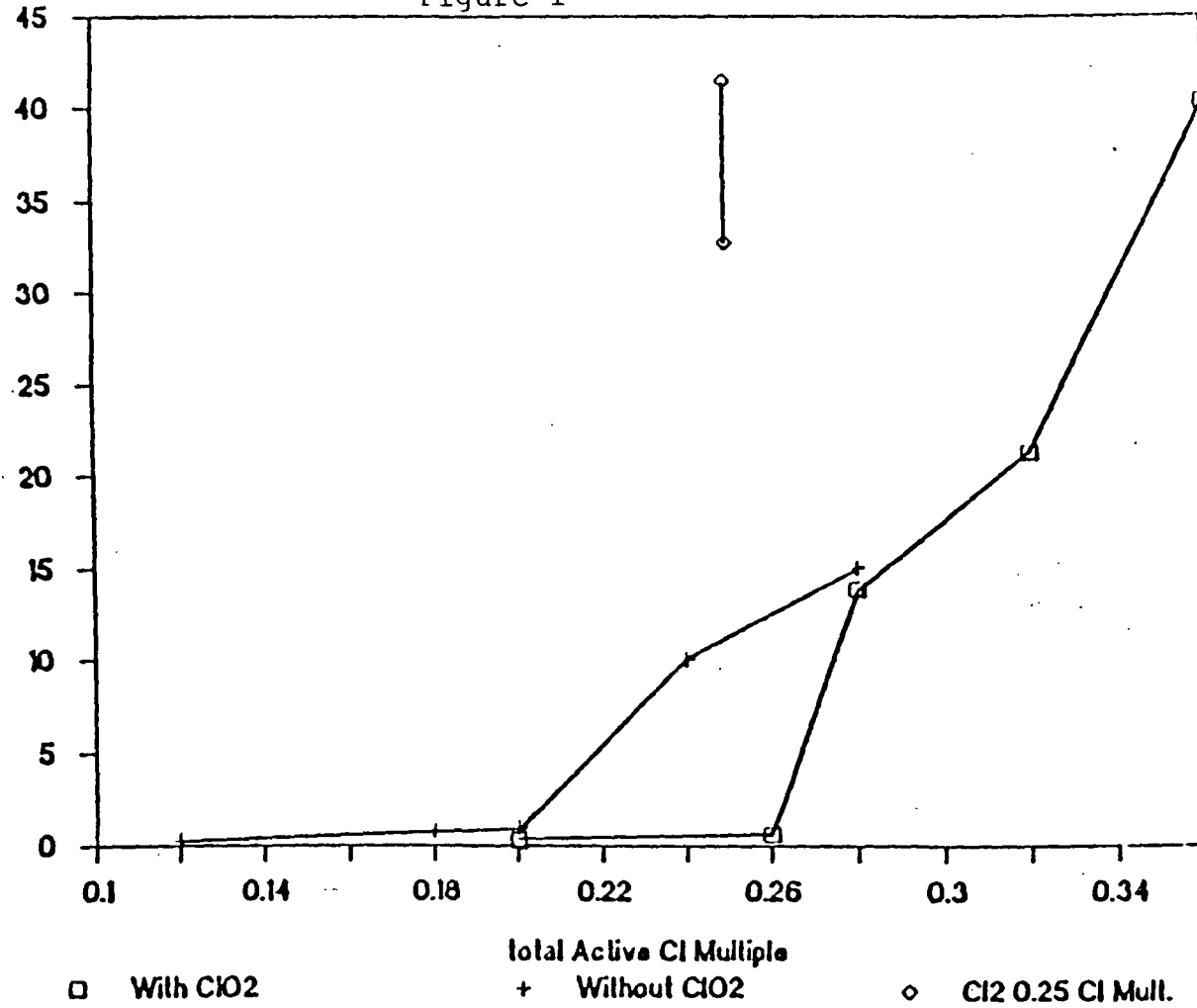
<u>Stg 1</u> <u>(Cl₂)</u>	<u>Stg 2</u> <u>(ClO₂)*</u>	<u>Stg 3</u> <u>(Cl₂)</u>	<u>Total</u> <u>Cl₂</u>
0.12	0.08	0.00	0.12
0.12	0.08	0.06	0.18
0.12	0.08	0.08	0.20
0.12	0.08	0.12	0.24
0.12	0.08	0.16	0.28
0.12	0.00	0.00	0.12
0.12	0.00	0.06	0.18
0.12	0.00	0.08	0.20
0.12	0.00	0.12	0.24
0.12	0.00	0.16	0.28
0.25	0.00	0.00	0.25
0.25	0.00	0.00	0.25

*As active chlorine

2378-TCDD vs Total Active Cl Multiple

Figure 1

2378-TCDD (ng/kg)



2378-TCDD Production vs Total Chlorine

Figure 2

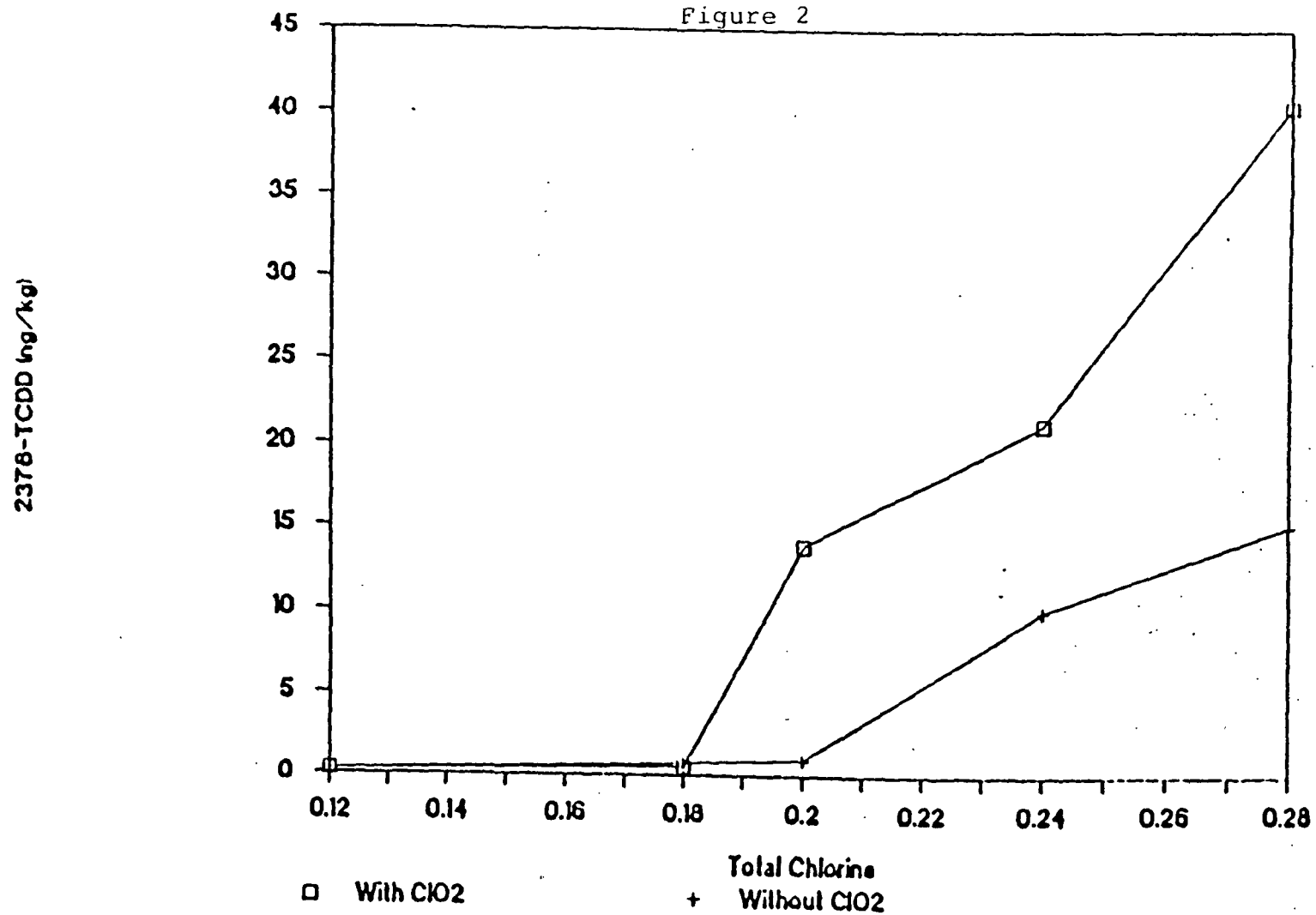


TABLE 2 CHLORINATION STAGE VARIABLES AND LEVELS

VAR LEVL COMB	CLO ₂ SEC AFTR Cl ₂	TEMP DEG C	C-ST FILT RCYC %	OXGN DLIG %	WASH LOSS L/KG
1	-15	30	0	0	6
2	15	30	0	0	0
3	-15	60	0	0	0
4	15	60	0	0	6
5	-15	30	30	0	0
6	15	30	30	0	6
7	-15	60	30	0	6
8	15	60	30	0	0
9	-15	30	0	50	0
10	15	30	0	50	6
11	-15	60	0	50	6
12	15	60	0	50	0
13	-15	30	30	50	6
14	15	30	30	50	0
15	-15	60	30	50	0
16	15	60	30	50	6

CE KAPPA NUMBER

$$\text{CE KAPPA} = 3.8 + 0.3(\text{XD}) + 0.2(\text{XT}) - 0.7(\text{XO}) + 0.2(\text{XL})$$

in which:

XD = -1 when ClO₂ is added 15 sec before Cl₂,
+1 " " " " " " " after " ;

XT = -1 when chlorination is done at 30 deg. C,
+1 " " " " " " " 60 " " ;

XO = -1 when none of the lignin is removed by oxygen before C,
+1 " 40% " " " " " " " " " " ;

XL = -1 when wash loss is 0 L/kg dry pulp.
+1 " " " " 6 " " " " ;

CE KAPPA NUMBER

$$CE \text{ KAPPA} = 3.8 + 0.3(XD) + 0.2(XT) - 0.7(XO) + 0.2(XL)$$

in which:

XD = -1 when CLO₂ is added 15 sec before Cl₂,
+1 " " " " " " " after ";

XT = -1 when chlorination is done at 30 deg. C,
+1 " " " " " " " 60 " ";

PROJECT 3664
CHLORINATION VARIABLES STUDY

CE KAPPA NUMBER

	<u>XT = XR = 0</u>	<u>XT = XL = +1</u>
XD	XO=-1 XO=+1	XO=-1 XO=+1
-1	3.9 2.5	4.6 3.2
+1	4.4 3.0	5.2 3.8

PROJECT 3664
 CHLORINATION VARIABLES STUDY

PRELIMINARY AOX ANALYSIS

$$\text{AOX, kg/T} = 4.2 + 0.4(\text{XR}) - 0.2(\text{XT}) - 1.1(\text{XO}) + 0.2(\text{XL}) \\
 + 0.2(\text{XR})(\text{XT}) - 0.3(\text{XO})(\text{XL})$$

in which:

XR = -1 when none of the C-stage filtrate is recycled,
 +1 " 30% " " " " " " " " ;

XT = -1 when chlorination is done at 30 deg. C,
 +1 " " " " " " 60 " " ;

XO = -1 when none of the lignin is removed by oxygen before C,
 +1 " 40% " " " " " " " " " " ;

XL = -1 when wash loss is 0 L/kg dry pulp,
 = +1 " " " " 6 " " " ;

**PROJECT 3664
CHLORINATION VARIABLES STUDY**

PRELIMINARY AOX ANALYSIS

$$\text{AOX, kg/T} = 4.2 + 0.4(\text{XR}) - 0.2(\text{XT}) - 1.1(\text{XO}) + 0.2(\text{XL}) \\ + 0.2(\text{XR})(\text{XT}) - 0.3(\text{XO})(\text{XL})$$

PROJECT 3664

CHLORINATION VARIABLES STUDY

PRELIMINARY AOX ANALYSIS

TOTAL AOX, kg/T

XO	XT = XR = 0		XR	XO=-1; XL=+1	
	XL=1	XL=+1		XT=-1	XT=+1
-1	4.8	5.8	-1	5.8	5.0
+1	3.2	3.0	+1	6.2	6.2

PROJECT 3664

CHLORINATION VARIABLES STUDY

PRELIMINARY AOX ANALYSIS

TOTAL AOX, kg/T

XO --	XT = XR = 0 -----			XO=-1; XL=+1 -----	
	XL=-1 -----	XL=+1 -----	XR --	XT=-1 -----	XT=+1 -----
-1	4.8	5.8	-1	5.8	5.0
+1	3.2	3.0	+1	6.2	6.2

CONCLUSIONS

- . Precursors other than DBD, DBF
- . DBD, DBF Also potentially Important
- . TCDD/F: Formed in C-Stage
 Stay with C-Pulp
 Survive Normal E-Stage
 Divide Between E-Pulp, E-Filtrate
- . ClO₂ does not readily destroy precursors
- . CE Kappa increased by delaying ClO₂
- . AOX decreased by O₂ ESP. when black liquor carryover is high
- . AOX decreased by opening C-stage ESP. when C-stage temp. is high

PROJECT 3474

ENVIRONMENTALLY COMPATIBLE

PRODUCTION OF BLEACHED PULP

PROJECT 3474

OBJECTIVE

DECREASE OR ELIMINATE THE NEED FOR CHLORINE IN BLEACHING

Table 1 Reactivity of vanillyl alcohol and veratryl alcohol on linter cellulose during NO₂ pretreatment.

Molar ratio of NO ₂ to model compounds	1.3	3.0	13	25
Vanillyl alcohol recovered, %	0	0	0	0
Veratryl alcohol recovered, %	-	100	-	90.3

Notes: Dosage of each model compound is 150mg on 10g of linter cellulose.
Reaction temperature: 20 C, reaction time: 10min.

PROJECT 3474

RESEARCH AREA:

Mechanisms of Oxygen Bleaching
Selectivity Improvement.

OBJECTIVE:

- (1) Understand Reactions of NO_2 That Accelerate Delignification and/or Retard Degradation.
- (2) Use this Information to find Better Ways to Improve Selectivity.

VALUE:

Will Allow Large Reduction in Chlorine Use and AOX Production.

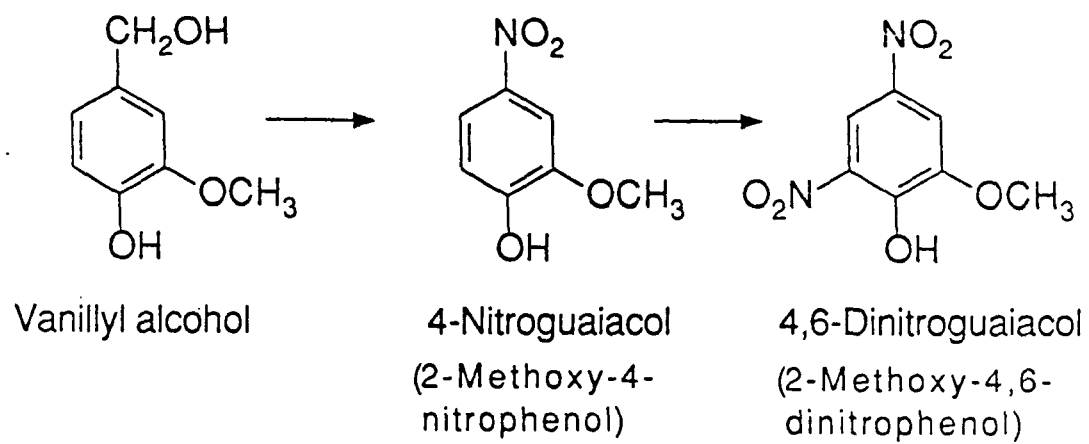


Fig. 1 Nitration of vanillyl alcohol in NO_2 pretreatment.

Table 2 Yields of nitrated products in NO₂ pretreatment of vanillyl alcohol on linter cellulose.

Molar ratio of NO ₂ to vanillyl alcohol	1.3	3.0	13	25
4-Nitroguaiacol, mol %	8.7	8.8	9.4	10.3
4,6-Dinitroguaiacol, mol %	0.5	2.8	14.6	15.8

Notes: Dosage of vanillyl alcohol is 150mg on 10g of linter cellulose.

Reaction temperature: 20 C, reaction time: 10min.

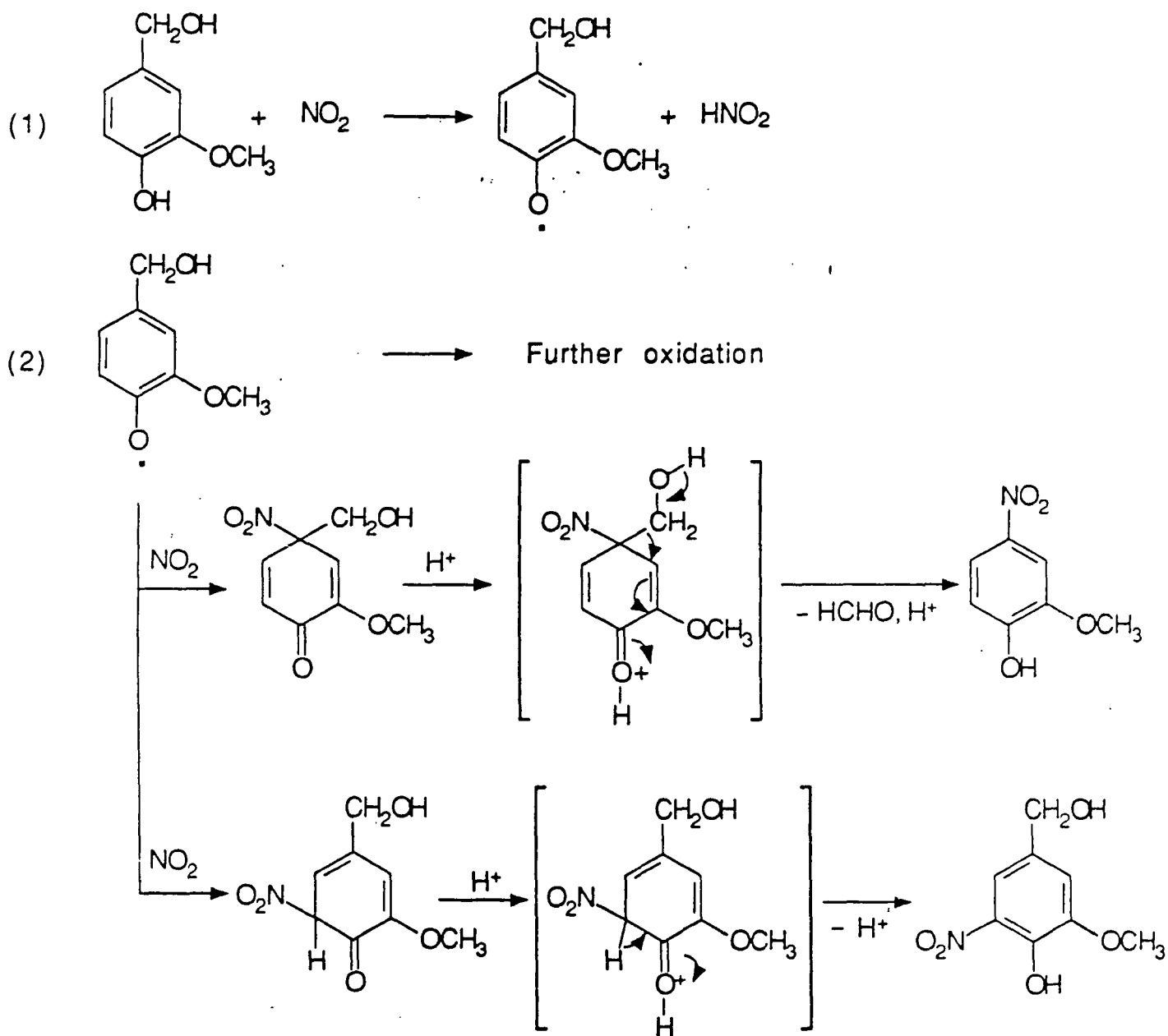


Fig. 2 Possible mechanism of nitration of vanillyl alcohol by NO_2 .

Table 5 NO₂ treatment of free phenolic lignin model compounds.

Lignin model compound	Condition (molar ratio to model)	Recovered yield, mol%	4-Nitroguaiacol yield, mol%	Nitrated vanillyl alcohol ^{a)} yield, mol%
Vanillyl alcohol	NO ₂ : (3) NaNO ₃ : (6)	0	5.8	8.6
Acetovanillone	NO ₂ : (3)	93	0.8	--

Legend: a): Molecular weight is 199.

Notes: Each model compound (1mmol) was dissolved in 10mL of dioxane, and then 30mL of water or 0.2M NaNO₃ was added.

Reaction temperature: 20 C, reaction time: 10min.

Table 6 Oxidation and nitration of veratryl alcohol by NO₂.

Condition	Recovered yield, mol%	Veratraldehyde yield, mol%	1,2-Dimethoxy-4-nitro- benzene yield, mol%
NO ₂ : 21mmol	81	11	0.4
NO ₂ : 21mmol, and HNO ₃ : 12mmol	79	13	1.1

Notes: Veratryl alcohol (1mmol) was dissolved in 10mL of dioxane, and then 30mL of water or 0.4M HNO₃ was added. Reaction temperature: 20 C, reaction time: 10min.

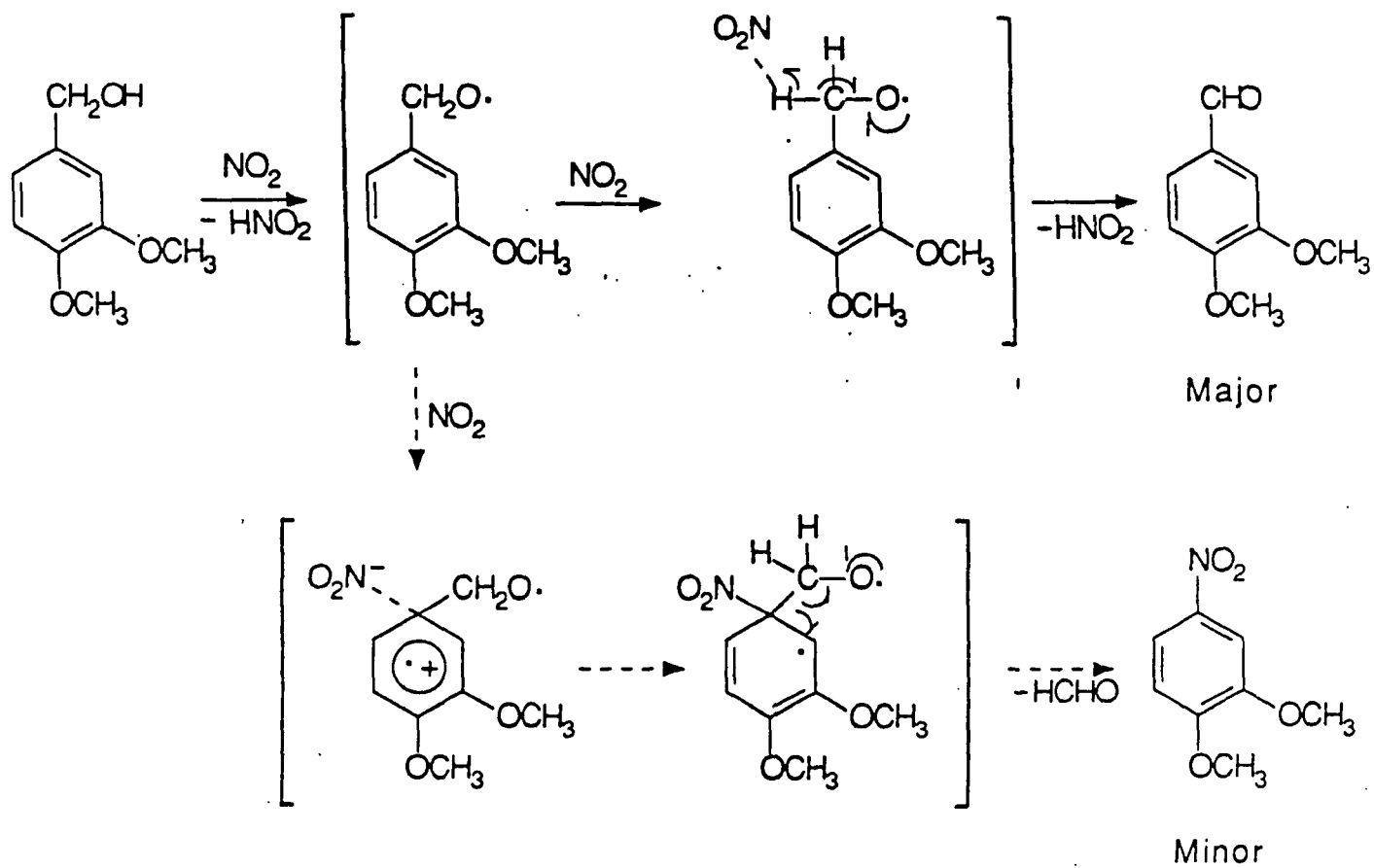


Fig.3 Oxidation and nitration of veratryl alcohol by NO_2 treatment.

Table 7 NO₂ treatment of 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)propan-1-ol.

Condition (molar ratio to model)	Recovered yield, mol %	α -carbonyl cpd. ^{a)} yield, mol %	Veratraldehyde yield, mol %	1,2-Dimethoxy 4-nitrobenzene yield, mol %
NO ₂ : (21)	67	25	4.7	trace
NO ₂ : (21) HNO ₃ : (12)	63	25	3.5	trace

Legend: a) 1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)propan-1-one

Notes: A starting compound (0.5mmol) was dissolved in 5mL of dioxane in a 500mL round flask, and then 15mL of water or 0.4M HNO₃ was added to it.

NO₂ treatment was carried out in the 500mL round flask.

Reaction temperature: 20 C, reaction time: 10min.

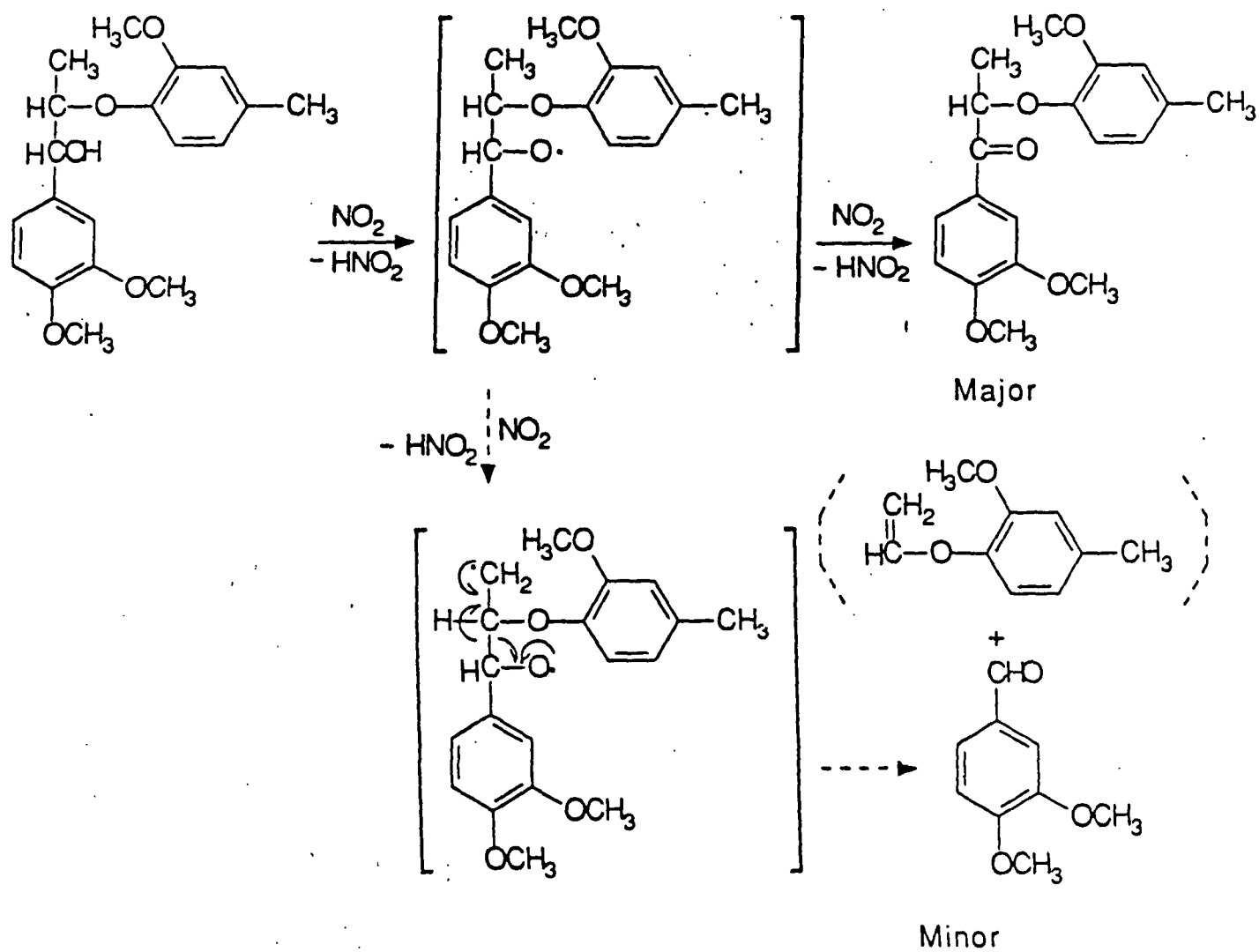


Fig. 4 Reaction of 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)propan-1-ol with NO_2 .

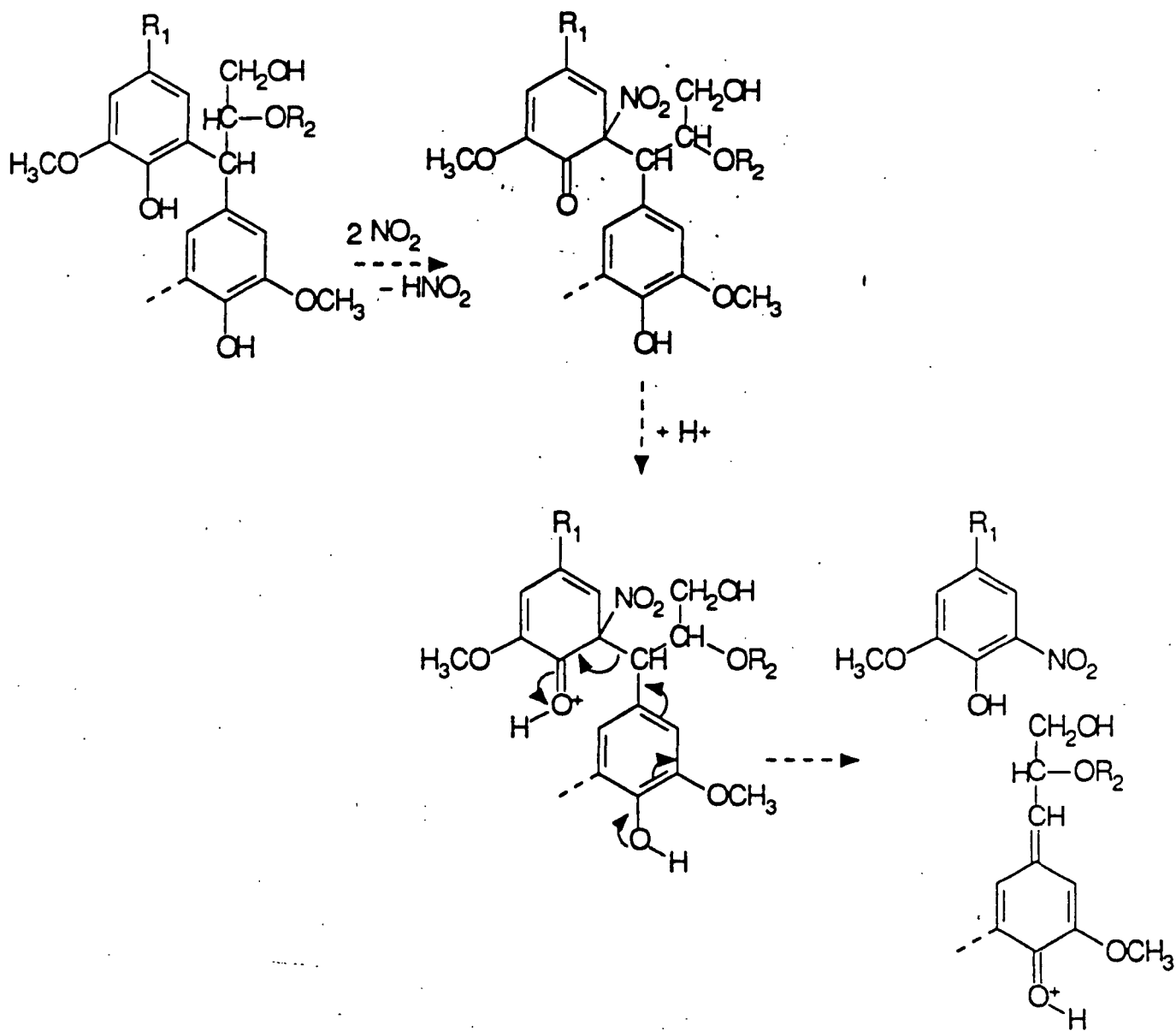


Fig. 5a A possible reaction of a condensed free phenolic lignin unit with NO_2 .

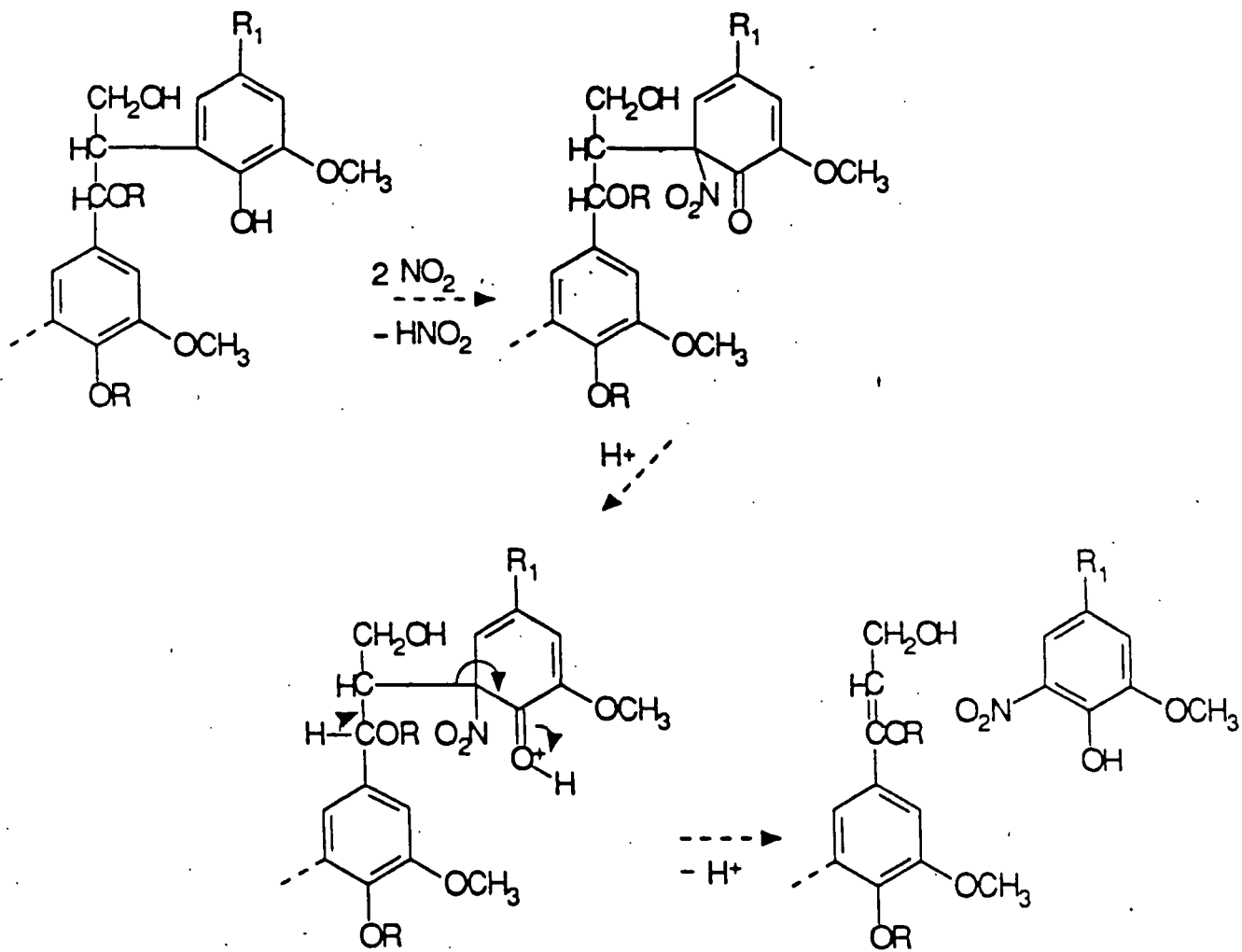


Fig. 5b A possible reaction of a condensed free phenolic lignin unit with NO_2 .

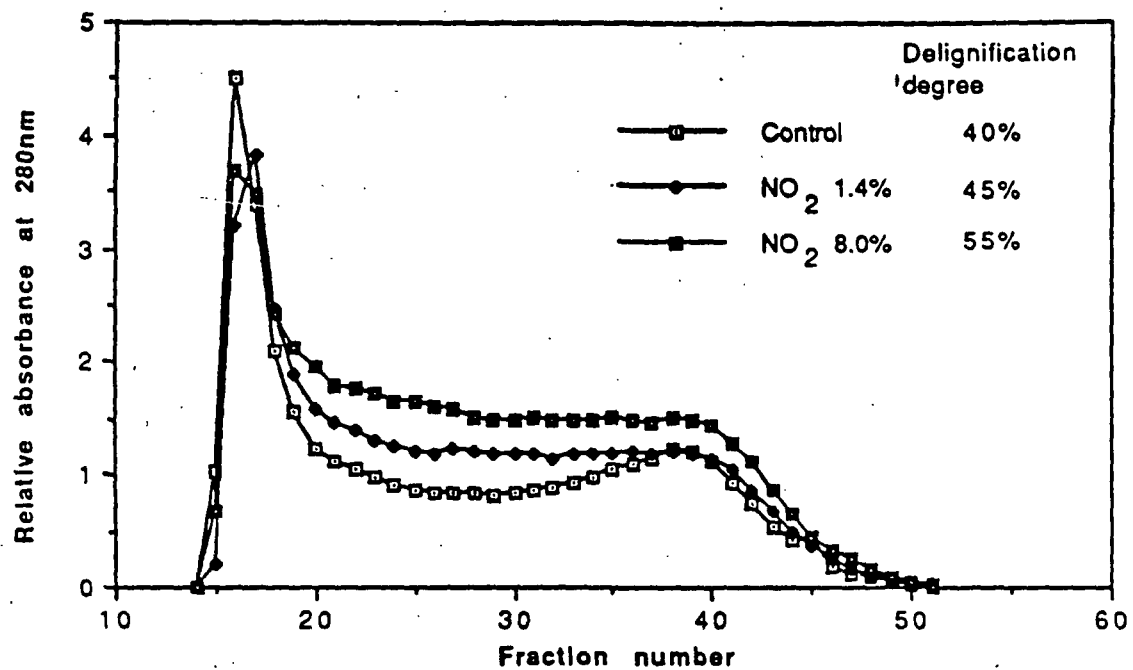


Fig. 6 Molecular weight distributions by GFC of lignins dissolved during oxygen bleaching.

Table 10 NO₂ pretreatment and O₂ bleaching of methylated kraft pulp.

NO ₂ dosage, % on pulp	Before oxygen bleaching		After oxygen bleaching	
	Lignin, %	Viscosity, cps	Lignin, %	Viscosity, cps
0	5.0	32.4	4.8	26.2
1.4	5.0	31.9	4.6'	25.1
8.0	5.0	31.1	4.5	25.1

Note: Oxygen bleaching conditions: pulp consistency: 27%, NaOH charge: 2%, Mg⁺² charge: 0.1%, reaction time: 30min (from 100 C to 112 C), oxygen pressure: 70psig at 45 C.

CONCLUSIONS

- (1) REACTIVITY: PHENOLIC >> NONPHENOLIC
- (2) PHENOLIC REACTIONS: NITRATION, OXIDATION
- (3) NITRIC ACID UNREACTIVE BUT CATALYTIC
- (4) NONPHENOLIC REACTION: ALPHA-OH TO ALPHA-C=O
- (5) BOTH (2) AND (4) OFFER LIGNIN DEGRADATION PATHWAYS
- (6) PRETREATMENT GIVES OXYGEN LIGNIN OF LOWER MOL
MASS
- (7) NITRO GROUP ASSISTED ETHER CLEAVAGE NOT
IMPORTANT

Fundamentals of Brightness Stability

Project 3524

A.J. Ragauskas

Brightness Reversion of High Yield Pulps

- Review Important Photo-Yellowing Parameters**
- Photo-Chemical Behavior of Lignin and Quinoid Structures**
- Current and Future Research Directions**

Fundamentals of Brightness Stability

Research Objective

- Investigate the fundamental chemical reactions which are initiated when high yield pulps are photolyzed.
- Devise new technologies to retard or stop the photo-yellowing process.

Research Significance

- Increase the usefulness of high yield fibers.
- Enhance our knowledge of the chemical behavior of lignin and its derivatives.
- Evaluate the effect that a solid matrix has on chemical reactivity.

Selected Highlights of

Brightness Reversion Process

- **Experimental Parameters**
- **Photo-Active Chromophores**
- **Reaction Mechanisms**

Photo-Yellowing of Mechanical Pulp

Experimental Yellowing Parameters

- * Frequency of light \Rightarrow 290 - 400 nm
- * Yellowing reactions are initiated by the absorption of a photon of light by the lignin component of mechanical pulp
- * Presence of O_2 is required
- * Phenolic hydroxyl groups accelerate the rate of yellowing, but are not an absolute requirement for yellowing
- * Post-irradiation yellowing of high yield pulps has been noted

Factors Moderating the Rate of Yellowing

- i) pH
- ii) metal salts
- iii) moisture and resin content
- iv) wood stocks
- v) bleaching procedures

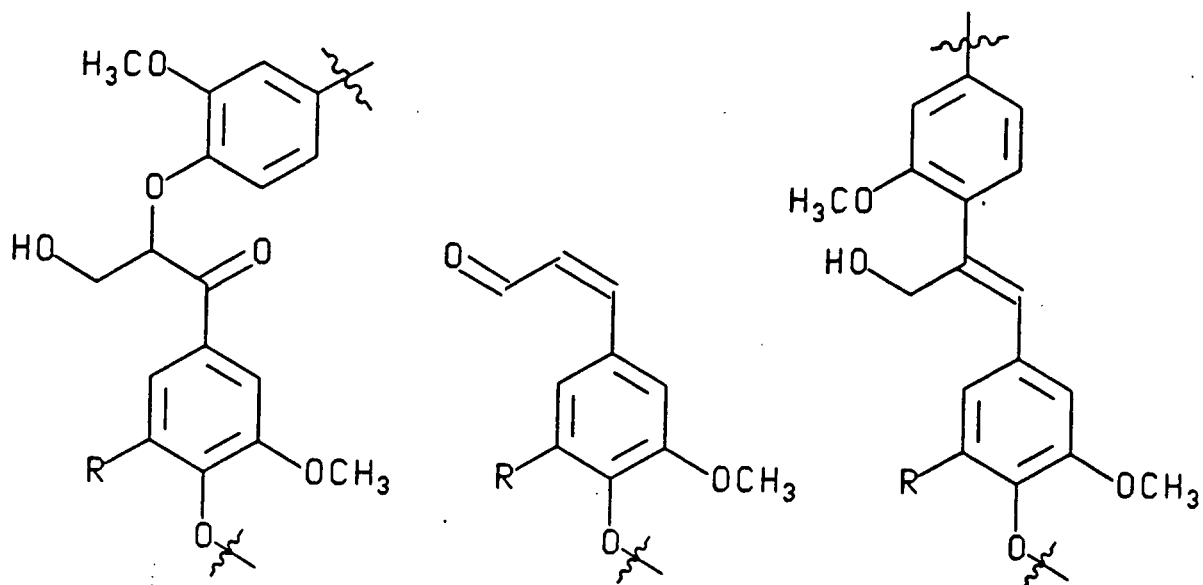
-to date these studies have failed to find manufacturing procedures which would significantly reduce the rate of brightness reversion.

Technical Difficulties

- i) chemical complexity of mechanical pulp
- ii) colored compounds formed only in trace amounts

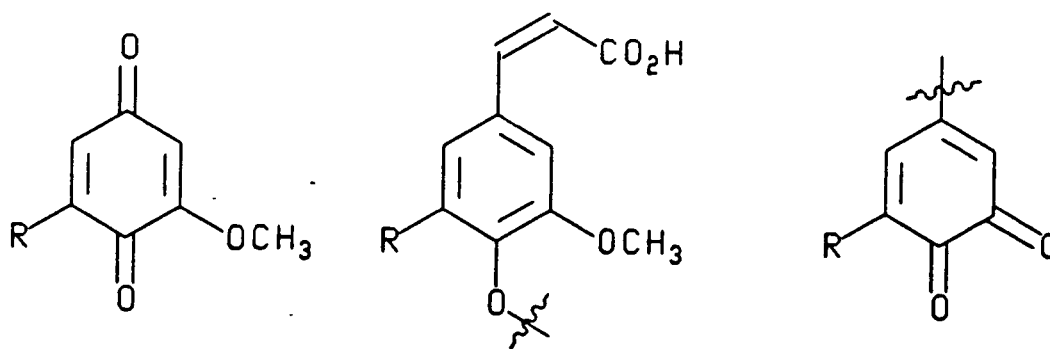
-due to these considerations the use of model studies has been employed to further enhance our knowledge of the photo-reversion process

Proposed Photo-Initiators



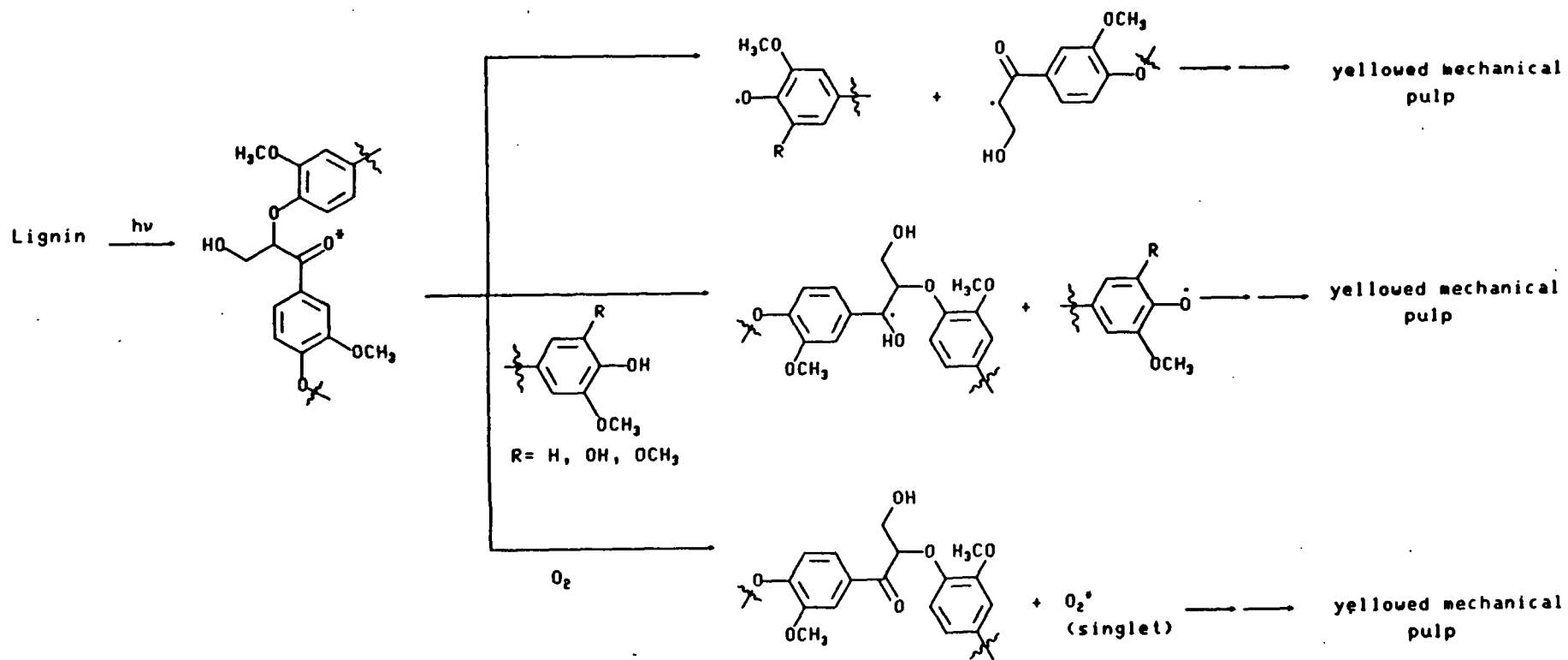
$\text{R} = \text{H}, \text{OCH}_3$

Proposed Yellowing Compounds



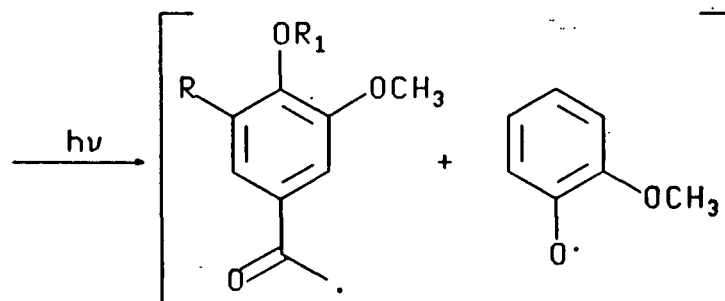
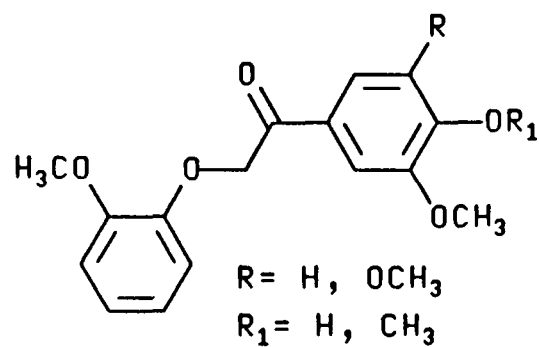
-quinones may also yield colored charge transfer complexes and/or condensed polymeric materials

Proposed Photo-Initiated Yellowing Reactions

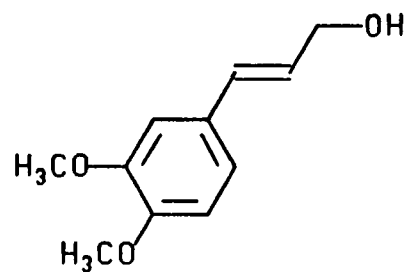


-it has been suggested that conjugated sites of unsaturation also undergo analogous reactions to those shown above

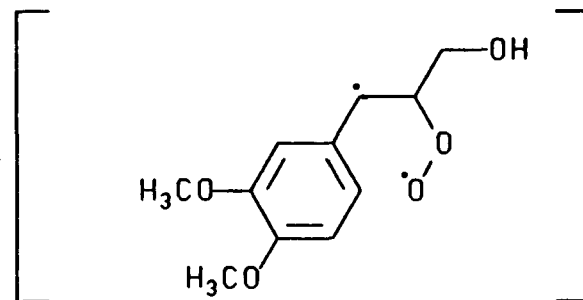
Photo-Yellowing Model Studies



→ → photoproducts
 Castellán et al



1) $h\nu$
 2) O_2



→ → photoproducts
 Forsskahl et al

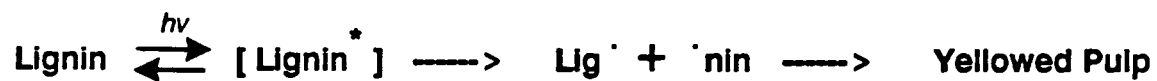
- modelling studies have provided a means of identifying important structures which may be involved in the brightness reversion process

Examination of Post-Irradiation Chemical Reactions

- Literature Survey**
- Purposed Research Activities**

Research Hypothesis: Post irradiation reactions are an important component of the photo-yellowing process.

ie/



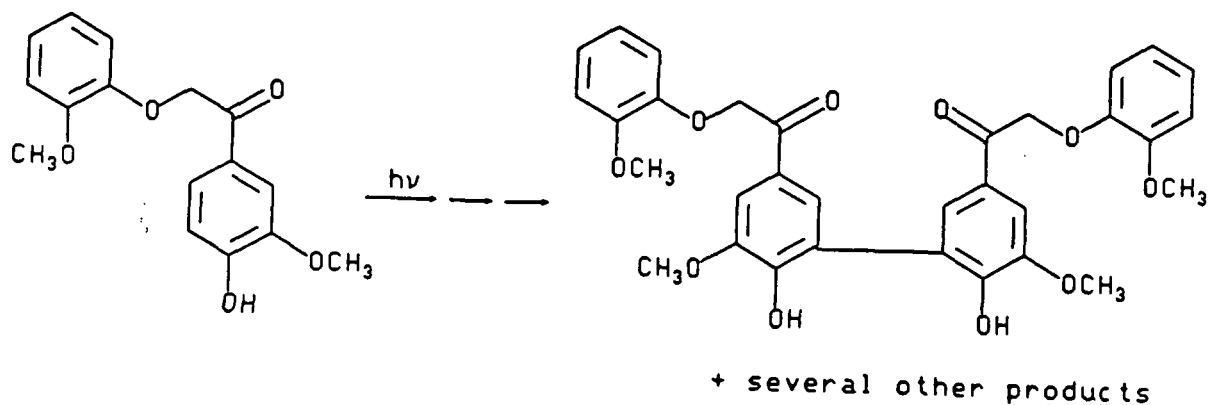
Supporting Experimental Observations

- i) post-irradiation yellowing of high yield pulps
- ii) detection of radicals in post-irradiated pulps

- to date, the nature of the reactions which occur after the initial photolysis step have not been properly defined.

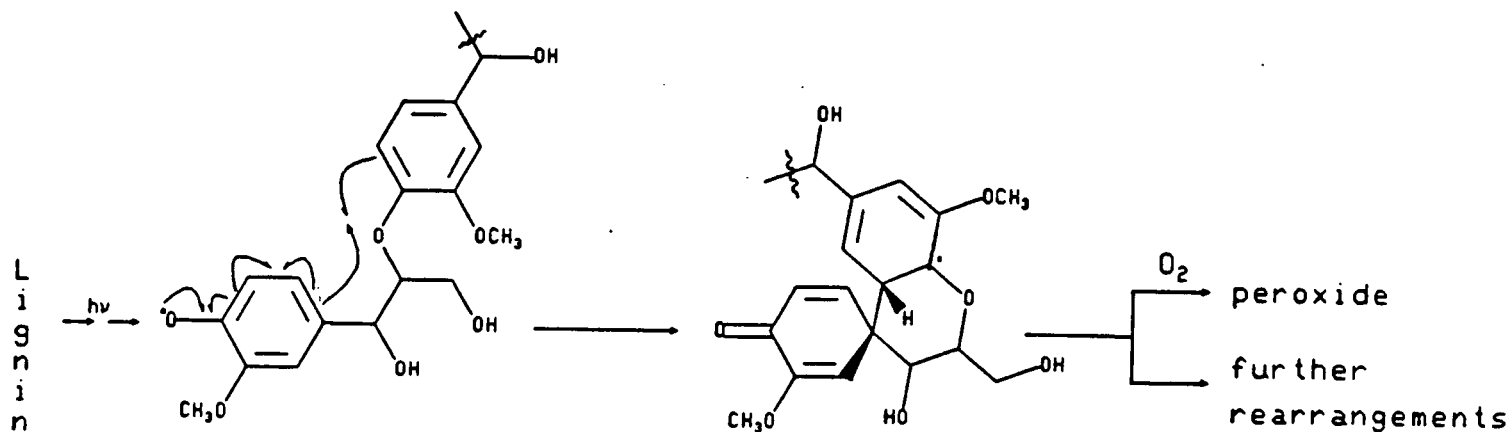
Problems With Current Model Studies

A/ Model Studies Do Not Properly Reflect the reaction Conditions Found in Mechanical Pulp



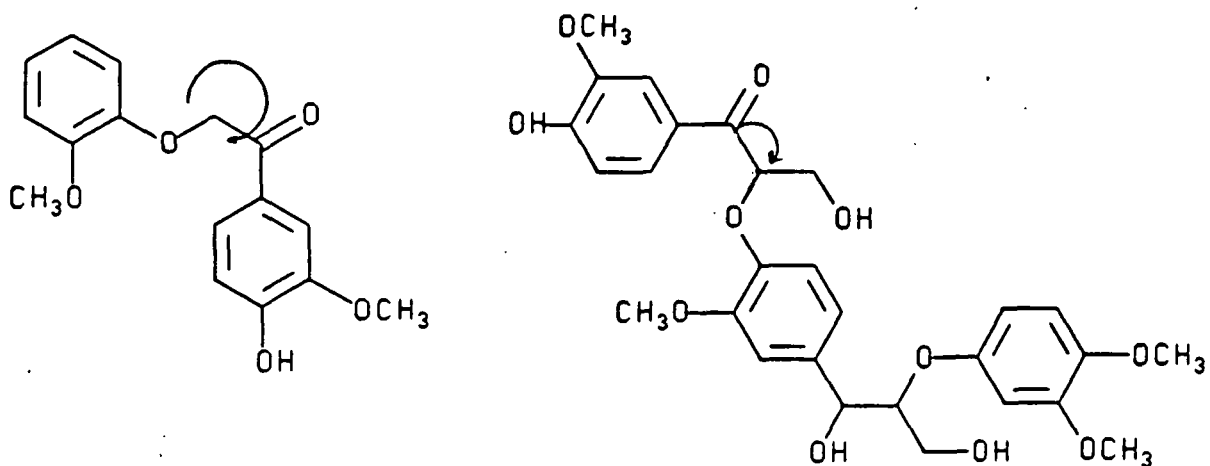
-radicals formed upon photolysis of mechanical pulp are present in low concentrations; therefore radical coupling reactions and/or reactions occurring with carbonyl groups are unlikely to occur

B/ Mono and Dimeric Models Compounds of Lignin Preclude The Possibility of Intra-Molecular Reactions Occurring After The Initial Formation of Radicals



NB: in principle these types of reactions could readily occur and yield condensed, unsaturated compounds (ie/ colored compounds).

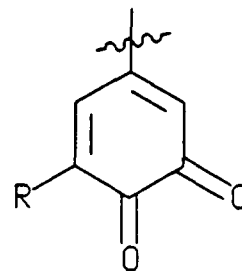
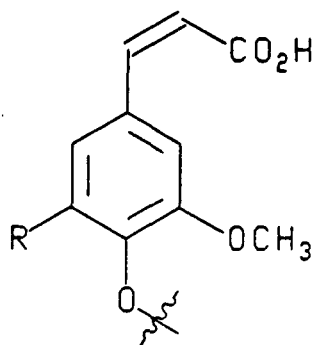
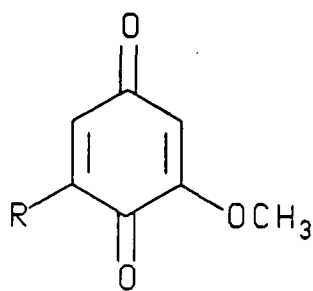
C/ Model Compounds are Conformationally Much Less Rigid Than Lignin



Note: Molecular Minimization Calculations (version two) suggest that the trimer lignin model has much less degrees of freedom than the dimer structure shown above; such differences in conformational energy could influence both the photolysis reaction and subsequent steps.

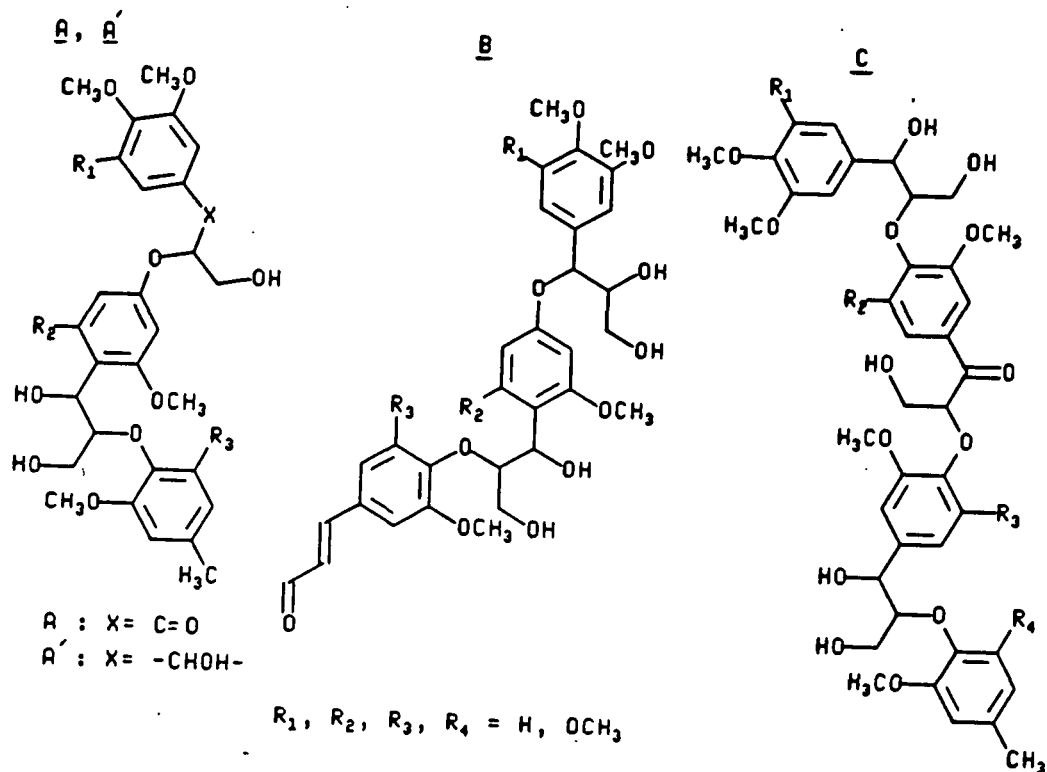
D/

**Proposed Yellowing Agents Are Not Found in The Product Mixtures
From Model Studies**



**Conclusion: Current model studies are presumably good at modelling
the initial photolysis reaction but not the subsequent steps.**

Compounds To Be Employed To Study The Photo-Yellowing Reaction

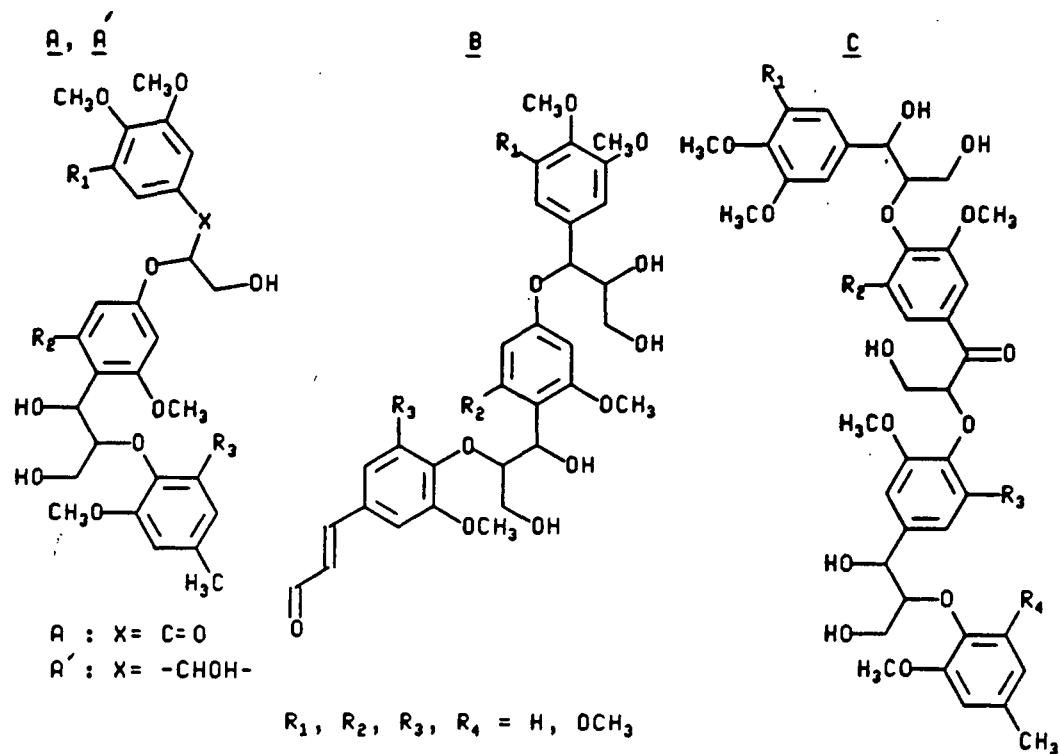


NB: All compounds will be photolyzed on a solid support

Advantages To Proposed Model Systems

- i) Initially formed radicals could undergo intramolecular rearrangements
- ii) Model compounds are conformationally more rigid than previous models
- iii) Photolysis of model compounds on a solid support will model reactions occurring in mechanical pulp
- iv) Irradiation of A/A', B/A' and C/A' will provide a means of modelling intermolecular reactions which may occur after the photolytic step

Experimental Conditions



Light Source

-Oriol Solar Simulator, Fluorescent Lamps, Medium Pressure Mercury Lamps

Solid Support Matrix

-Cotton Linters, Cellobiose, Model Compounds Grafted onto a Polymer

Product Analysis

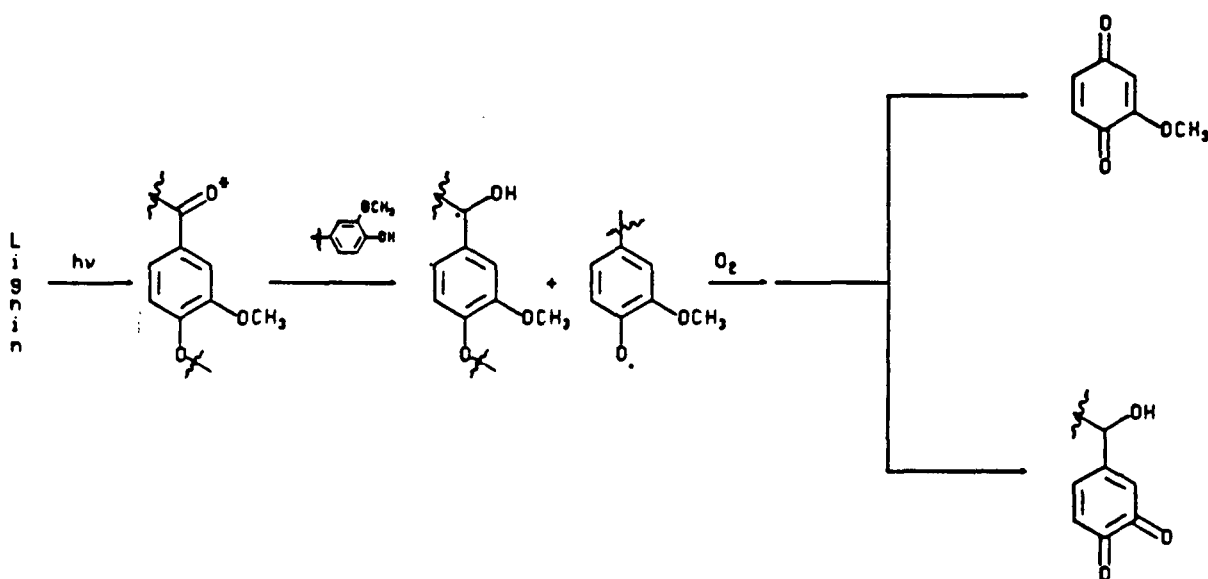
-HPLC, GLC, NMR, IR, UV, MS

Photo-Reactivity of Quinones

- **Contribution to Yellowing**
- **Proposed Investigative Studies**

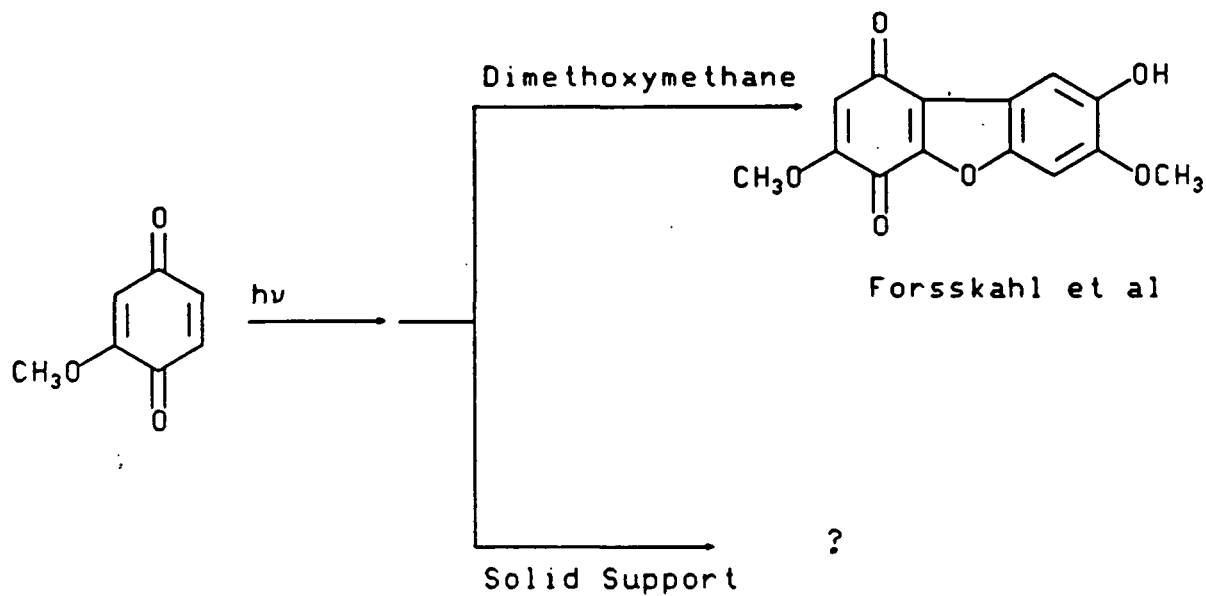
Photochemistry of Quinones

In Situ Formation



NB: Para-quinones are formed by a chain cleavage process, ortho-quinones can be formed attached to the lignin polymer

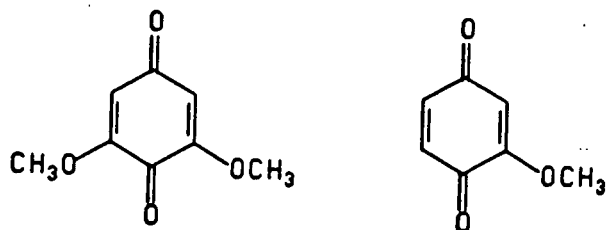
Photochemistry of Quinones



-literature clearly suggests that ortho and para-quinones are photo-reactive under the brightness reversion conditions; currently the effect of a solid support matrix on the reaction profile is unknown.

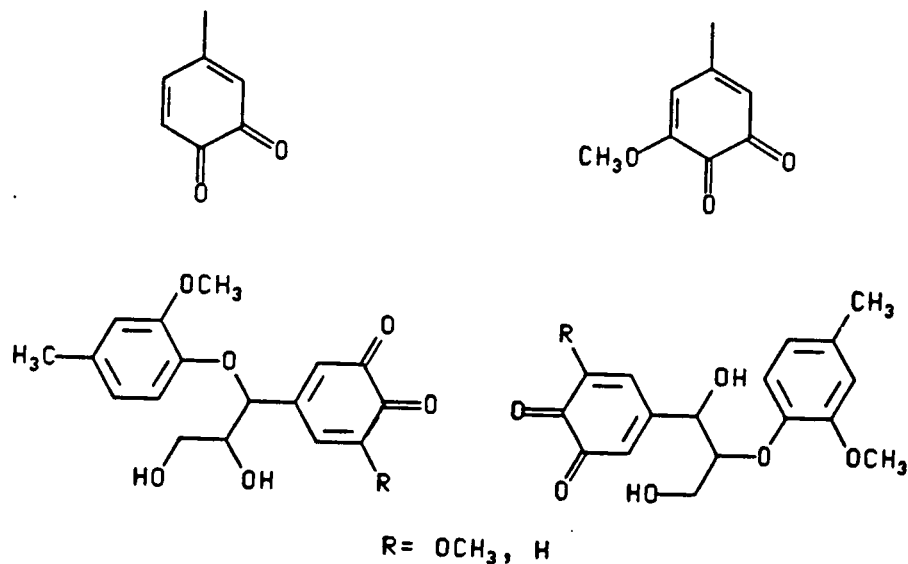
Proposed Compounds To Be Synthesized and Photolyzed

Para-Quinones



-structures are analogous to those proposed to be formed in mechanical pulp.

Ortho-Quinones



-compounds are simplified models of proposed structures formed in high yield pulps

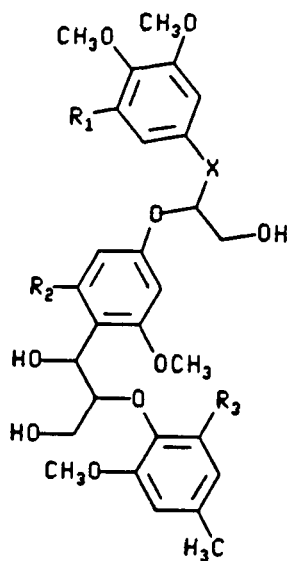
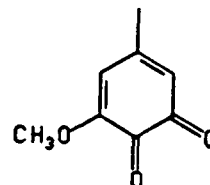
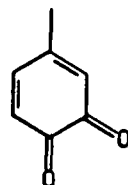
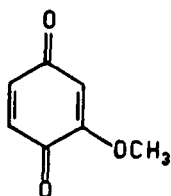
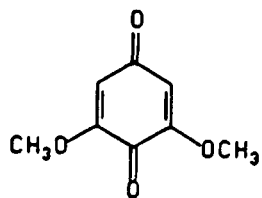
Experimental Photochemical Reaction Conditions

-Quinones are to be absorbed onto a solid support matrix and irradiated under the brightness reversion conditions

-Above reactions will be repeated in the presence of A'

Current Research Activities

Synthetic Efforts



A : X = C O

A : X = -CHOH-

$R_1, R_2, R_3, R_4 = H, OCH_3$

Summary

- proposed lignin model compounds will provide valuable physical chemistry data (ie/ NMR chemical shifts, conformational analysis, ...)
- photolysis of lignin and quinone structures will further probe several important aspects of the photoyellowing reaction
- as our knowledge of the photoyellowing process evolves it is anticipated that novel methodologies will develop that will successfully retard or stop the photo-reversion process.

H I G H Y I E L D P U L P S
o f
H I G H a n d S T A B L E B R I G H T N E S S

Alan W. Rudie

O B J E C T I V E S :

Develop a cost effective method to produce high
brightness and stable brightness high yield pulps.

P O T E N T I A L V A L U E

O F

H I G H A N D S T A B L E B R I G H T N E S S H I G H Y I E L D P U L P S

- * M A R K E T E X P A N S I O N S : B C T M P i n t o W h i t e P a p e r s
 T M P / S G W i n t o # 3 L W C
 B l e a c h e d B o a r d

- * C O S T R E D U C T I O N S : B C T M P , a l l g r a d e s
 T M P / S G W , L W C a n d S C g r a d e s
 H i g h B r i g h t n e s s N e w s

PLANS FOR
PRELIMINARY EXPERIMENTS

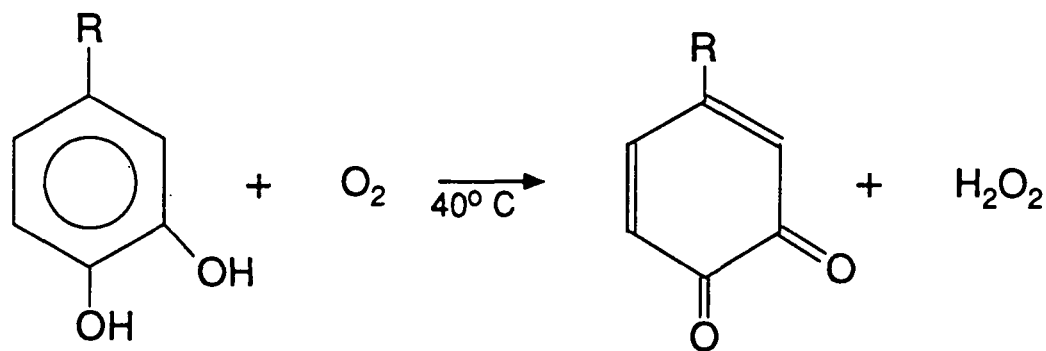
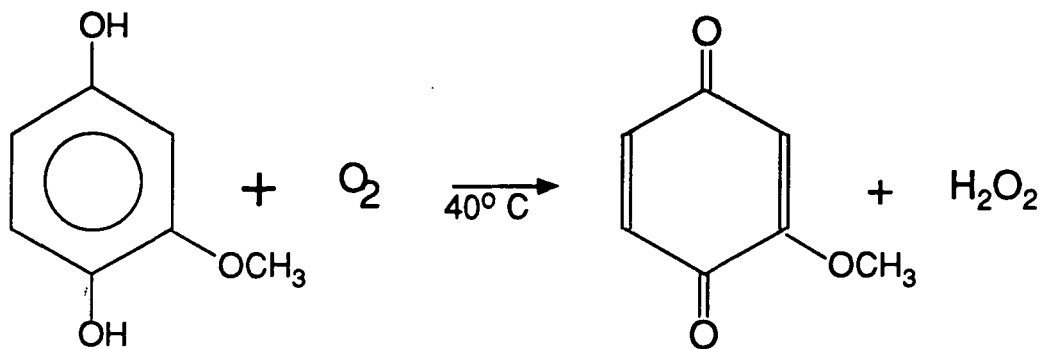
EVALUATE:

- * Oxygen
- * Oxygen Followed by Peroxide
- * Oxygen Mixed With Peroxide

FOR BLEACHING:

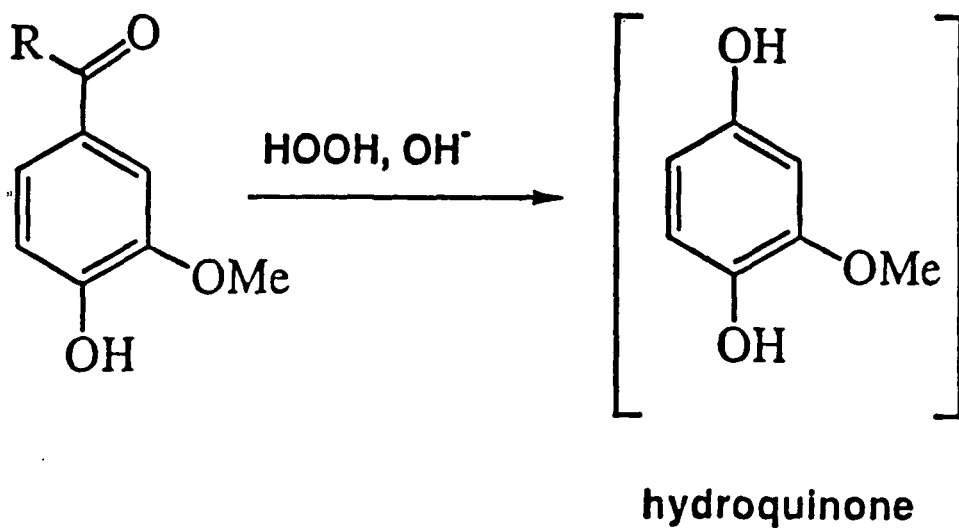
- * Southern Pine TMP and CTMP
- * Hardwood TMP and CTMP

AUTOXIDATION OF HYDROQUINONES AND CATECHOLS



R = t - Butyl

Oxidation of Lignin Models



Tappi, 1965, 48, 121

Tappi, 1969, 52, 491

PROJECT 3566

STRONG, INTACT HIGH YIELD FIBERS

Alan W. Rudie

Tom J. McDonough

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.

P O T E N T I A L V A L U E
O F
H I G H S T R E N G T H , H I G H Y I E L D P U L P S

- * Wood Savings
- * Market Expansion
- * Environmentally Benign

P I L O T P L A N T S T A R T - U P A C T I V I T I E S

- * Familiarize operating personnel with the pilot plant and research procedures
- * Identify and replace worn and suspect parts
 - * CD 300 shaft seal
 - CD 300 main bearing
 - First impregnator lift screws (rebuild top flights)
- * Establish system capabilities and idiosyncrasies

PLANNED ACTIVITY, FISCAL YEAR 1990

CONSORTIUM PROJECT 1-2: THERMOMECHANICAL and CHEMITHERMOMECHANICAL
PULPING of JUVENILE and MATURE SOUTHERN PINES

OBJECTIVE:

Characterize the response of juvenile and mature wood from the southern pines to thermomechanical and chemithermomechanical pulping.

INDEPENDENT VARIABLES:

Juvenile Wood Project

Chip source/Tree age

Average Chip Size

Presteamng Conditions

Specific Refining Energy

Refining Consistency

Production Rate

Chemical Addition (CTMP)

DEPENDENT VARIABLES:

Juvenile Wood Project

Freeness

Shives

Handsheet Properties

Fiber Length Distribution

Optical Properties
(includes brightness reversion)

S T A R T - U P E X P E R I M E N T S :

ALKALINE PEROXIDE MECHANICAL PULPING OF DENSE HARDWOODS

OBJECTIVES:

Evaluate fiber quality after screw compression impregnation.

Evaluate the influence of metal ions (Al^{3+} and Ca^{2+}) on APMP

INDEPENDENT VARIABLES:

Steam or Plug Screw Impregnation

Atmospheric Pre-steaming Temperature

Hand Sheet conditions (metal ion content)

* Total chemical addition to be held constant.

DEPENDENT VARIABLES:

Freeness (chemically treated pulps)

Fiber Length (mechanical)

Short Span Tensile (mechanical pulps)

Handsheet Properties (mechanical and chemically treated pulps)

Optical Properties (mechanical pulp)

F I B E R S T R E N G T H T E S T I N G :

PREMISE:

- * Single fiber testing is time consuming, tedious and biased toward whole (longer and stronger) fibers

ALTERNATIVES:

- * Evaluate chemical treatment of mechanical pulps to develop bond strength for testing
 - Ozone
 - Chlorite/Chlorine Dioxide
- * Evaluate short span and zero span tensile testing on whole pulps and long fiber fractions to separate the fiber bonding and fiber strength contributions to sheet strength.

C O N C L U S I O N S T O D A T E :

- * High Strength Pulps are Obtainable with Mechanical and Chemimechanical Pulping Methods
- * TMP is Currently Manufactured to Bond Strength and Brightness Limits.

BLACK LIQUOR COMBUSTION FUNDAMENTALS

PROJECT 3473-1 (IPST FUNDING)
PROJECT 3473-6 (DOE FUNDING)
PROJECT 3605 (IPST FUNDING)

Jeff Empie
Ken Nichols
Bob Horton
Steve Lien

PRESENTATION FOR PAC MEETING

MARCH 20, 1990

by

Jeff Empie

OBJECTIVE:
(1984-1989)

Advance our understanding and knowledge of the internal chemical and thermal processes which occur during black liquor combustion in kraft recovery boilers. This will be accomplished by:

1. Developing laboratory-scale flow reactor systems which will enable the study of both state-of-the-art and advanced recovery systems;
2. Studying gas phase and char bed mechanistic processes under realistic and controlled environments with advanced optical and spectroscopic techniques;
3. Developing a data base that will bridge the gap between on-going fundamental research and commercial application of the resultant findings, culminating in increased thermal efficiency, productivity, and capital effectiveness.

VALUE:

- . Increased thermal efficiency potential estimated at 0.7 MM BTU/ADT, or about \$100 MM/yr.
- . Increased process productivity potential of 5% through operation improvements and minimized downtime, equivalent to about \$500 MM/yr.
- . Enhanced potential for equipment design and process control improvements.

STATUS:

Project was completed in four phases:

- Phase 1. In-flight chemical and thermal processes
- Phase 2. Char bed processes
- Phase 3. Inorganic fume formation processes
- Phase 4. Recovery furnace simulation

Major Conclusions:

1. Rate equation based on single drop studies of drying, pyrolysis and burning of individual black liquor drops confirmed by continuous flow reactor data.
2. Char bed burning rate data were shown to be oxygen mass transfer limited. Measured mass transfer coefficients were found to be consistent with values calculated from standard mass transfer correlations.
3. Fume deposition was shown to be governed by thermophoresis at low gas velocities.
4. A three-dimensional recovery furnace model has developed providing significant insight into recovery furnace physical and chemical processes.

OBJECTIVE:
(1990-1994)

Develop a recovery furnace model based upon fundamental chemical and engineering principles and supported by laboratory data. Model must be accurate, credible, and usable by the industry as a tool for increasing the energy efficiency and productivity of kraft recovery boilers.

FIRST YEAR DELIVERABLES:

- * Submodel for single particle combustion
- * State-of-the-art model of a kraft recovery furnace
- * Definition of transport process at the combustion zone/char bed interface
- * Diagnostic recovery boiler probe for velocity and temperature measurements
- * Equipment design and purchase for measuring fume deposition rates under typical furnace conditions

SUBMODEL FOR SINGLE PARTICLE COMBUSTION

- * Quantitative prediction of combustion rate of black liquor droplets falling to char bed
- * Target quantities include
 - droplet surface temperature
 - solids content at ignition
 - time to ignition
 - residual carbon content of char
- * Work performed by W.J. Frederick, IPST Adjunct Professor, presently at Abo Akademie in Finland
- * One year time frame

TRANSPORT PROCESSES AT CHAR BED SURFACE

- * Continuation of previous study of char bed burning
- * Information on gasification reactions, NO formation, fuming, and particle entrainment to be generated as supporting input data for the furnace model
- * Influence of char bed shape on transport processes will be examined
- * DOE flow reactor used previously has been reinstalled and will be used for this study

KRAFT RECOVERY FURNACE MODEL

- * Combustion model revision and simplification to be done with fixed flow field (IPST funded)
- * Improved computational fluid dynamics (CFD) code to be developed by the University of British Columbia
- * Integration of combustion and fluid dynamics models will result in rigorous model for black liquor combustion in variable flue gas flow field
- * Project to be overseen by IPST Adjunct Professor, T. Grace

RECOVERY BOILER DIAGNOSTICS

- * Actual operating data on furnace gas velocity, temperature, and chemical composition as a function of location are needed to establish model credibility
- * Intrusive and non-intrusive techniques to be screened and the most promising developed
- * Testing of prototype to be done on DOE flow reactor prior to mill site measurements

FUME DEPOSITION RATE MEASUREMENTS

- * Boiler tube pluggage due to fume deposition is major operating problem
- * Deposition rate data taken under representative conditions needed for modeling input
- * Present DOE flow reactor with some modifications to be used for study

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY
(Project 3473-1)
Ken Nichols
Assistant Professor

IPST PROJECT ADVISORY COMMITTEE MEETING
Atlanta, GA
March 20, 1990

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY
(Project 3473-1)

Overall Objective: A comprehensive understanding of black liquor combustion and application of that knowledge to improve recovery boiler performance.

- * FT-IR Diagnostics Pat Medvecz, Ph.D. student,
Denise Martin, M. S. student
- * Char Gasification Stacy Lee, M. S. student
- * Fume Formation Chris Verrill, Ph. D. student
- * Fume Measurement by Laser Scattering

FT-IR Diagnostics

Objective: Develop and apply FT-IR (Fourier Transform-Infrared Spectroscopy) to measure gas concentrations (CO, CO₂) and Temperatures during lab-scale combustion of Black Liquor Char.

Value: Will provide data needed for mathematical modeling of bed-burning. Non-intrusive method will not disturb reaction environment.

Prior Results

- * FT-IR equipment selected, purchased, set-up at IPST
- * Temperature controlled reaction cell designed, constructed, tested
- * CO absorption spectra obtained at gas temperatures up to 1000 °C
- * Improvements in method for calculating temperatures from CO spectra

Recent Results

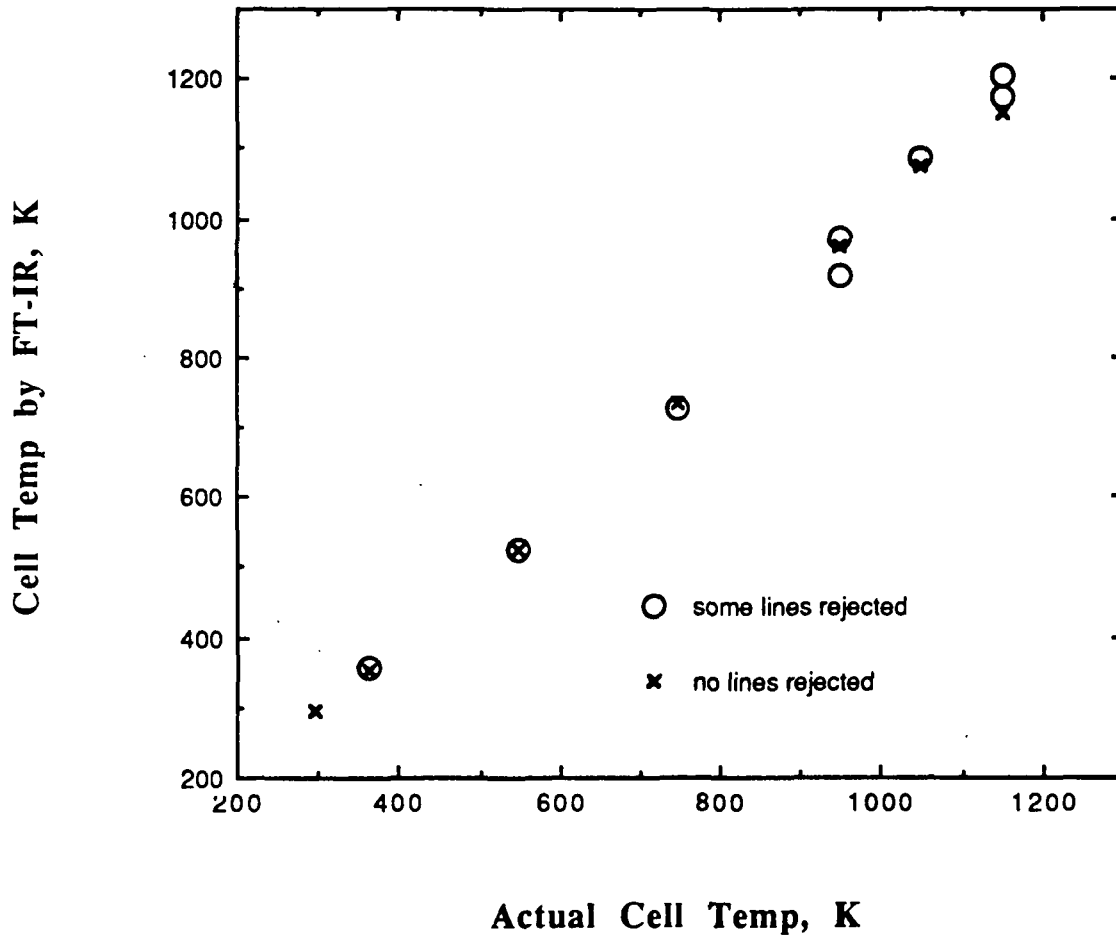
- * Temperature measurements up to 1000 °C
- * Temperature profiling of gas cell with thermocouples
- * Completion of initial design for optics to implement FT-IR equipment onto Black Liquor Flow Reactor

ACTUAL VS. MEASURED TEMPERATURES

<u>Actual Temp. K</u>	<u>FT-IR msd Temp. K</u>		<u>% difference</u>	
295	---	(295) ^b	---	(0.1)
361	357 ^a	(354)	1.1	(1.9)
547	526	(524)	3.8	(4.2)
748	726	(735)	2.9	(1.7)
950	917	(960)	3.5	(1.0)
950	972	---	2.3	---
1049	1085	(1073)	3.3	(2.3)
1151	1174	(1152)	2.0	(0.1)
1151	1203	---	4.3	---

- a) some spectral lines rejected
- b) no spectral lines rejected

ACTUAL VS. MEASURED TEMPERATURES



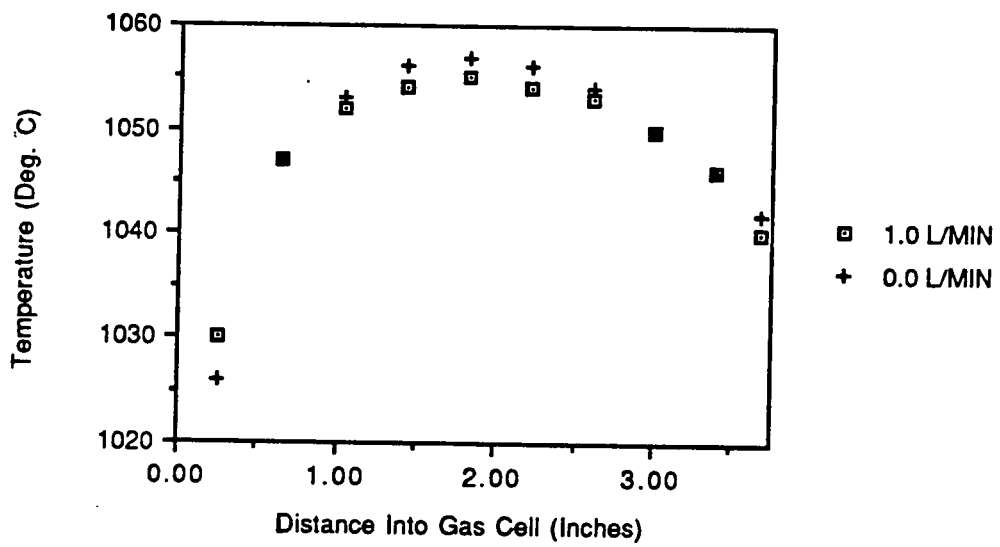


Fig. 10 Temperature profile of gas cell at 1000°C at 1.0 and 0.0 L/min., thermocouple entered gas cell from front wall

Conclusions

- * Accuracy of FT-IR method is 0-4% error for combustion Temperature measurements up to 1000 °C
- * Temperature profile in test cell is acceptably low (<1% at 1000 °C) indicating temperature is constant throughout cell volume

Future Plans

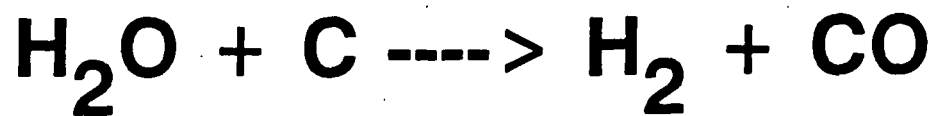
- * Improve accuracy by reducing emission from cell
- * Conduct gas concentration measurements (CO, CO₂)
- * Perform char combustion experiments
- * Implement FT-IR instrumentation to Black Liquor Flow Reactor

Char Gasification

Objective: Determine the rates of oxidation of Black Liquor Char carbon with CO_2 and H_2O over a range of temperatures. Determine the temperature range in which mass transfer (of oxidizer to the char surface) controls the rates. Compare the relative importance of gasification reactions to the oxidation of char carbon by O_2 .

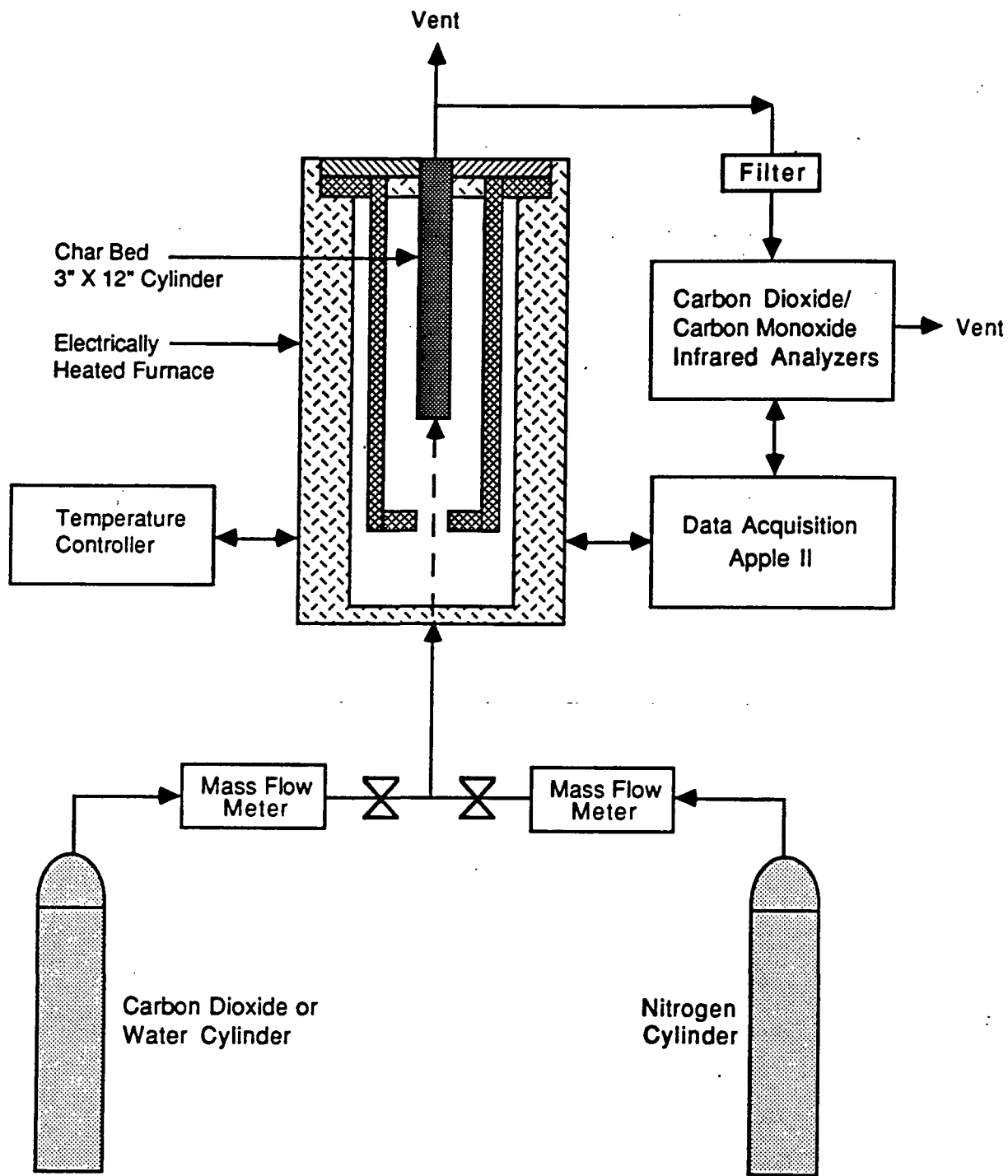
Value: Gasification rate data are presently very limited. Knowledge of these rates is required for mathematical modeling of recovery furnaces.

GASIFICATION REACTIONS



Prior Results

- * Kinetics reactor was designed, constructed
- * Demonstration testing performed to verify control of temperature and gas flowrates
- * Char was made by treating black liquor in Flow Reactor



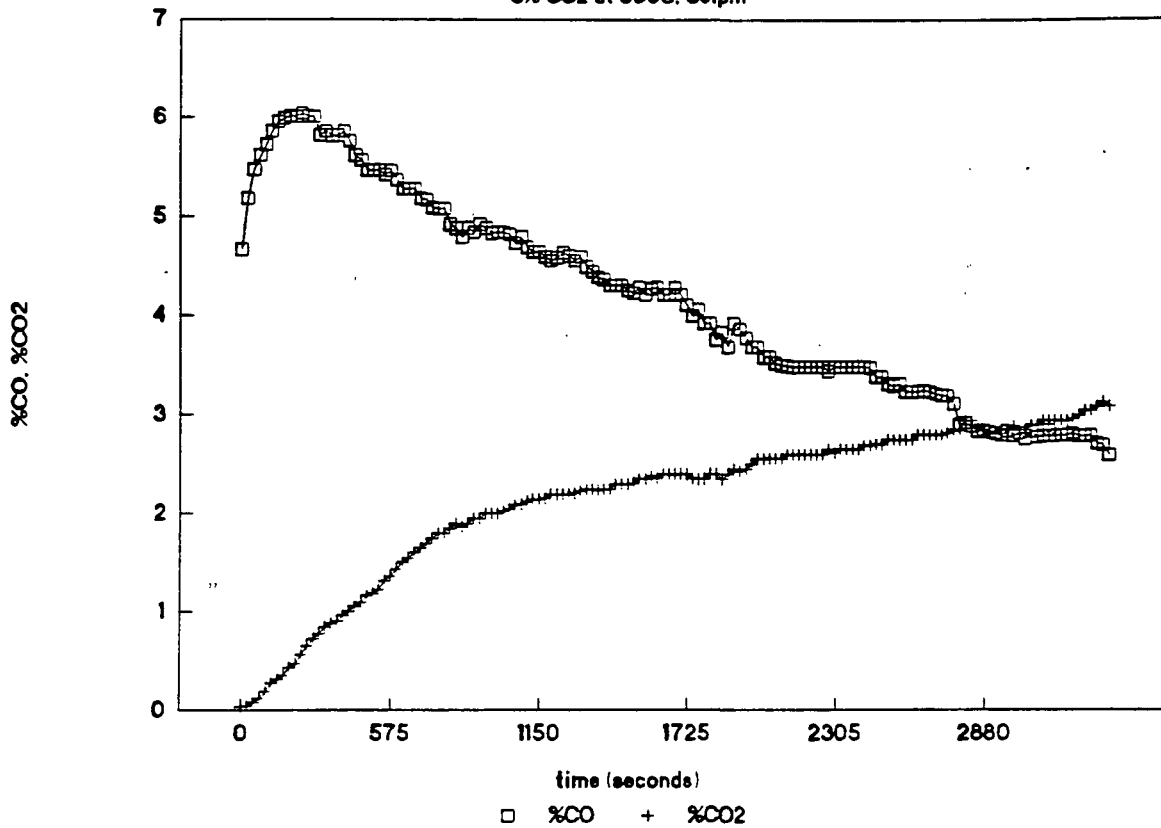
Experimental System
For Measurement of Gasification Rates

Recent Results

- * A test matrix of 12 experiments was completed
- * Preliminary rate data obtained for the reaction
 $\text{CO}_2 + (\text{BL-char-C}) \rightarrow 2\text{CO}$

Experiment #5: B.L. Char Gasification

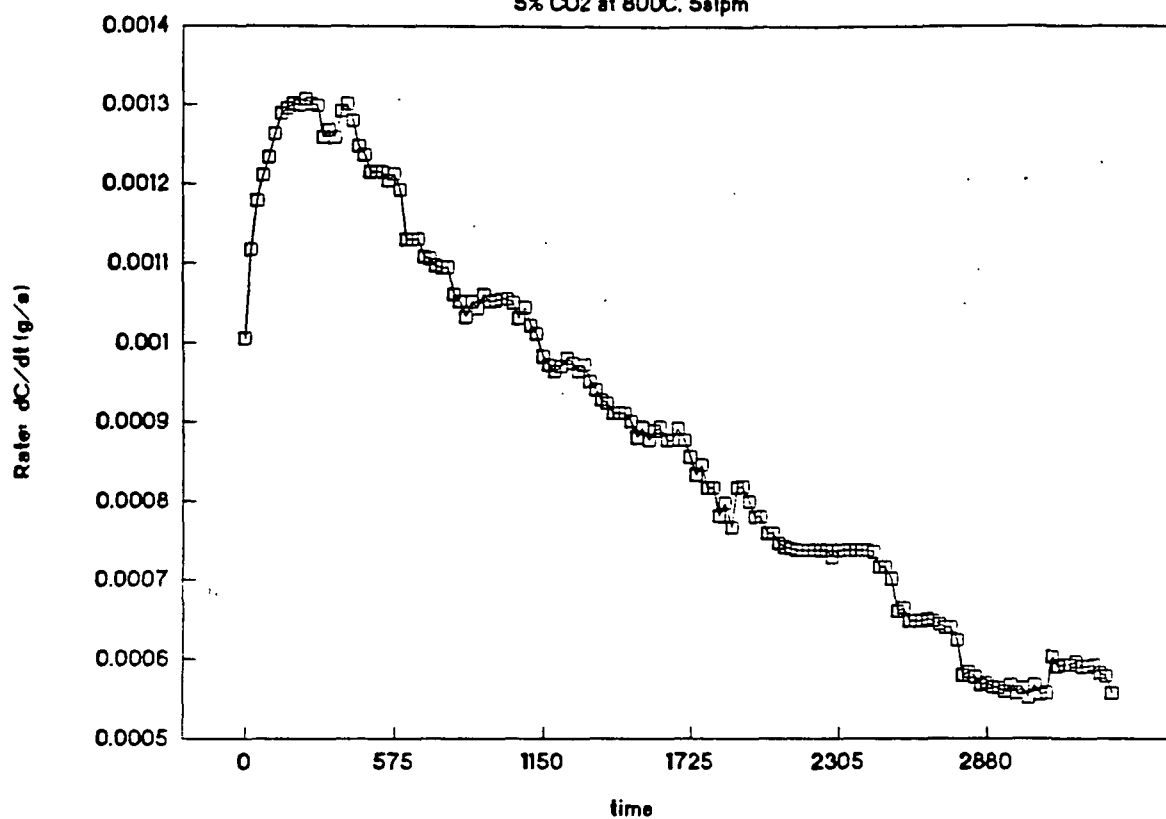
5% CO₂ at 800C, 5slpm



Sample of the raw data collected for for each gasification test.

Experiment #5: B.L. Char Gasification

5% CO₂ at 800C, 5slpm



Rate of CO₂ + (BL-char-C) ---> 2CO, as determined from CO concentration data.

Future Plans

- * Continue analysis of present data
- * Determine (if possible) from this data whether observed gasification rate is limited by mass transfer
- * CO₂ gasification rate at temperatures above 800 °C
- * H₂O rate measurements
- * Gasification rates for other Kraft Black Liquor chars

Fume Formation

Objective: To determine when and to what extent fuming occurs during the different stages of black liquor droplet combustion. To hypothesize mechanisms of fume formation. To determine the effects of combustion conditions on fuming rate.

Value: Fuming rate is expected to increase with increasing levels of solids firing. Controlling fuming rate may require knowledge of the mechanism of fume formation. Empirical knowledge of fuming rates is required if sodium species are to be included in mathematical modeling of recovery furnaces.

Prior Results

- * Droplet combustion furnace designed and constructed
- * Several trials of black liquor droplet combustion conducted over a range of flow conditions (600-900 °C, 2-6 ft/s)

Future Plans

- * Construct and install fume filter tape drive mechanism
- * Compare furnace response and operation with past data
- * Obtain liquors with known compositions
- * Conduct experiments to determine time and duration of fuming events
- * Hypothesize mechanisms of fume formation

Fume Monitoring by Laser Scattering

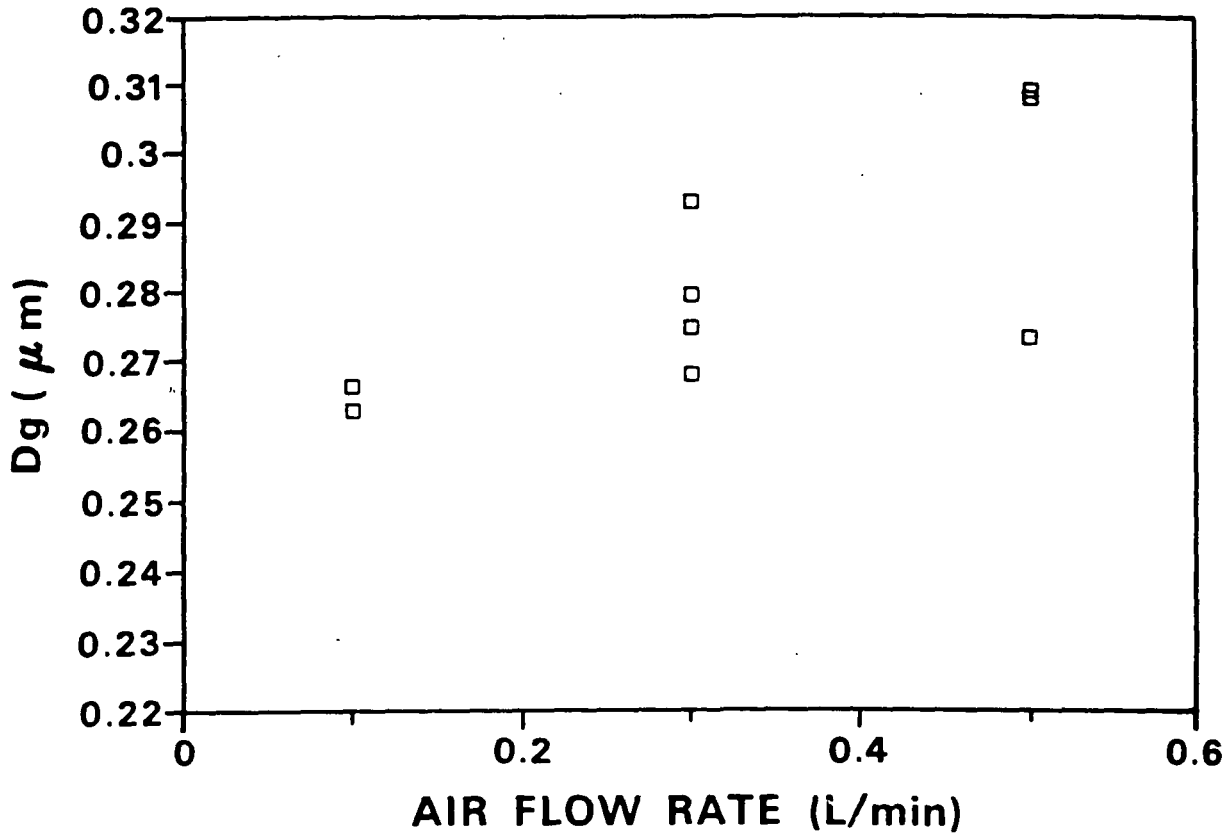
Objective:

- To develop a non-intrusive fume sensor for use on the Black Liquor Flow Reactor.
- To quantify fuming rate, particle size, and particle size distribution

Value:

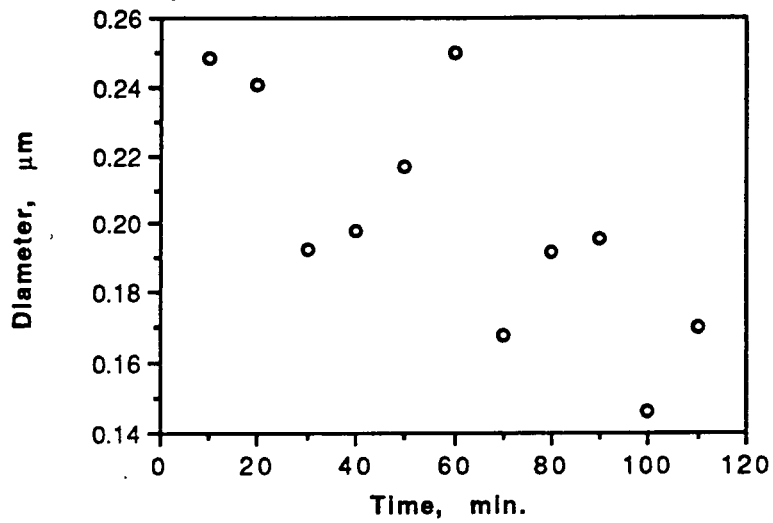
- Continuous monitoring of fume
- No agglomeration or other effects associated with filters

AIR EFFECT ON FUME PARTICLE SIZE



Laser scattering measurement of synthetically generated fume. Each data point required a single angle measurement, since a value for standard deviation was assumed.

Variation in Fume Diameter



Laser scattering measurement of synthetically generated fume. Each data point required two measurements, one at each of two angles, so that particle size and standard deviation could be determined simultaneously.

Conclusions

- * Laser scattering method has yielded reproducible data from synthetic fume when standard deviation and refractive index of particles are known (or assumed)
- * Accuracy of multiple-angle measurements is unacceptable

Present Status

Utility of the method may not be worth the time and expense required for continued development

- Method will have limited application, laboratory only
- Remaining development work will be extensive, with unknowns
- Other methods are available for fume size and concentration measurements

Feasibility of Incineration of Concentrates
From Bleach Plant Effluents

(Project 3671, NCASI funded)

Ken Nichols

Assistant Professor

IPST Project Advisory Committee Meeting

Atlanta, GA

March 20, 1990

Incineration of Bleach Plant Effluents

Objective: Evaluate potential technologies for thermal destruction of chlorine-containing concentrated streams from closed cycle processes in a device other than the kraft recovery furnace.

Value: Treatment methods such as ultrafiltration and reverse osmosis which could be used to treat bleach plant effluents have not been widely accepted, in part due to a lack of acceptable means of disposal of the concentrate which is produced

Recent Activity

- * Bleach plant effluents (C_D and E₁) obtained from a kraft pulp mill
- * Lab-scale filtration device leased, capable of ultrafiltration and reverse osmosis

Future Plans

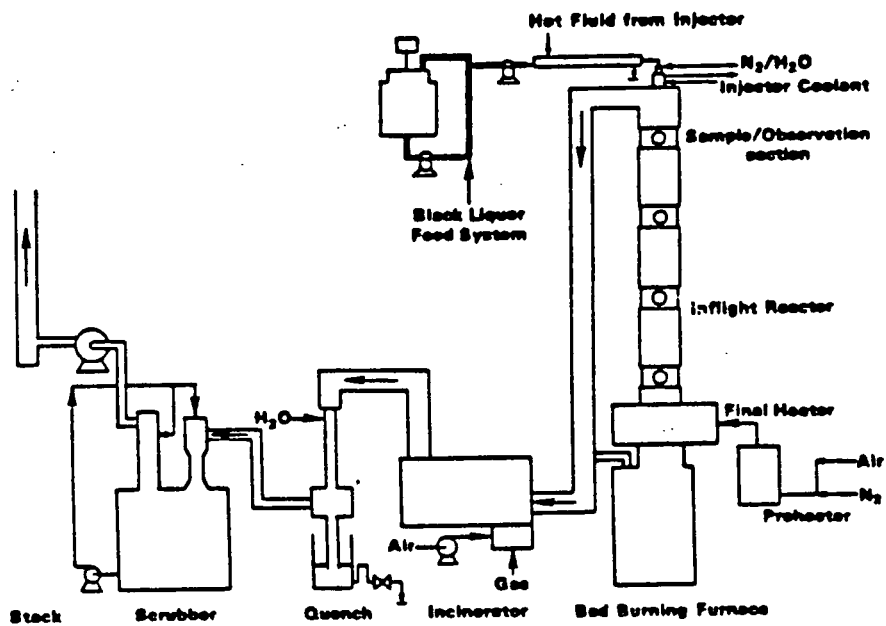
- * Treat effluents with lab-scale ultrafiltration and reverse osmosis.
- * Characterize concentrates
 - elemental composition (C,O,H,Na,Cl,S,)
 - physical properties (heating value, viscosity)
 - combustion behavior
 - determination of thermal destruction behavior
 - ash composition and melting temperature
 - determination of fate of chlorine

PROJECT 3473-6
(DOE FUNDED)

IN-FLIGHT DROPLET DRYING WITH HIGH
SOLIDS BLACK LIQUOR

OBJECTIVE: Measure in-flight droplet processes

- at high solids (<70%)
- vary feed liquor viscosity by adjusting feed liquor solids and temperature



IPC Phase I process flow reactor system in upflow mode.

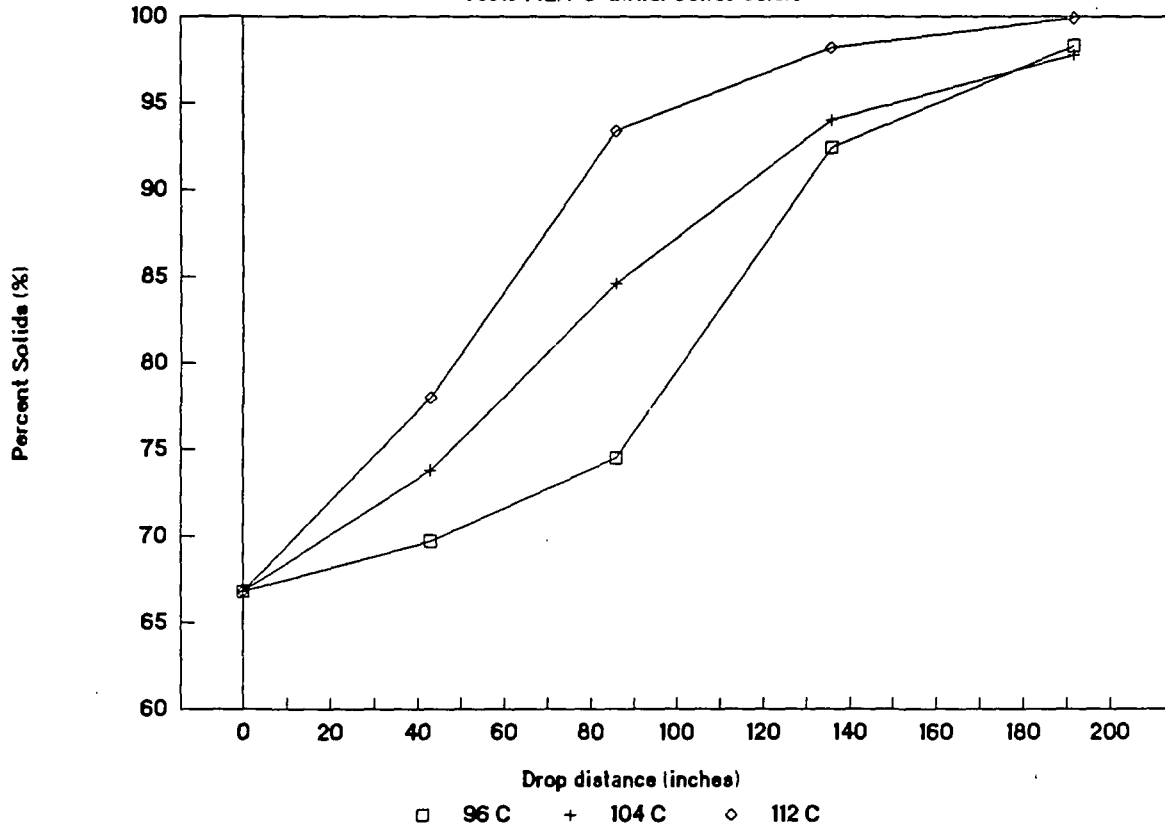
TEST CONDITIONS:

Initial Black Liquor Solids (%)

	66.8%	71.0%	74.9%
	-----	-----	-----
Temperature	96	104	112
	100	108	117
	112	120	127

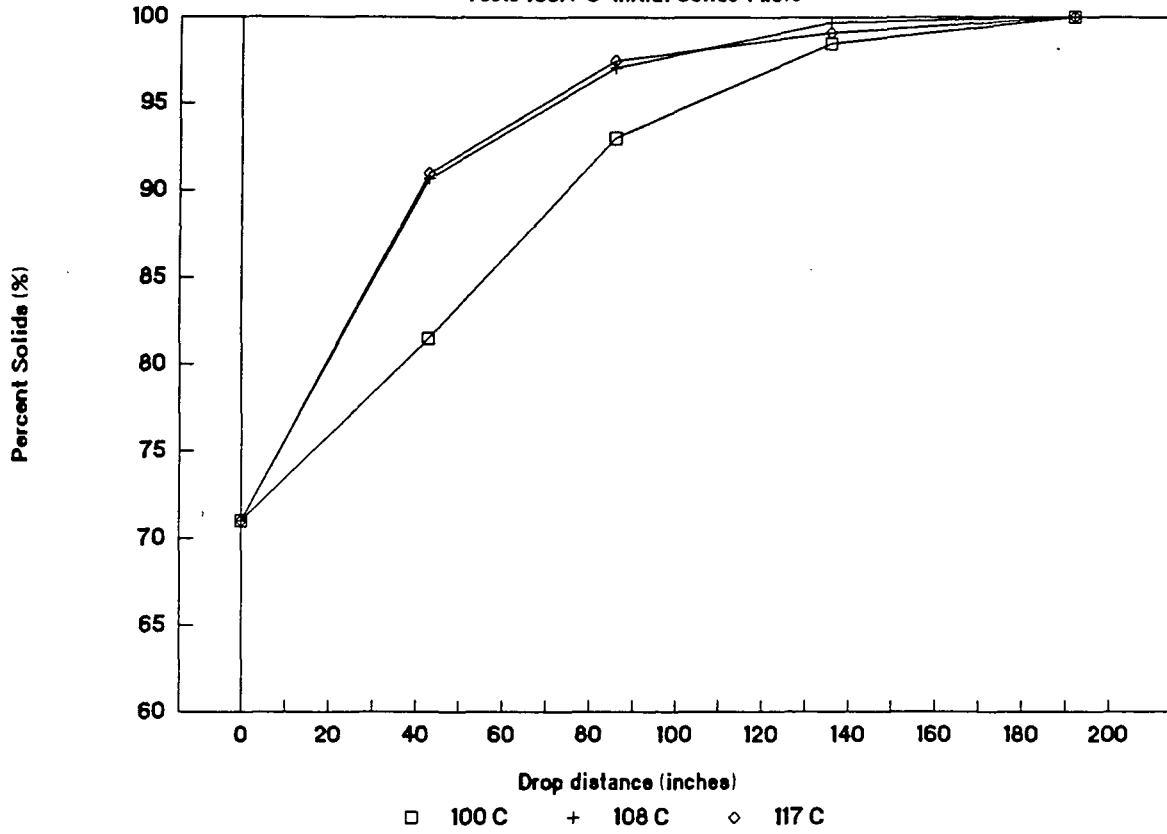
DROPLET DRYING

Tests 142A-C Initial Solids 66.8%



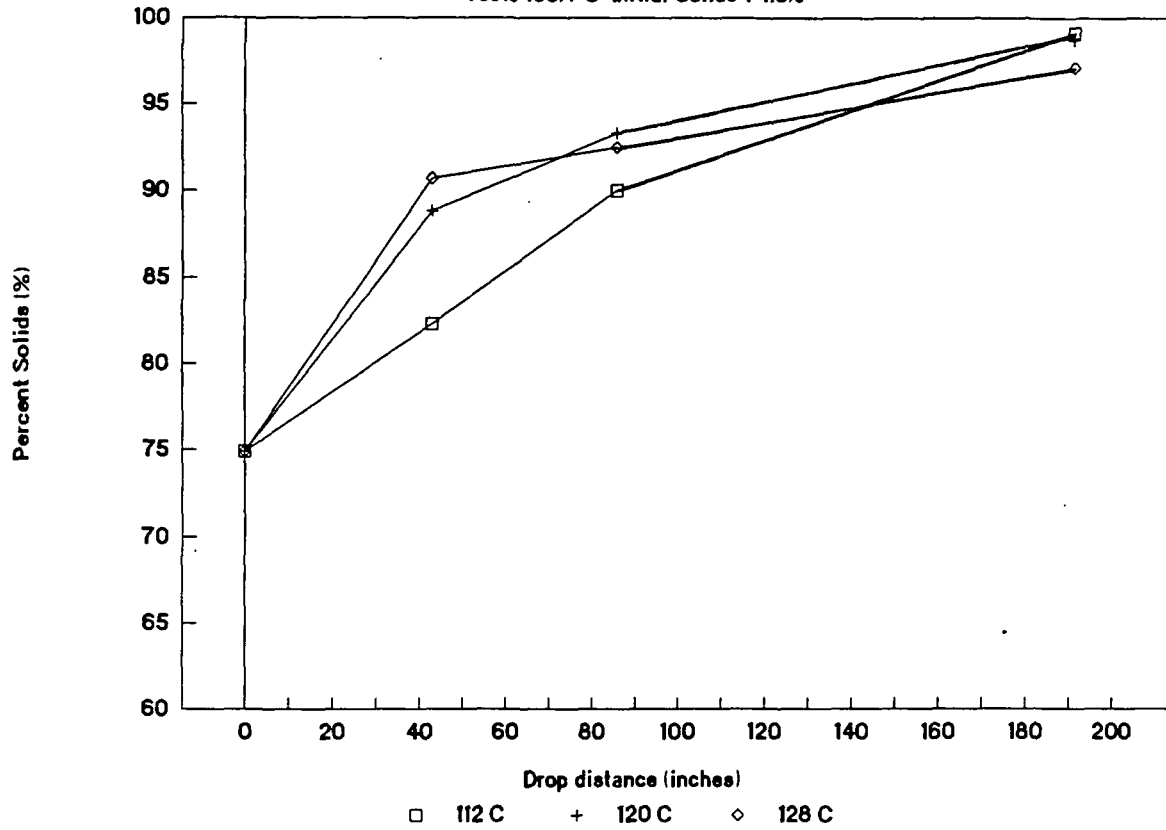
DROPLET DRYING

Tests 166A-C Initial Solids 71.0%



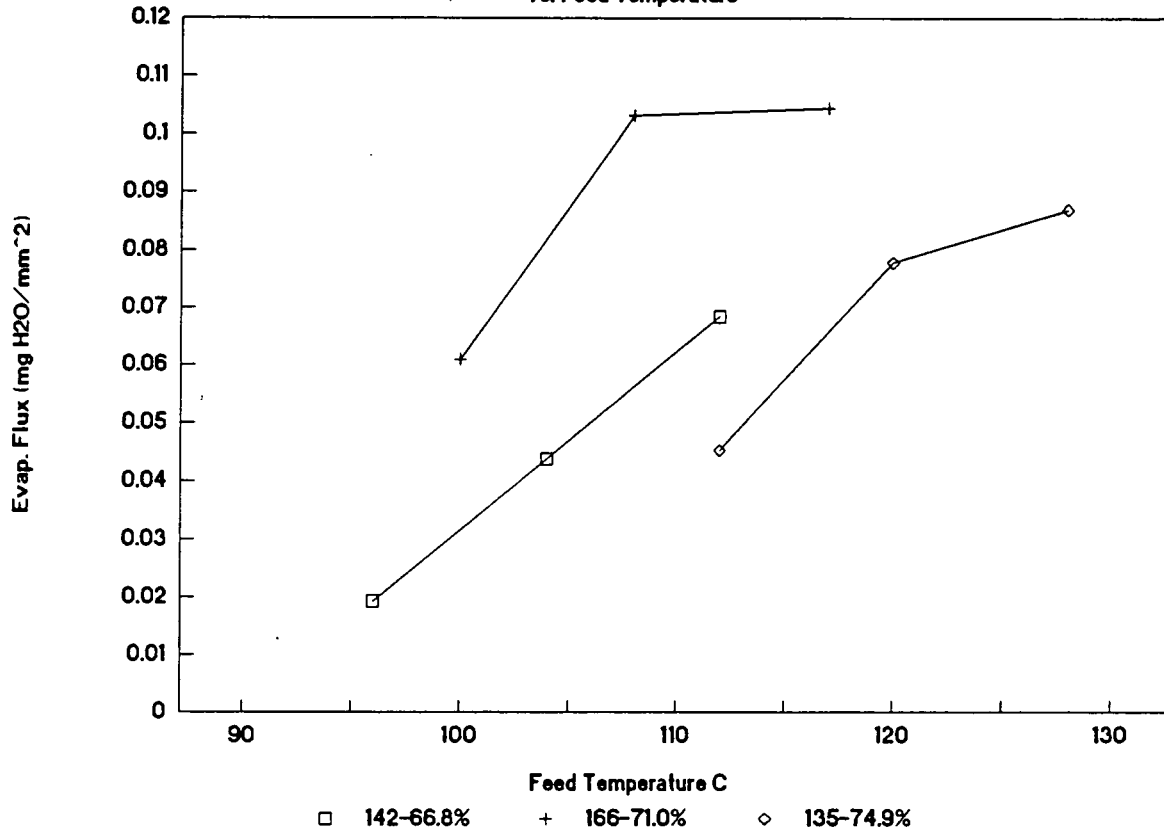
DROPLET DRYING

Tests 135A-C Initial Solids 74.9%



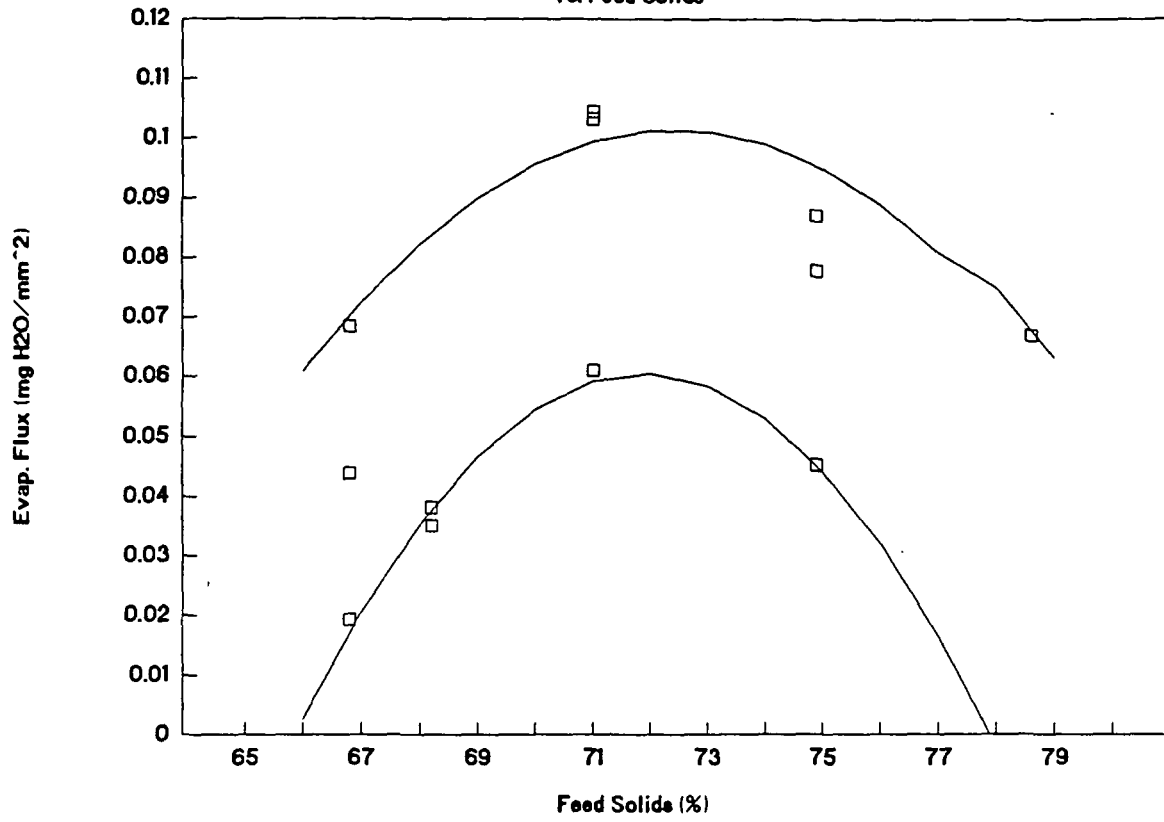
Drop Drying Rate

Vs. Feed Temperature



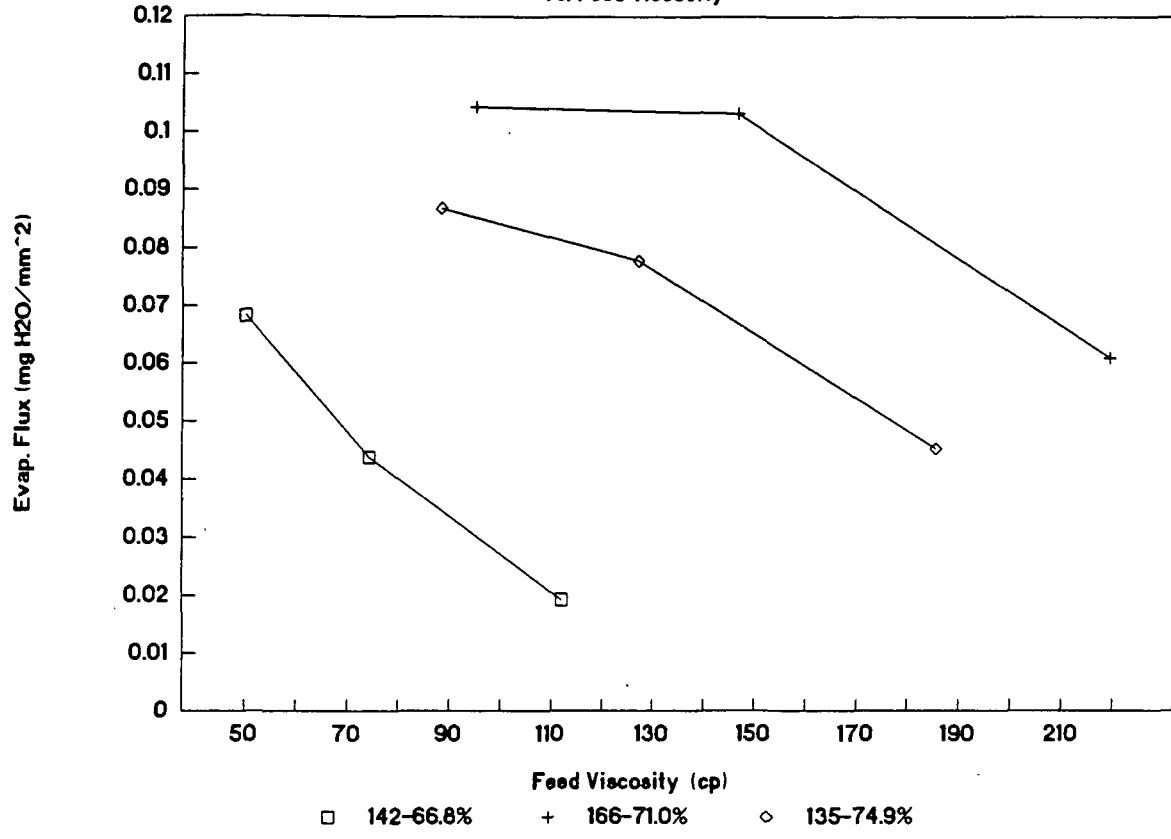
Drop Drying Rate

Va. Feed Solids

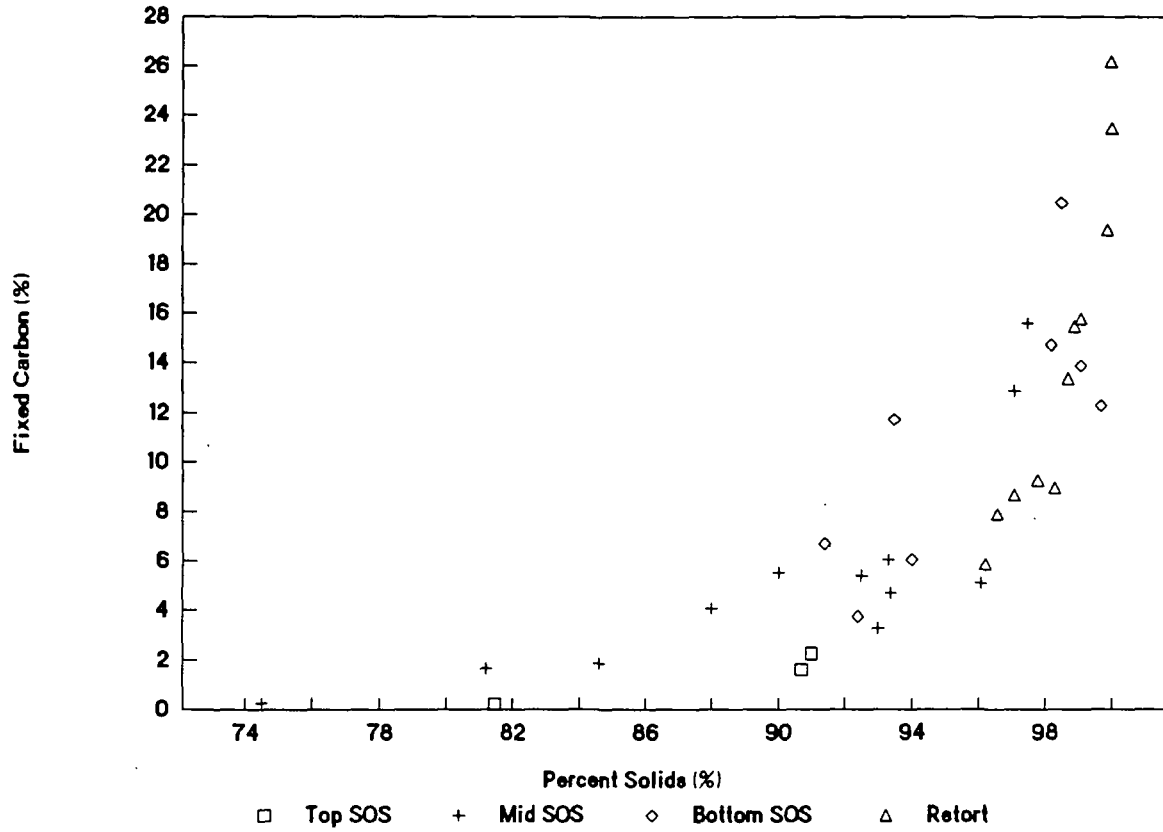


Drop Drying Rate

Va. Feed Viscosity



Fixed Carbon vs. Solids



CONCLUSIONS

1. Higher black liquor feed temperatures increase the droplet drying rate.
2. This data indicates that there is a maximum drying rate at about 71% solids.
3. Pyrolysis starts when drops have dried to at least 80% solids and proceeds rapidly above 90% solids

BLACK LIQUOR DELIVERY SYSTEMS
(Project 3657-2)

Terry Adams
Tom Spielbauer

PAC Meeting Presentation
March 20, 1990

Jeff Empie

Objective: Develop the optimum black liquor delivery system for the current kraft recovery boiler by establishing the conditions for obtaining a controlled, well-defined, narrow droplet size distribution.

Technical Basis:

- * Flow/Pressure Drop Characteristics
- * Fluid Sheet Thickness
- * Droplet Size Distribution

VALUE:

- . Increased thermal efficiency potential estimated at 0.7 MM BTU/ADT, or about \$100 MM/yr.
- . Increased process productivity potential of 1%, equivalent to about \$100 MM/yr.
- . Enhanced potential for equipment design and process control improvements

FLOW/PRESSURE DROP CHARACTERISTICS

Flow Coefficient:

$$P = C_f \rho Vn^2/2$$

Where: P = pressure drop (Pa)

C_f = flow coefficient
(unitless)

ρ = fluid density (kg/m³)

Vn = fluid velocity at the
minimum flow area (m/s)

Function of Reynolds No:

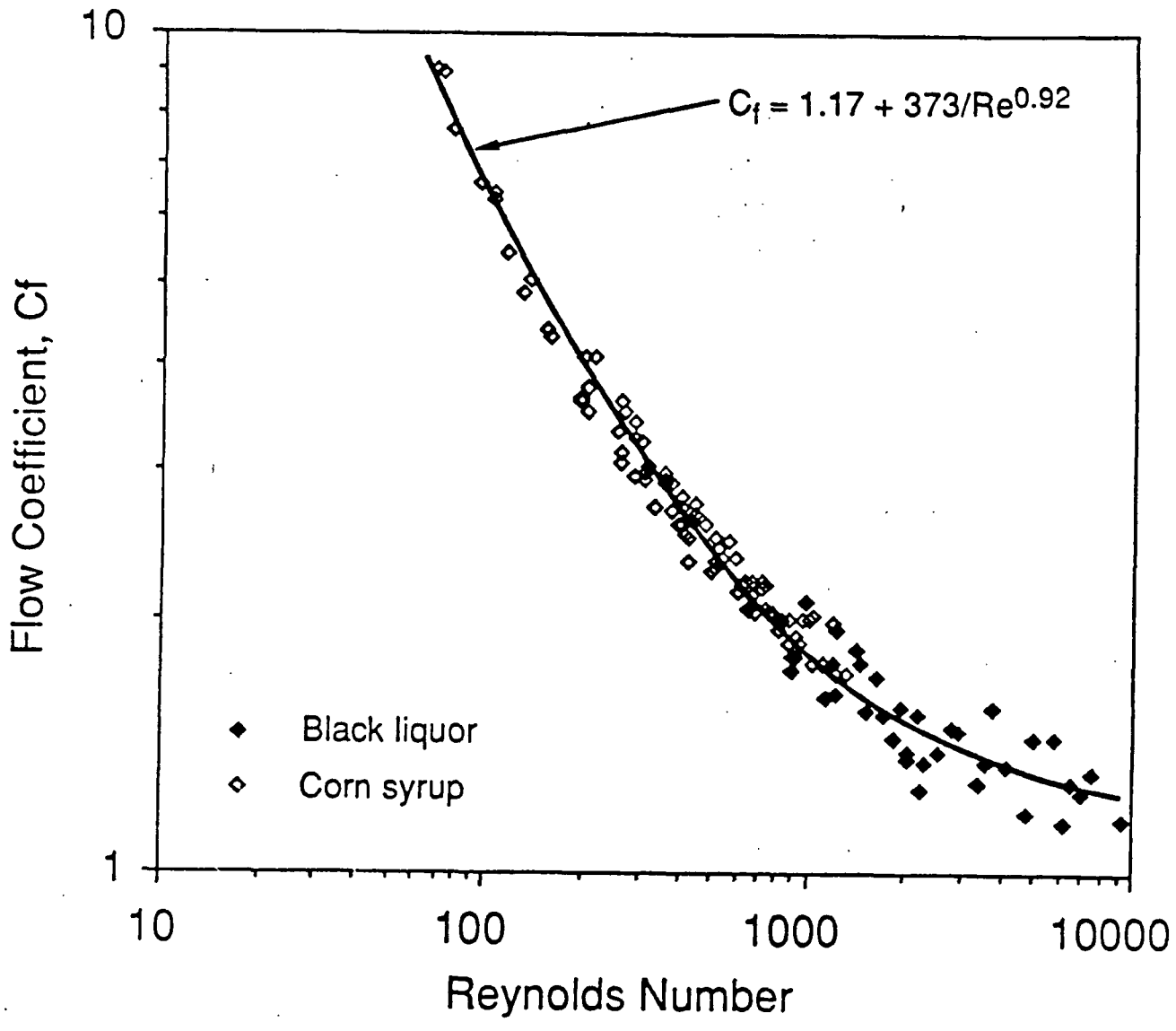
$$Re = DVn \rho/\mu$$

Where: D = diameter

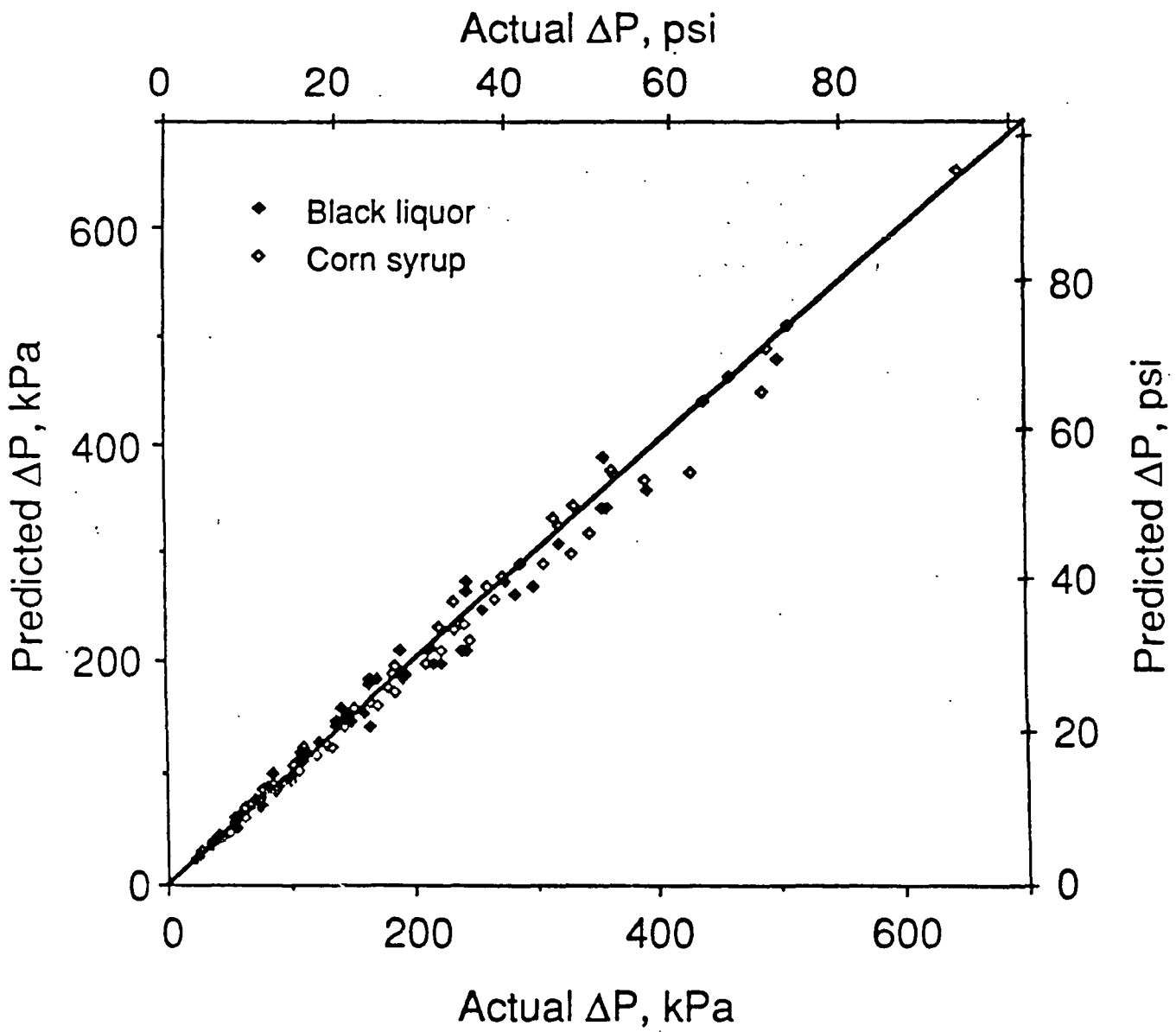
μ = fluid viscosity (kg/ms)

$$C_f = A + B \cdot Re^\alpha$$

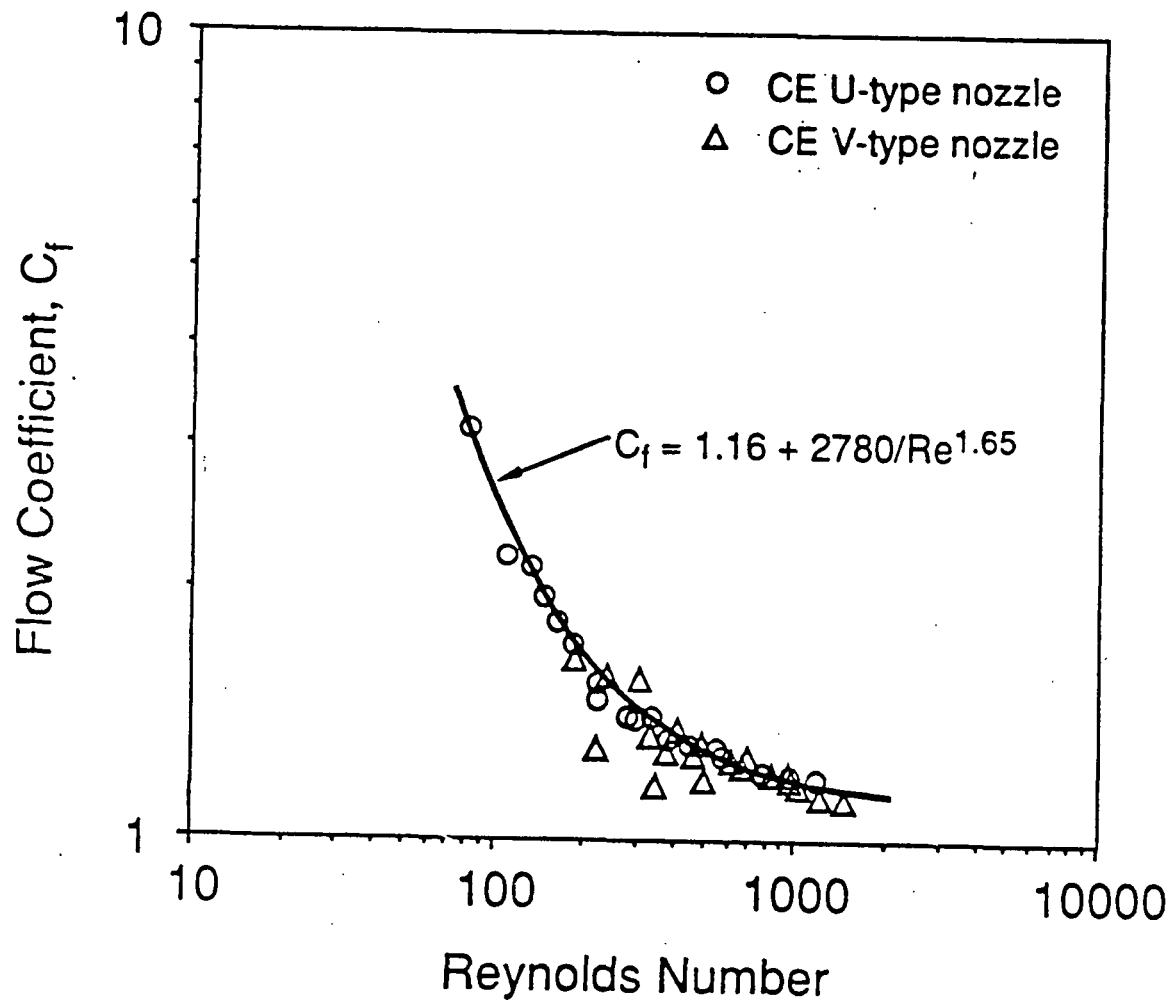
Where: A, B, α = constants



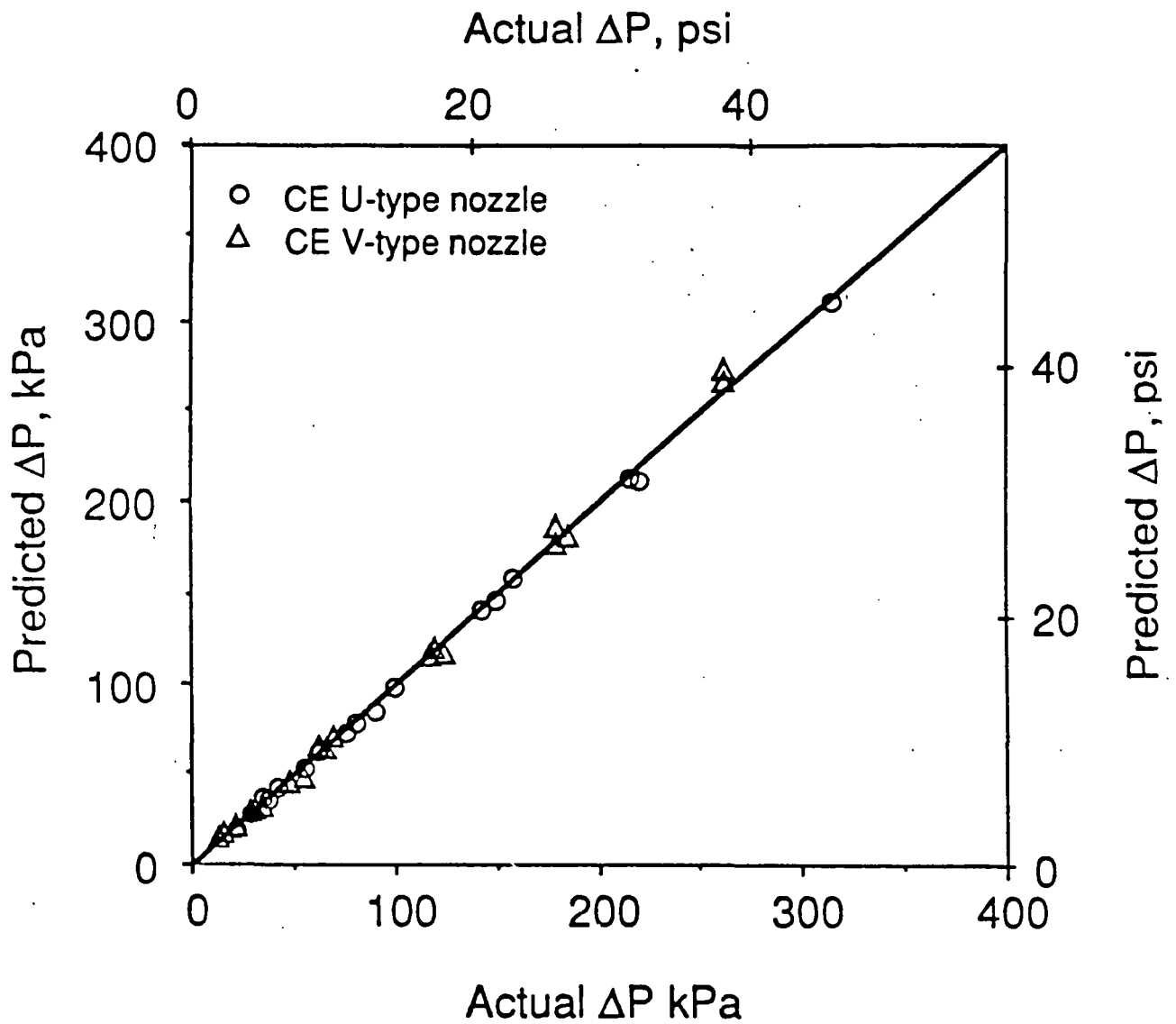
Flow coefficient data and correlation for two B&W splashplate nozzles using two working fluids -- black liquor and corn syrup.



Comparison of actual and predicted pressure drop for two B&W splashplate nozzles using two working fluids -- black liquor and corn syrup.



Flow coefficient data and correlation for a CE U-type and a V-type nozzle using corn syrup as a working fluid.



Comparison of actual and predicted pressure drop for a CE U-type and V-type nozzle using corn syrup as a working fluid.

CONCLUSIONS ON FLOW/ Δ P CHARACTERISTICS

- * Flow/ Δ P characteristics correlate with Reynolds Number
- * Flow coefficient correlates with two-term fit representing inertial acceleration and viscous losses
- * Viscous loss term is negligible at lower end of normal mill operating conditions
- * Because of constant acceleration term, B & W and CE U- and V- type nozzles should be insensitive to fluctuations in black liquor properties
- * CE swirl cone nozzle likely to be more sensitive; but more data are needed
- * Black liquor characterized well by low-shear Newtonian viscosity.

FLUID SHEET THICKNESS

Droplet Formation Mechanism (Splashplate Nozzle):

- * Splashplate produces a fluid sheet
- * Sheet expands as it moves away from nozzle
- * Sheet thins out
- * Aerodynamic forces produce waves in sheet
- * Perforations develop to random locations
- * Liquor between perforations collapses to form droplets

DATA CORRELATION

Reduced Sheet Thickness (Yr)

$$Yr = Y/D$$

Where: Y = sheet thickness
D = nozzle exit diameter

Reduced Surface Velocity (Vr)

$$Vr = V/Vn$$

Where: V = surface velocity
Vn = nozzle exit velocity

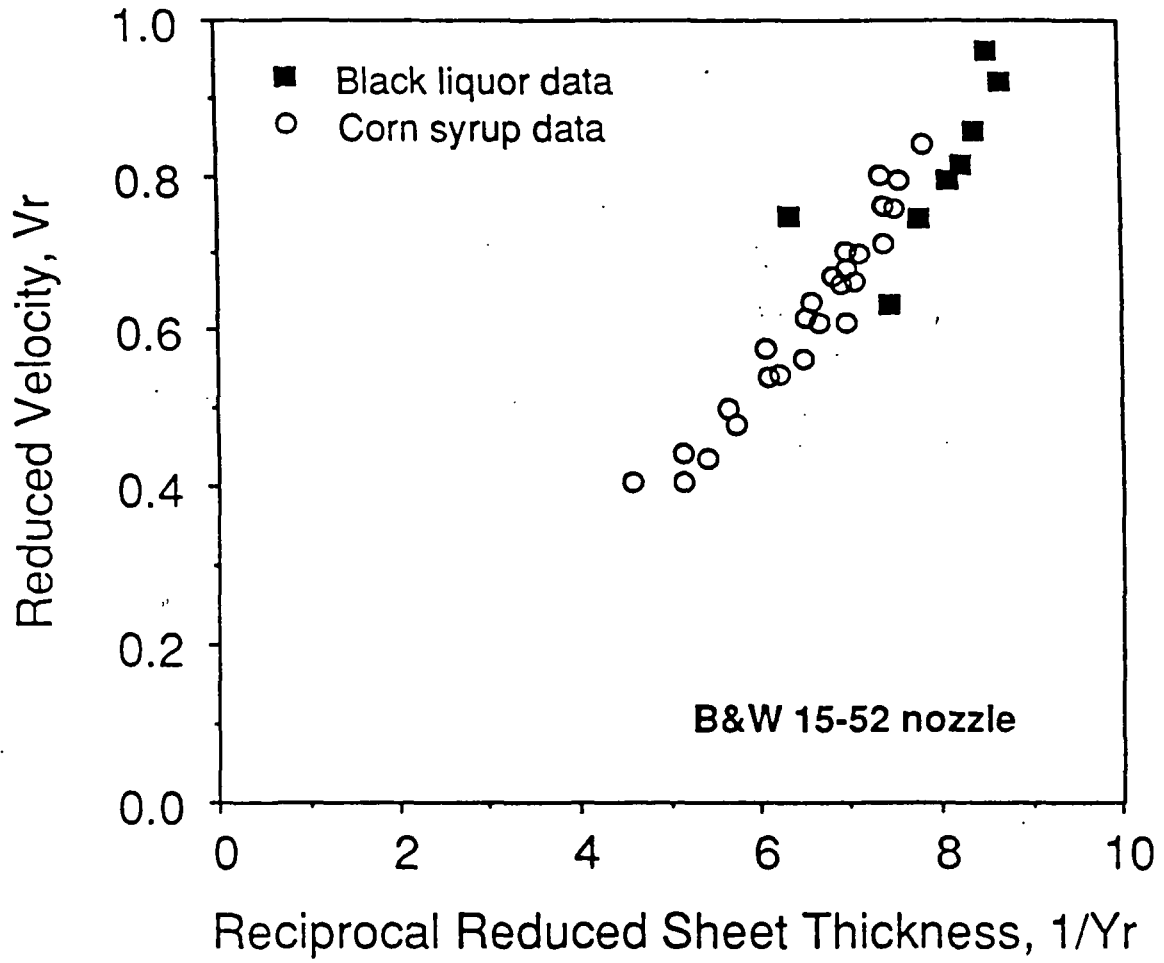
Assuming:

- * A linear velocity profile through sheet thickness
- * All viscous losses occur after point where sheet velocity is parallel to plate surface

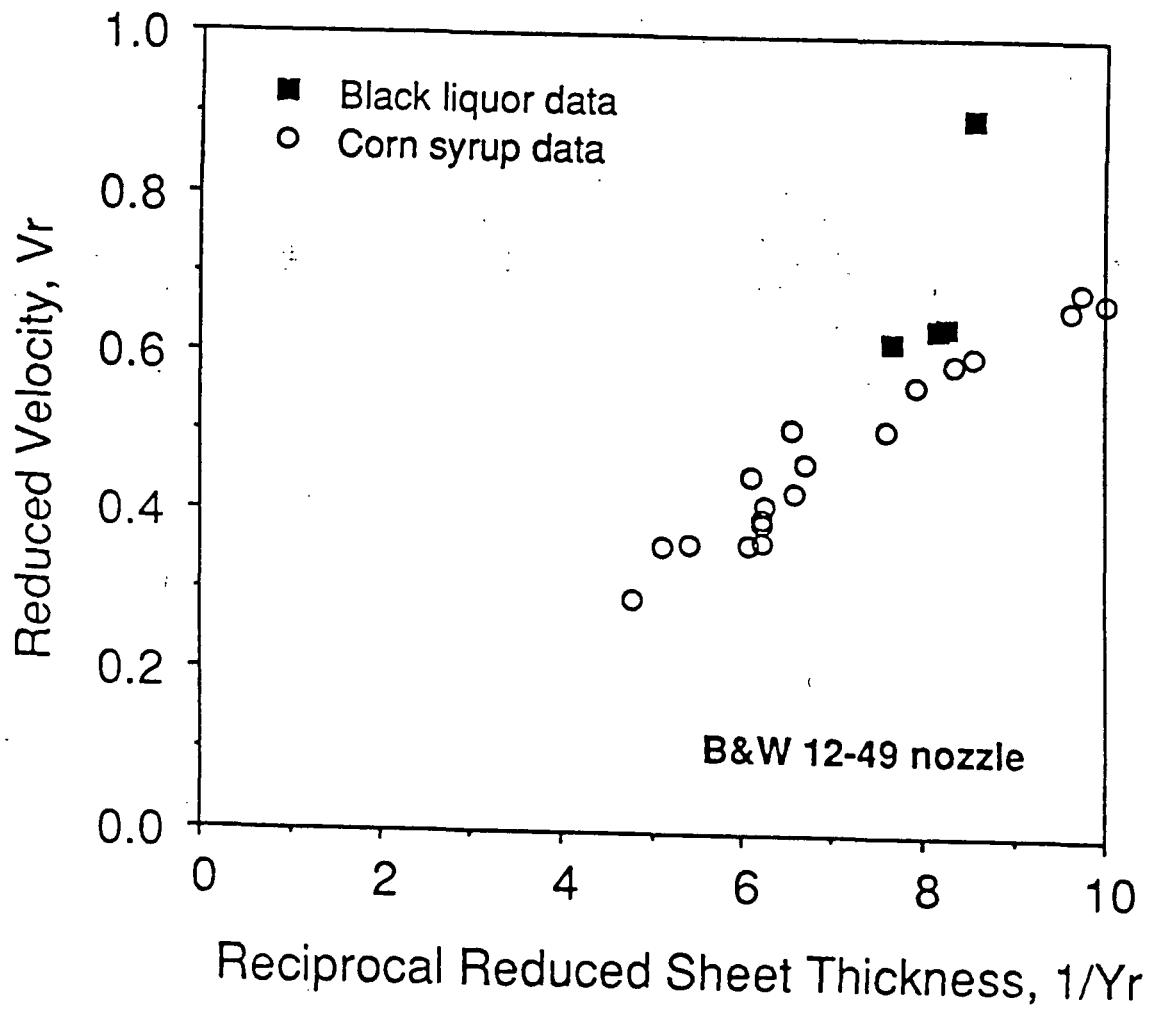
Continuity Considerations yield:

$$Vr = \frac{D}{8R Yr}$$

Where: R = radius along plate from stagnation point



Correlation between reduced sheet velocity and reduced sheet thickness based on the continuity equation for the B&W 15-52 nozzle.



Correlation between reduced sheet velocity and reduced sheet thickness based on the continuity equation for the B&W 12-49 nozzle.

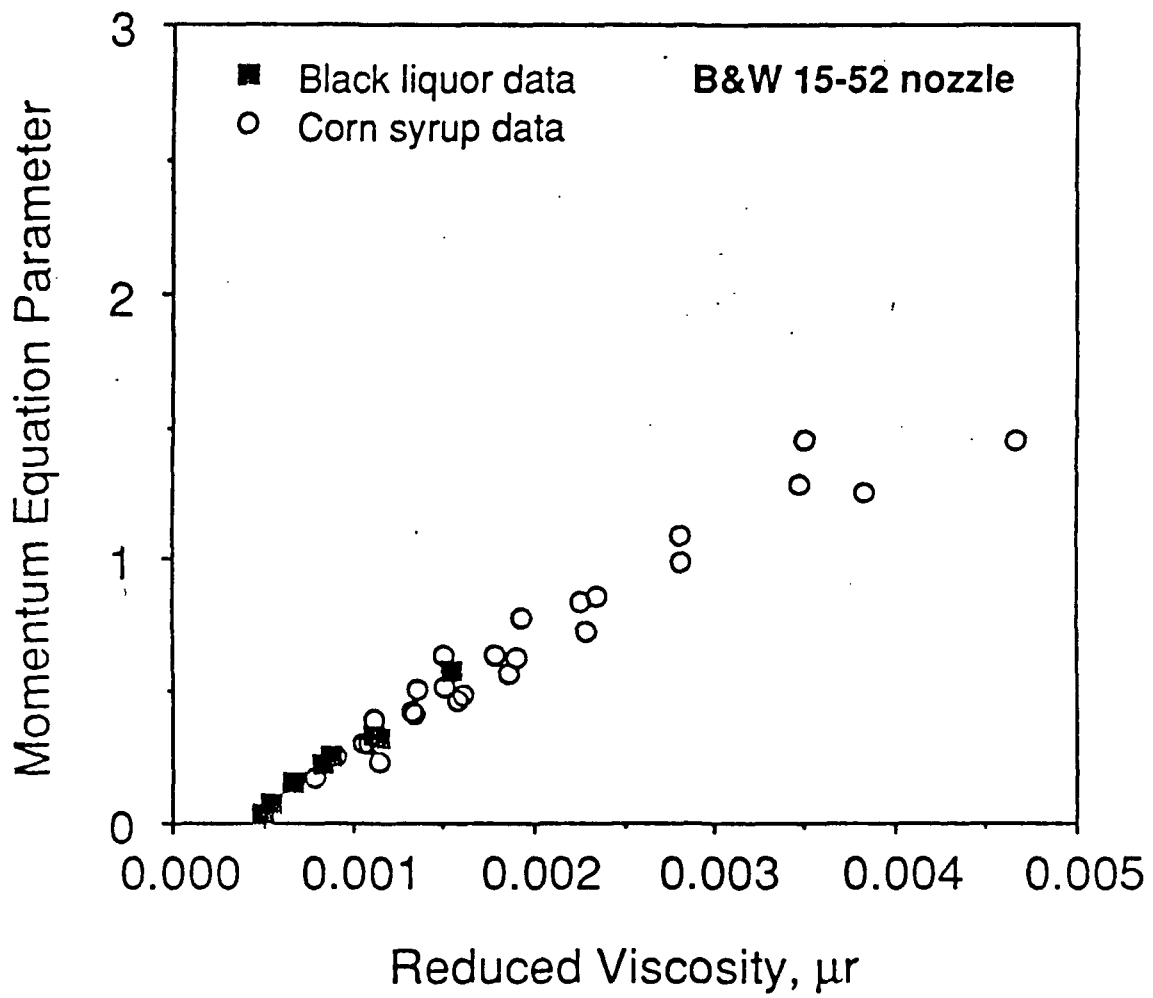
Momentum Considerations yield:

$$\frac{1}{V_r} = \mu_r C_1 + C_2$$

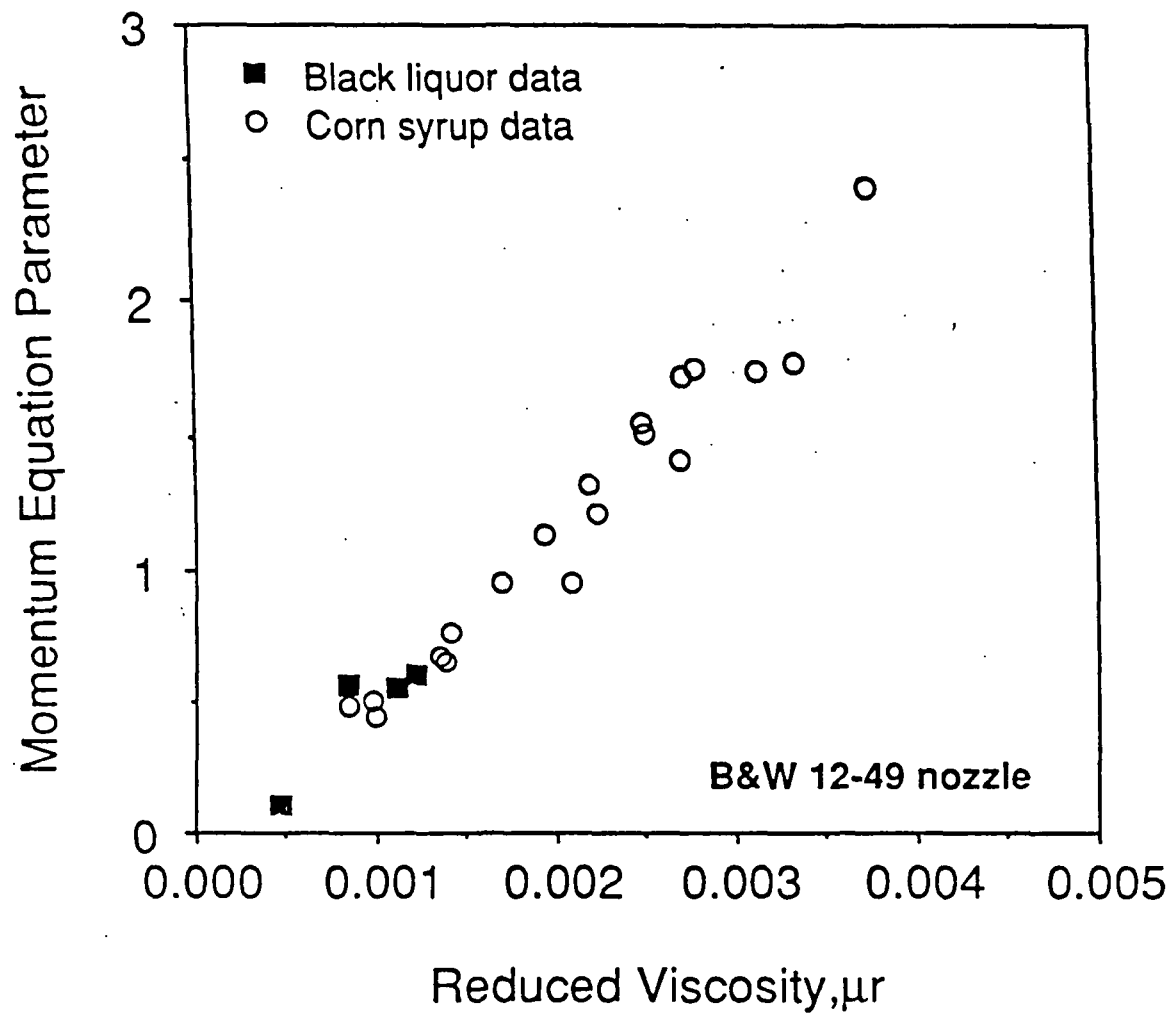
$$Y_r = \mu_r C_3 + C_4$$

$$Y_r(1-V_r) = \mu_r C_5 + C_6$$

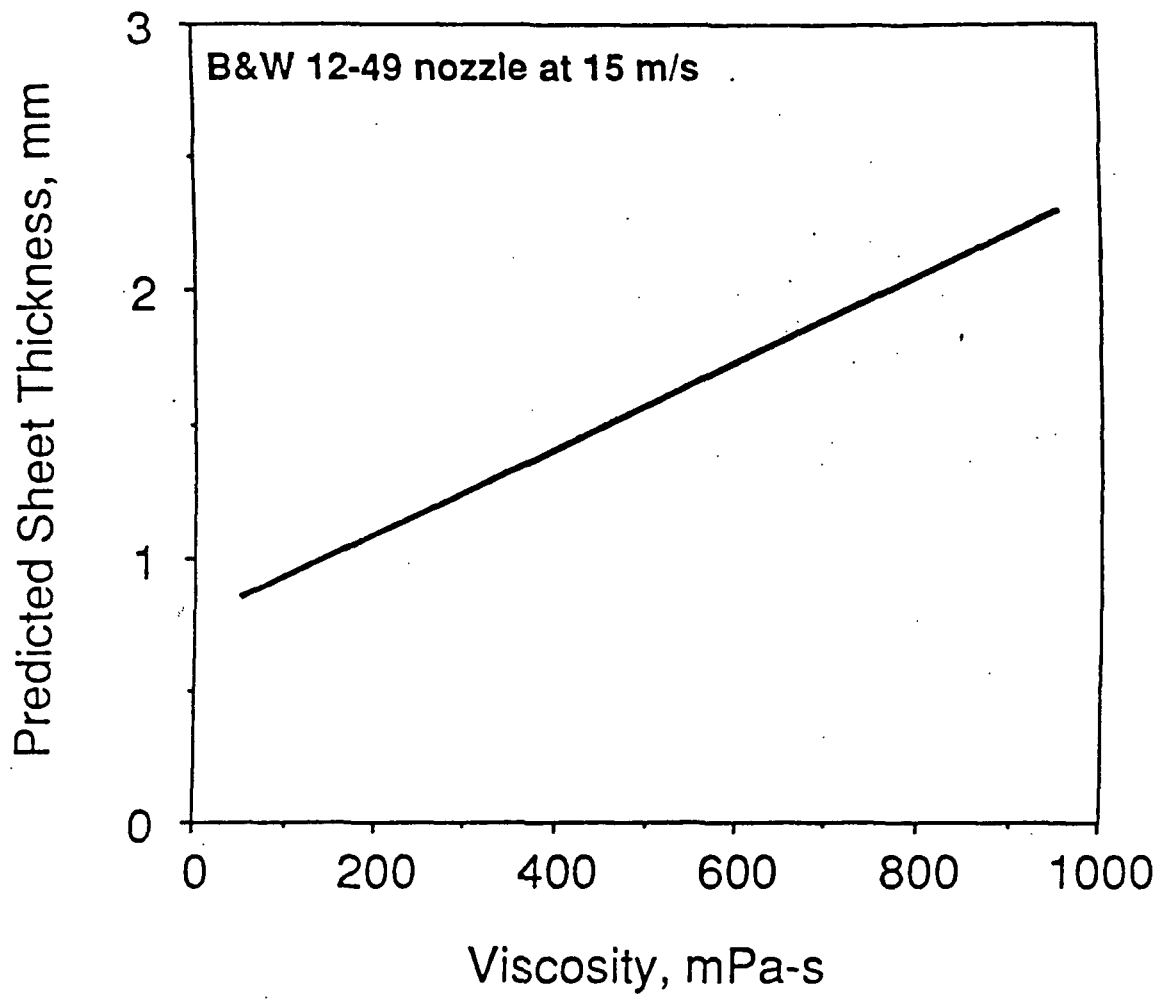
Where: μ_r = reduced viscosity
$$= \frac{\mu}{\rho D V_n}$$



Momentum equation parameter, $1/Vr-1$, as a function of the reduced viscosity for the B&W 15-52 nozzle.



Momentum equation parameter, $1/Vr-1$, as a function of the reduced viscosity for the B&W 12-49 nozzle.



Calculated sheet thickness as a function of fluid viscosity for a B&W 12-49 nozzle operating at 15 m/s (17 gpm).

CONCLUSIONS ON FLUID SHEET CHARACTERISTICS

- * Fluid sheet thickness and surface velocity decrease as the angle from the spray centerline increases
- * As viscosity increases, sheet thickness increases and surface velocity decreases
- * Sheet thickness and surface velocity are governed by mass and momentum balances
- * Sheet thickness is not very sensitive to fluid viscosity

DROPLET SIZE DISTRIBUTION

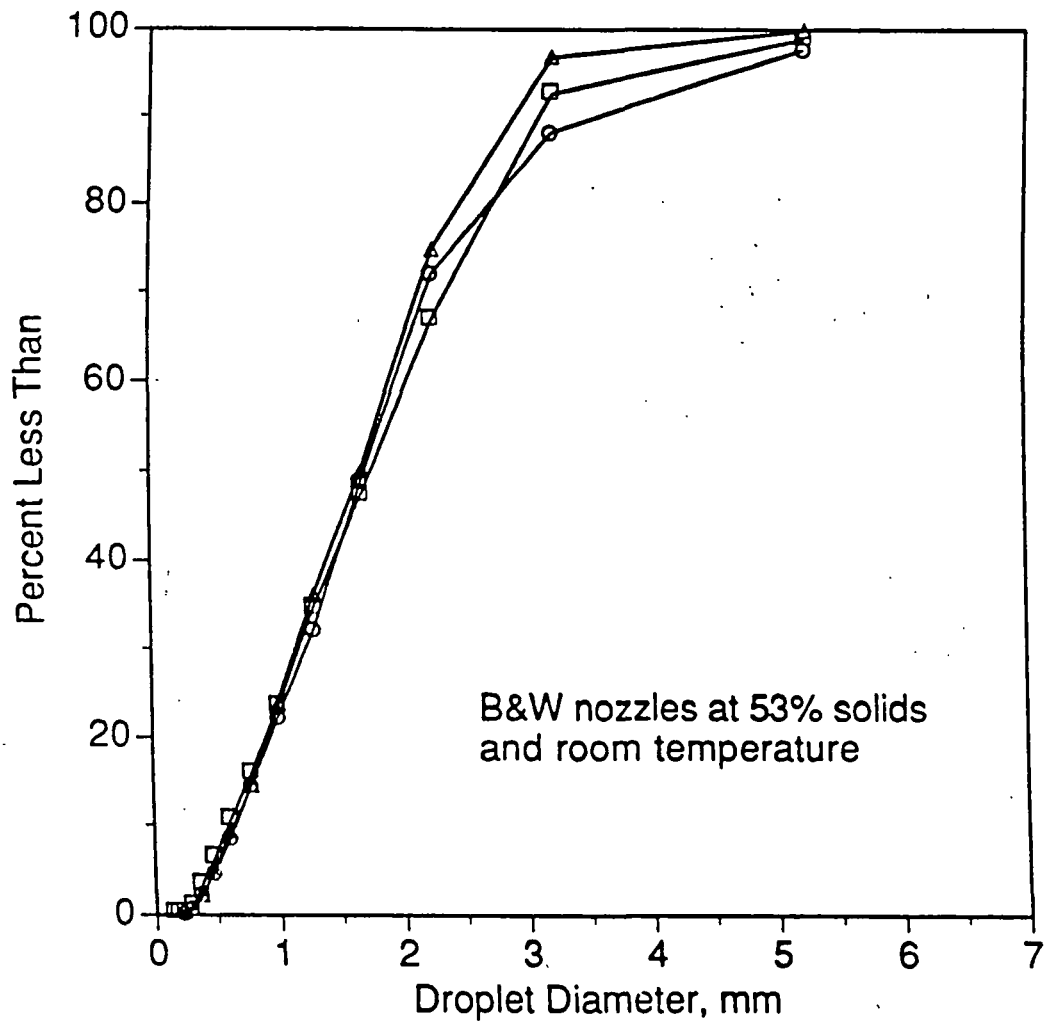
Tests conducted at IPST and B & W Alliance Research Center

Droplet size measured

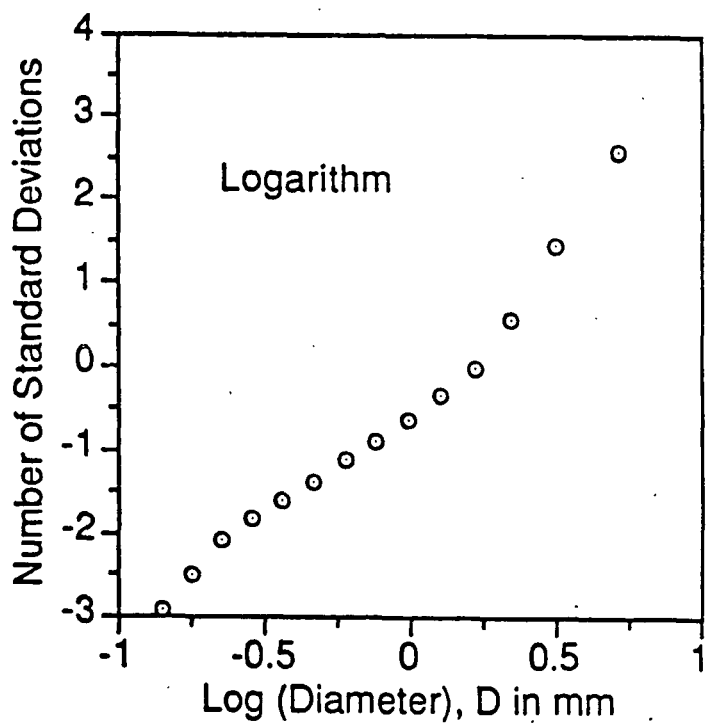
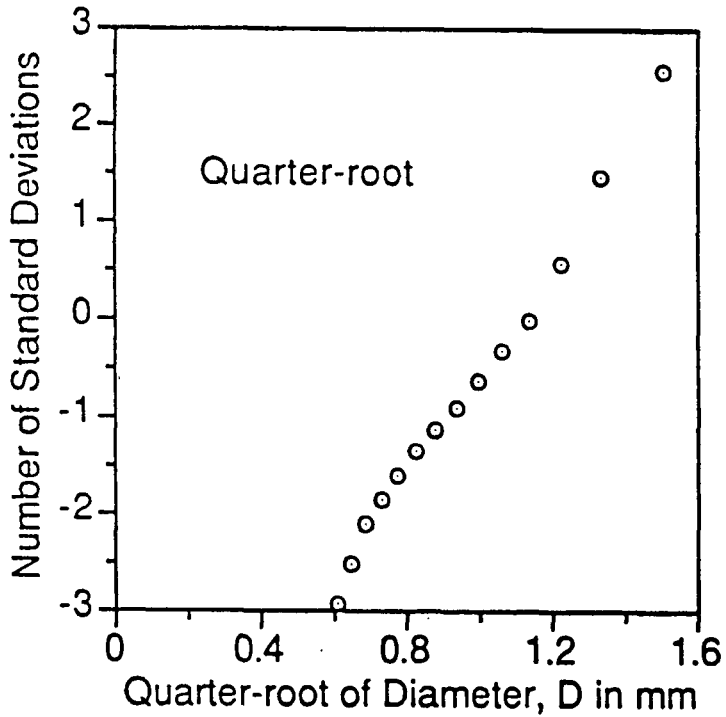
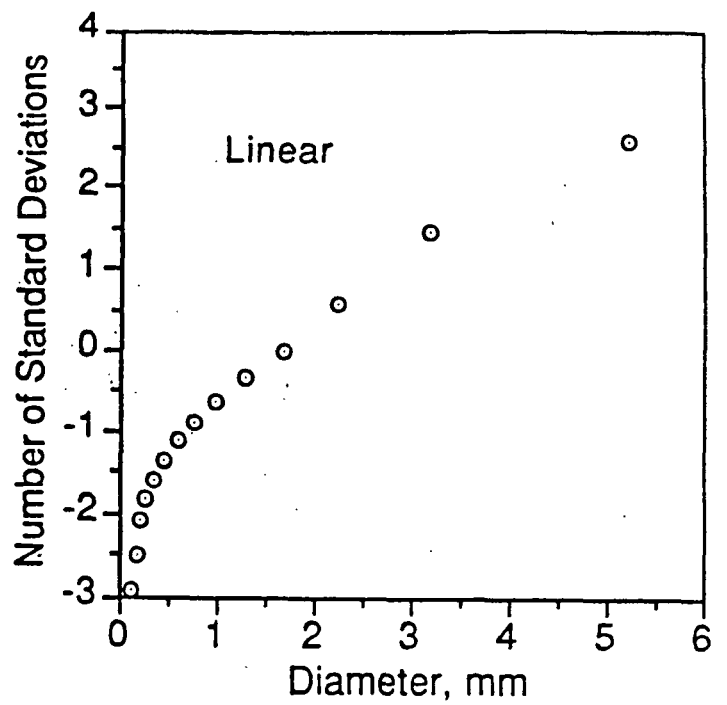
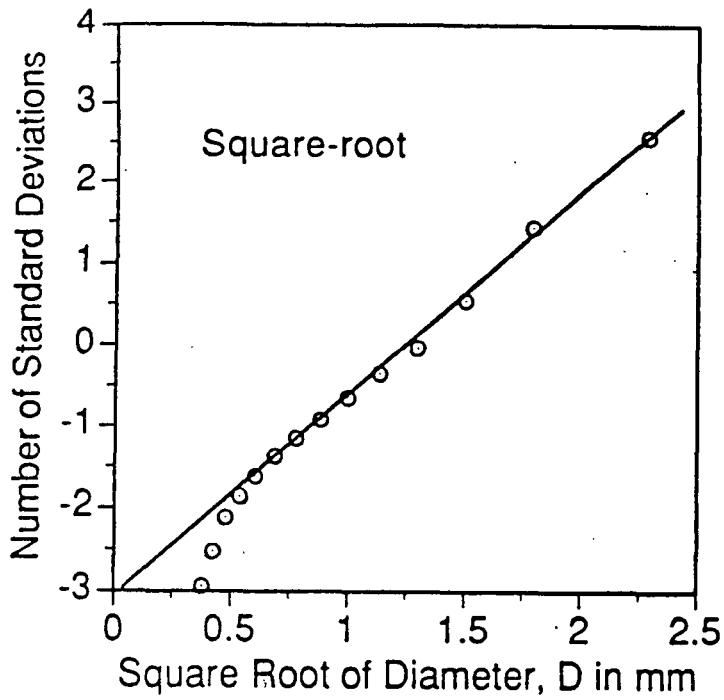
- 1.2m downstream of splashplate
- at spray centerline, edge, and intermediate location
- by Malvern ST2600 Droplet and Particle Size Analyzer
- using black liquor of 150 cP viscosity

Distributions examined

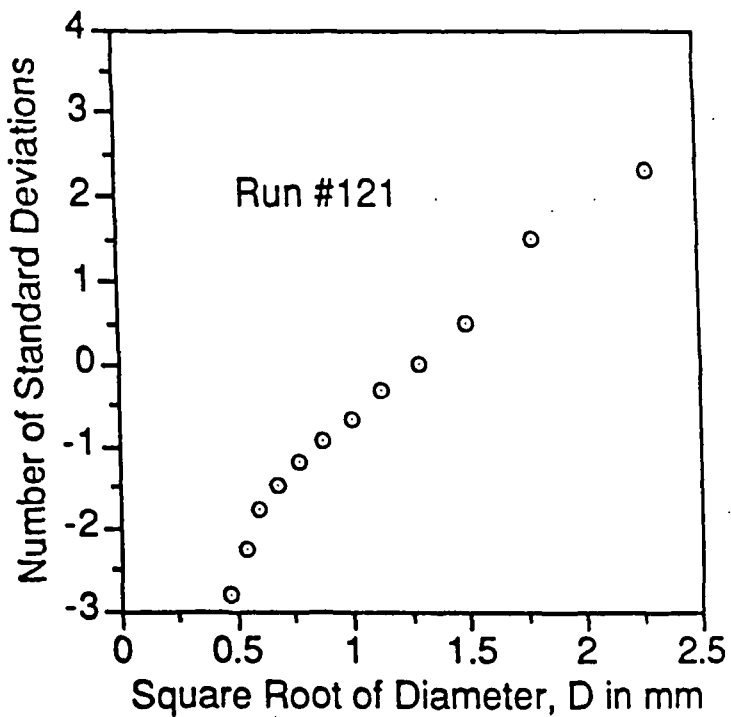
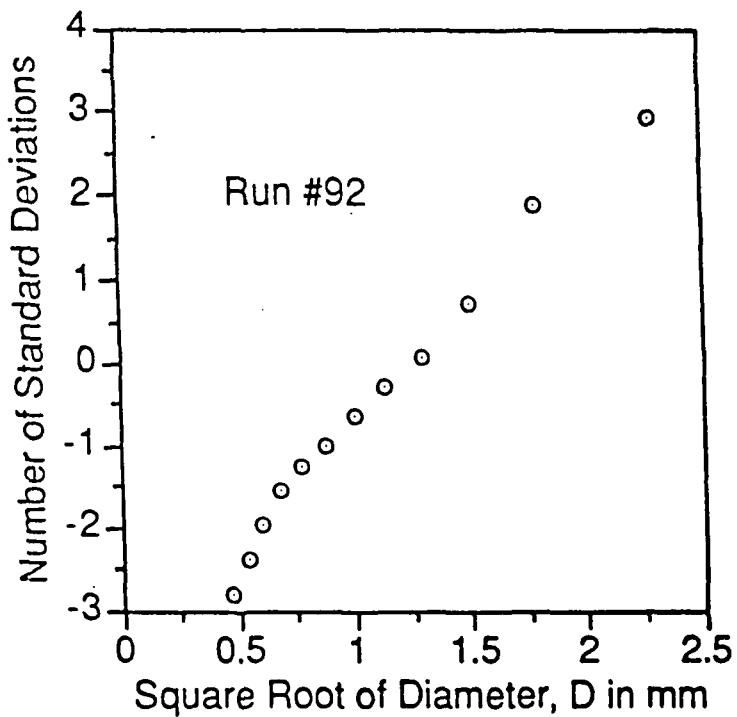
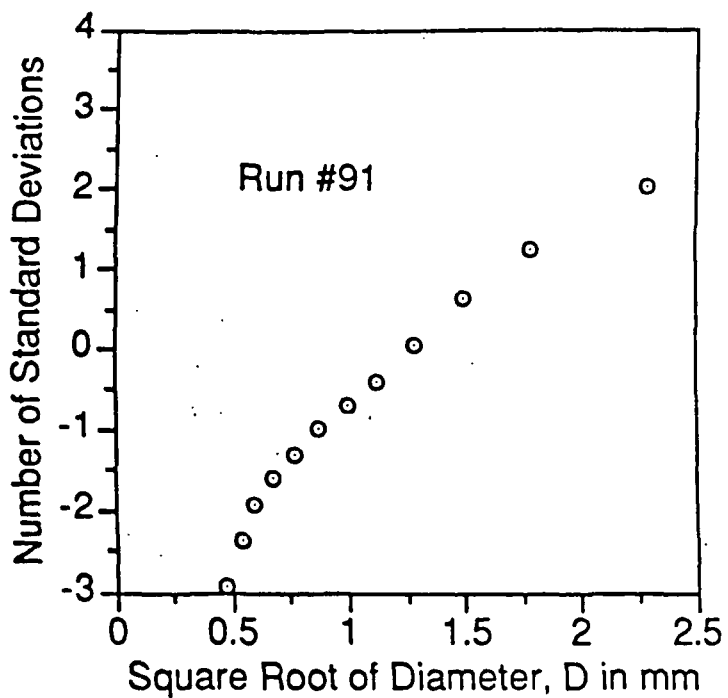
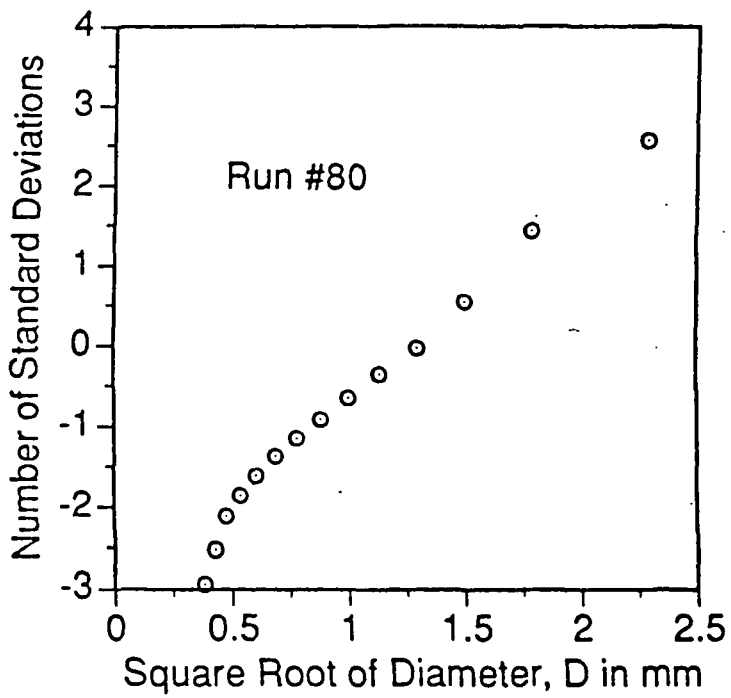
- Square root - normal
- Linear - normal
- Quarter root - normal
- Log - normal



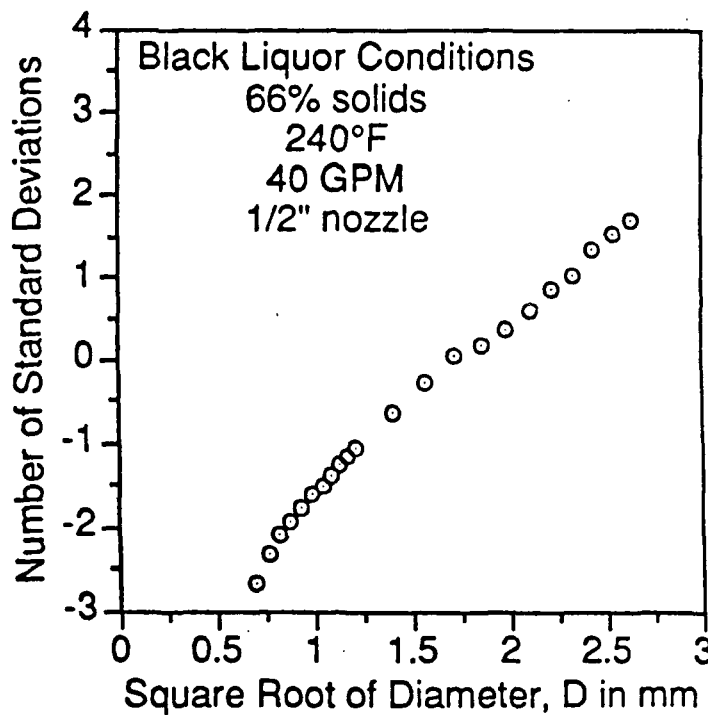
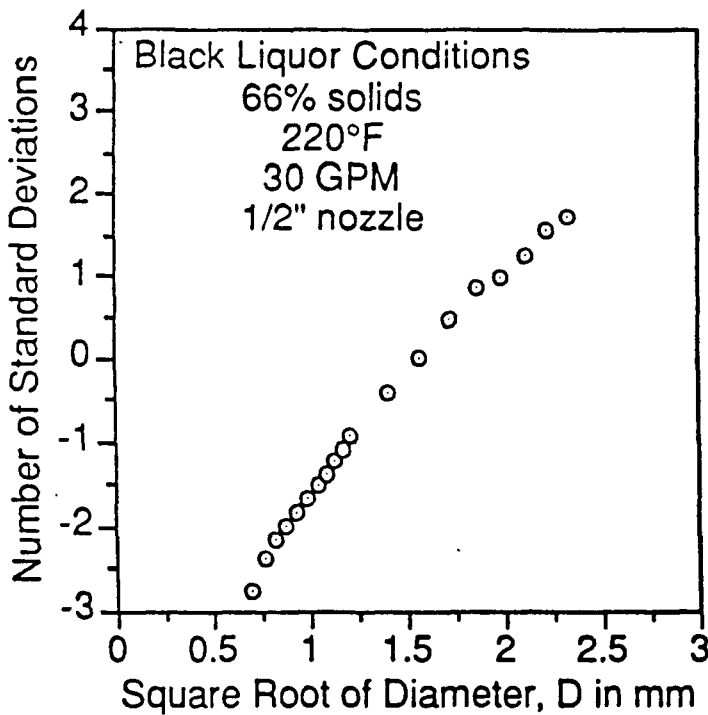
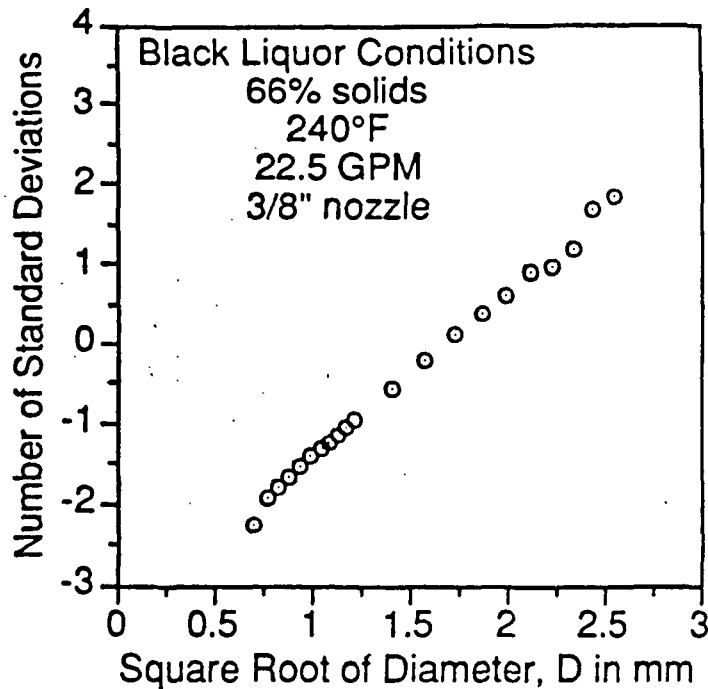
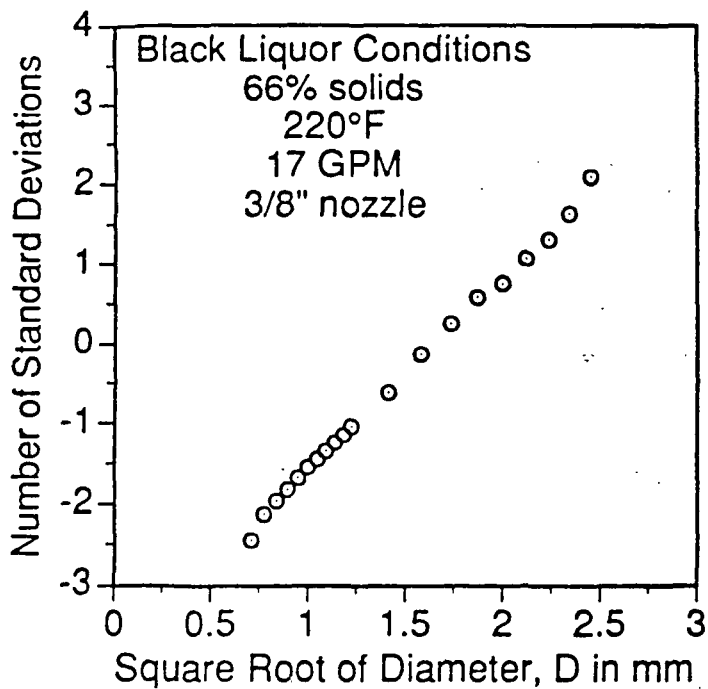
Sample plots of black liquor spray size distribution for two B&W splashplate nozzles taken by B&W Alliance Research Center using a Malvern Analyzer.



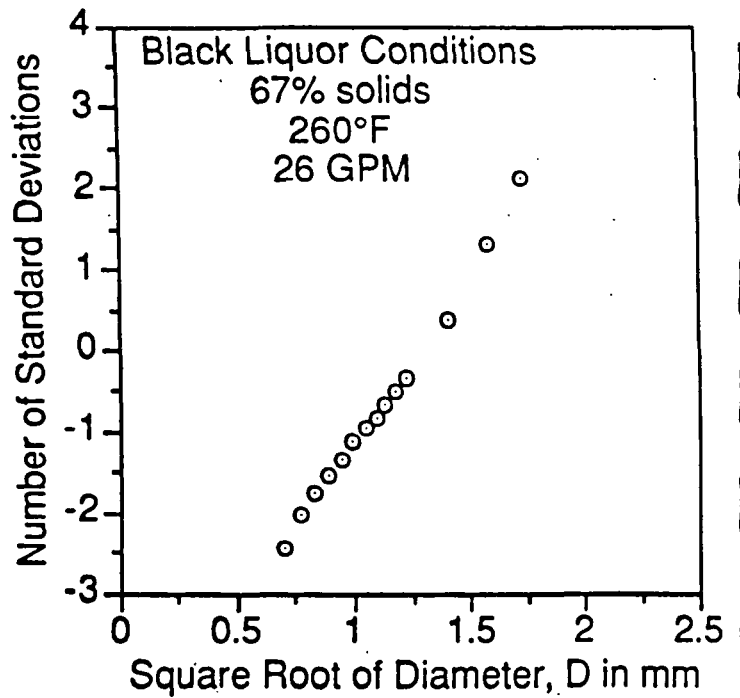
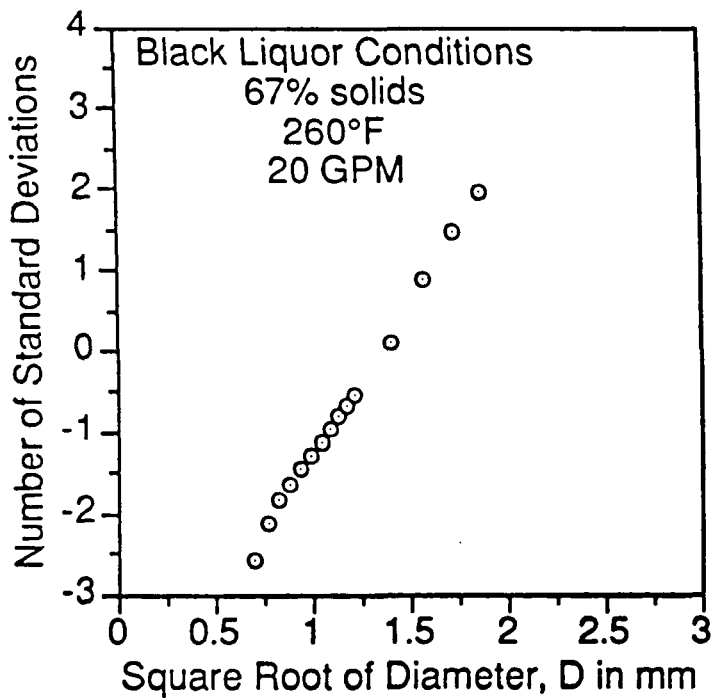
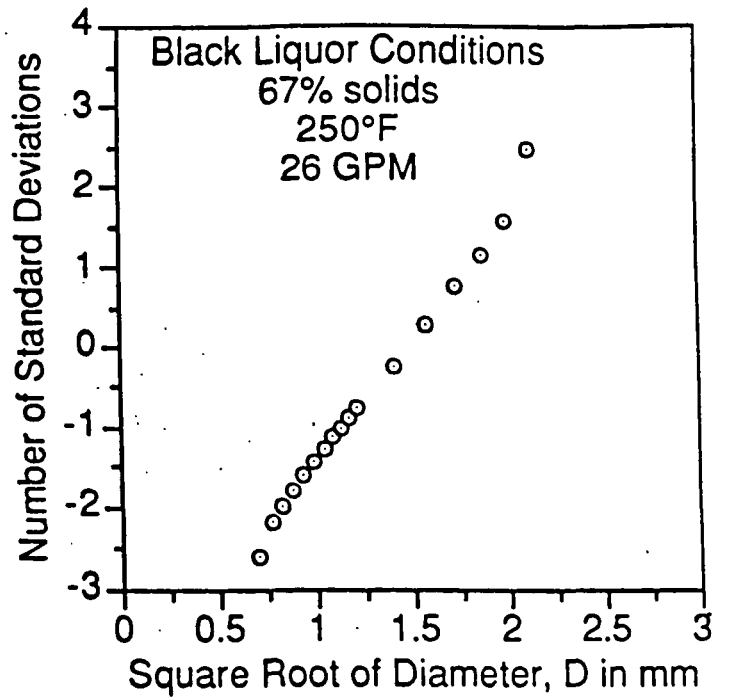
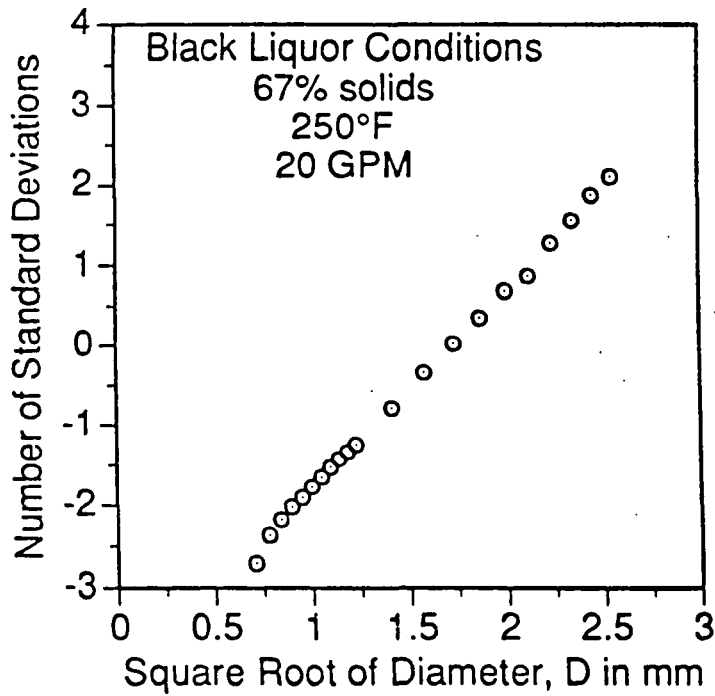
Data for one B&W black spray size distribution
 plotted using four assumed scales -- square-root, linear,
 quarter-root, logarithm.



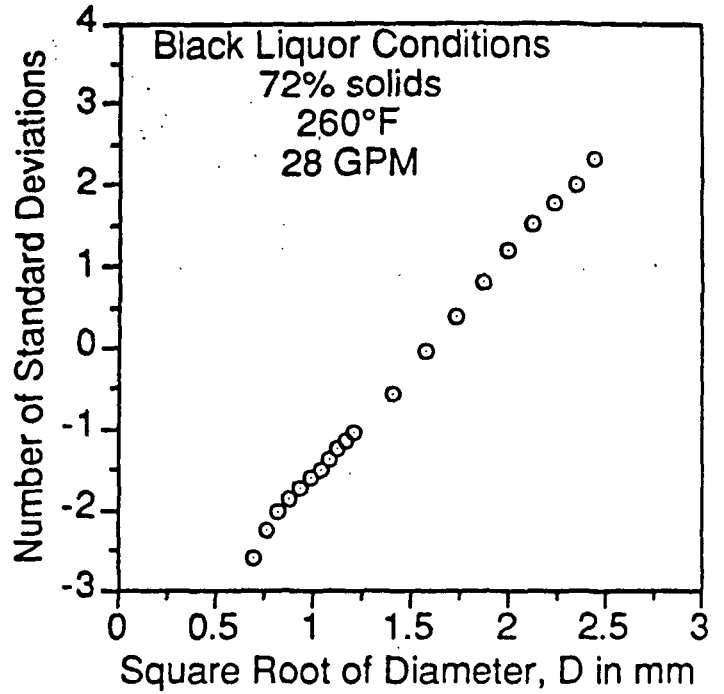
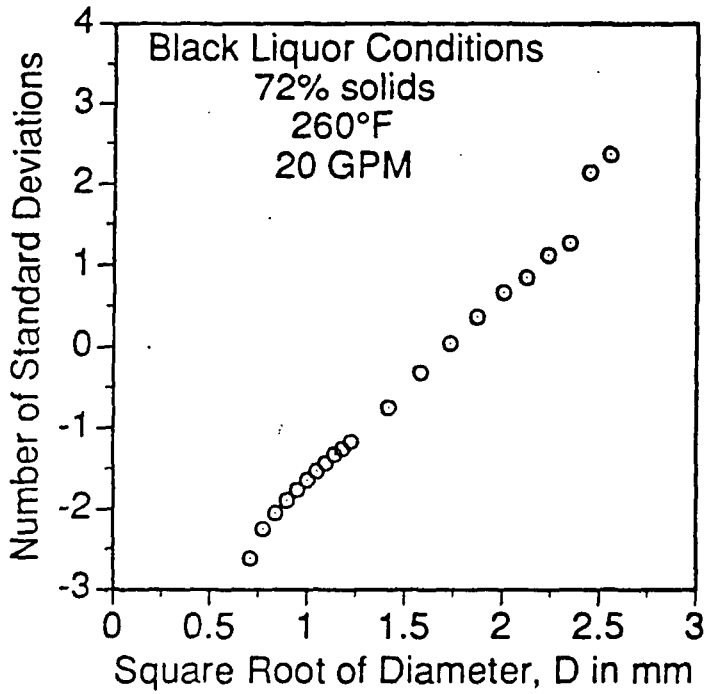
Square-root normal plots of four B&W black liquor spray size distributions.



Square-root normal plots of four IPST black liquor spray size distributions for two B&W splashplate nozzles operating at 66% solids.



Square-root normal plots of four IPST black liquor spray size distributions for a 1/2 inch CE swirl cone nozzle.



Square-root normal plots of four IPST black liquor spray size distributions for a 1/2 inch CE swirl cone nozzle operating with 72% black liquor solids.

CONCLUSIONS FROM SIZE DISTRIBUTION DATA

- * Square root - normal size distribution function provides good correlations of black liquor spray size distributions
- * Only two parameters needed are mass median drop diameter and normalized standard deviation
- * Normalized size distribution appears virtually independent of nozzle geometry, flow conditions, and fluid parameters; however more data is needed to substantiate this

1990 PROGRAM

- * Complete reinstallation of IPST spray facility
- * Test commercial nozzles with black liquors and model fluids
- * Test commercial nozzles with black liquors at one or more mill locations
- * Commence testing of new nozzle (commercially available) types using black liquor and model fluids

Computer Model of Recovery Furnace

(project 3605)

Robert R. Horton
Assistant Professor

IPST Project Advisory Committee Meeting

Atlanta, GA

March 20, 1990

Presentation Outline

Objectives

Value and Applications

Personnel

Current Status and Results

Project Directions

Conclusion

IPST Personnel

Faculty

Bob Horton	(Proj. Ldr.)
Jeff Empie	(Group Ldr.)
Earl Malcolm	(Div. Mngr.)
Tom Grace	(Adjunct prof.)

Graduate Students (Grad. date)

Andrew Jones	Spring 1989
Allan Walsh	Spring 1989
Dan Sumnicht	Summer 1989
Tom Kindler	Spring 1990

Project Objectives

To Date: Develop a computer-based 3-dimensional model of the recovery furnace process using commercially available CFD code.

Current: Determine if a practical and functional computer model is possible using current approach to allow simulation of the effects of different operating conditions.

Future: Develop customized CFD code and model the recovery furnace in modules that is credible and useable to allow an increase in efficiency and productivity.

Project Value and Applications

Process Variables

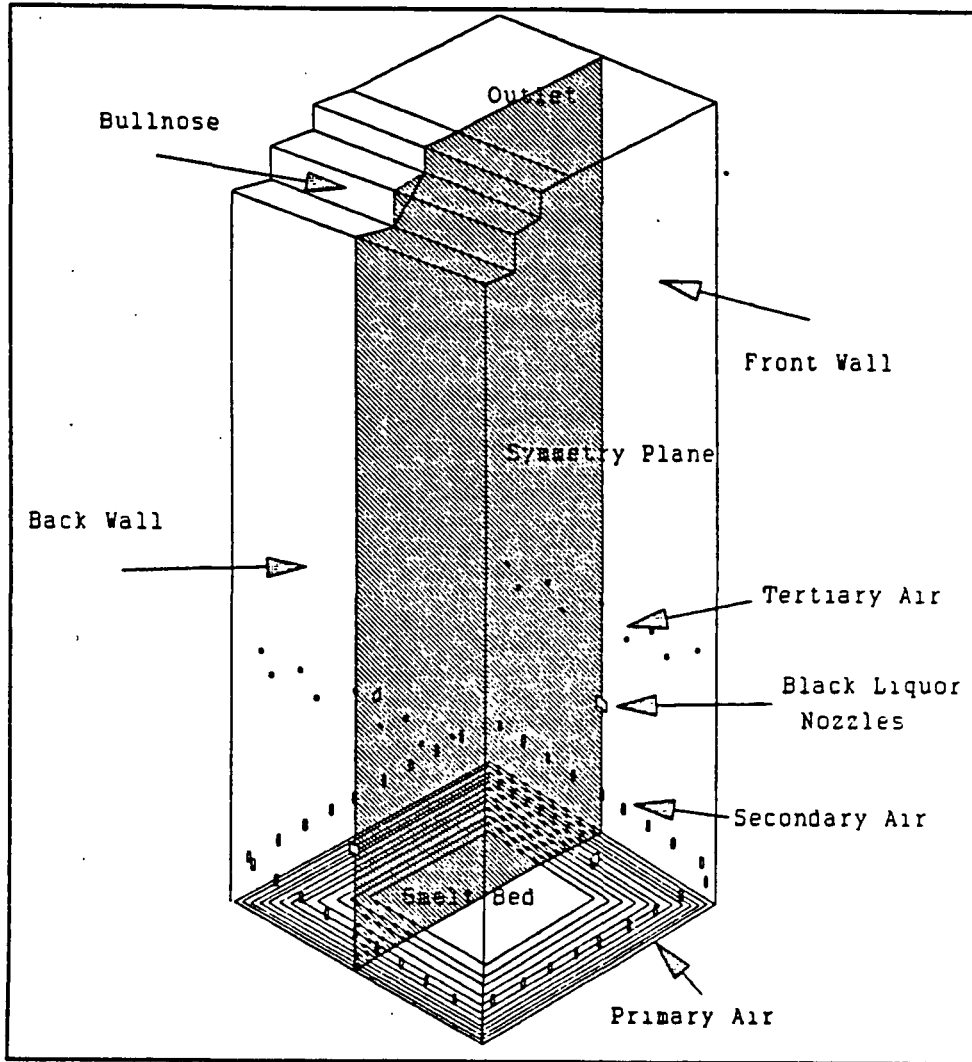
- Furnace Geometry (B.L. and air inlet location, angle)
- Black Liquor Quality (%solids, droplet size)
- Inlet Flow Rates (B.L., air)
- Bed Shape

Performance Parameters (to be simulated)

- Carry Over
- Temperature
- Species Concentrations
- Reduction and Combustion Efficiencies
- Flow Patterns

Applications

- Improve Heat Transfer Performance
- Improve Combustion Efficiency
- Minimize Corrosion
- Assist in Retrofitting
- Suggest Large-scale Design Improvements



Schematic of Base Case

Current Recovery Furnace Model Description

-Approach

Use commercially avail. CFD software
Solve entire problem at once

-50,000 nodes (max.)
hardware limitation (16 Meg RAM)
50 x 40 x 25 grid
poor resolution at jets
ill-conditioned system of equations

-Plane of Symmetry
symmetric flow & temp. patterns in horiz. plane
no tangential jets

-Convergence time
Three Months! (slow Computer)
3500 + Iterations (inefficient CFD algorithms)

Model Status and Results

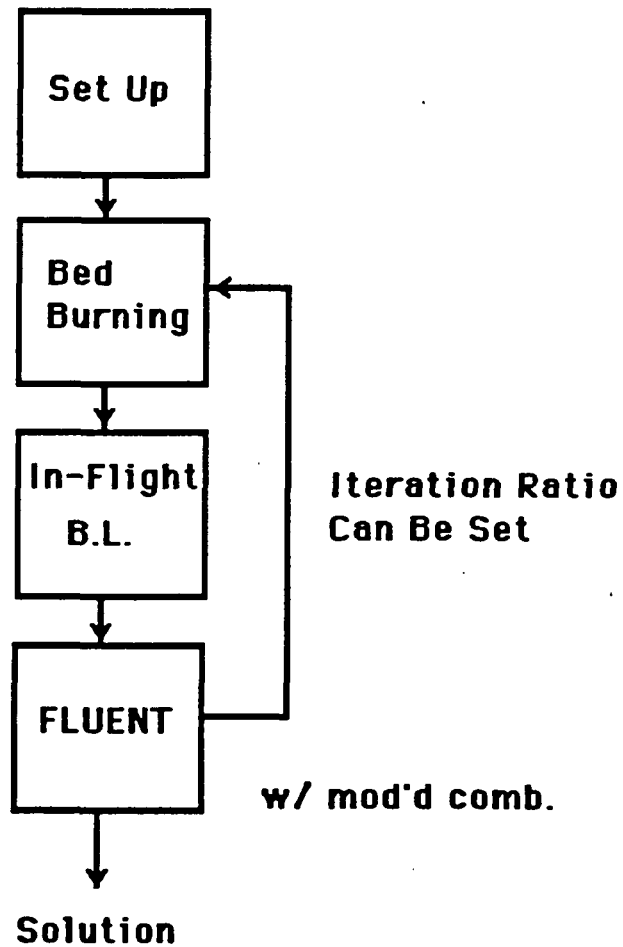
Current IPST Model includes:

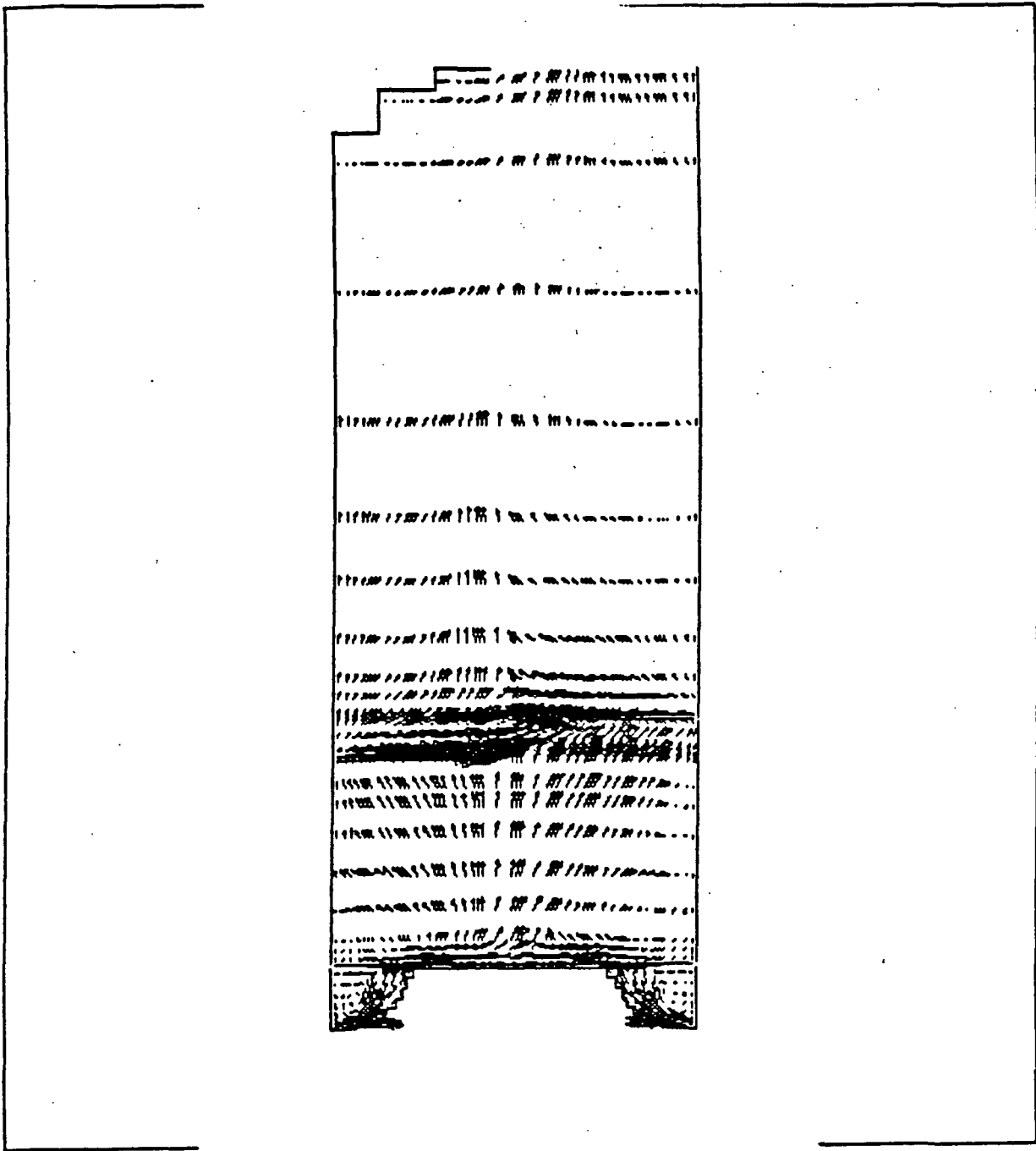
Bed Burning

In-Flight Black Liquor Trajectories

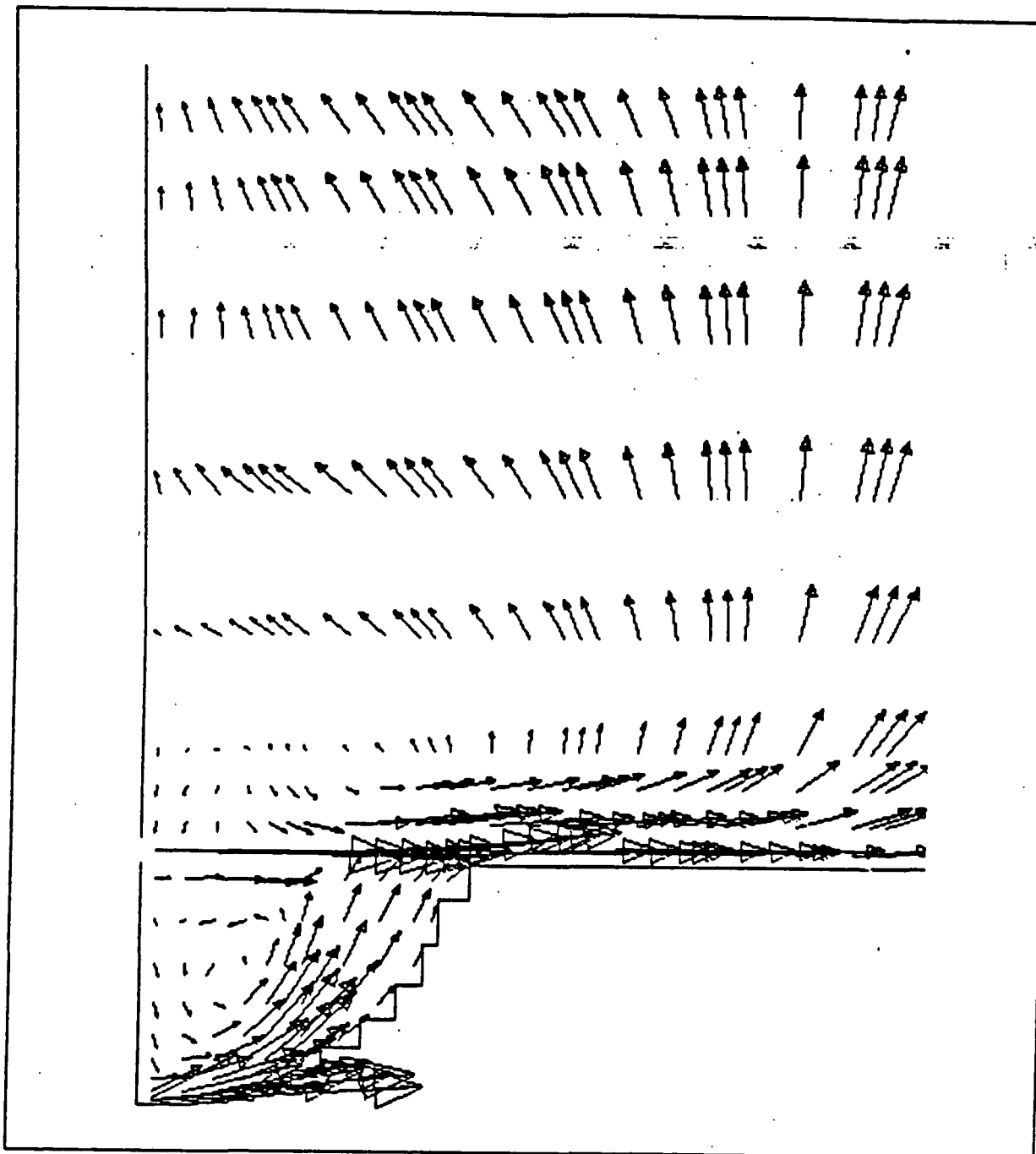
Combustion

Schematic Diagram:



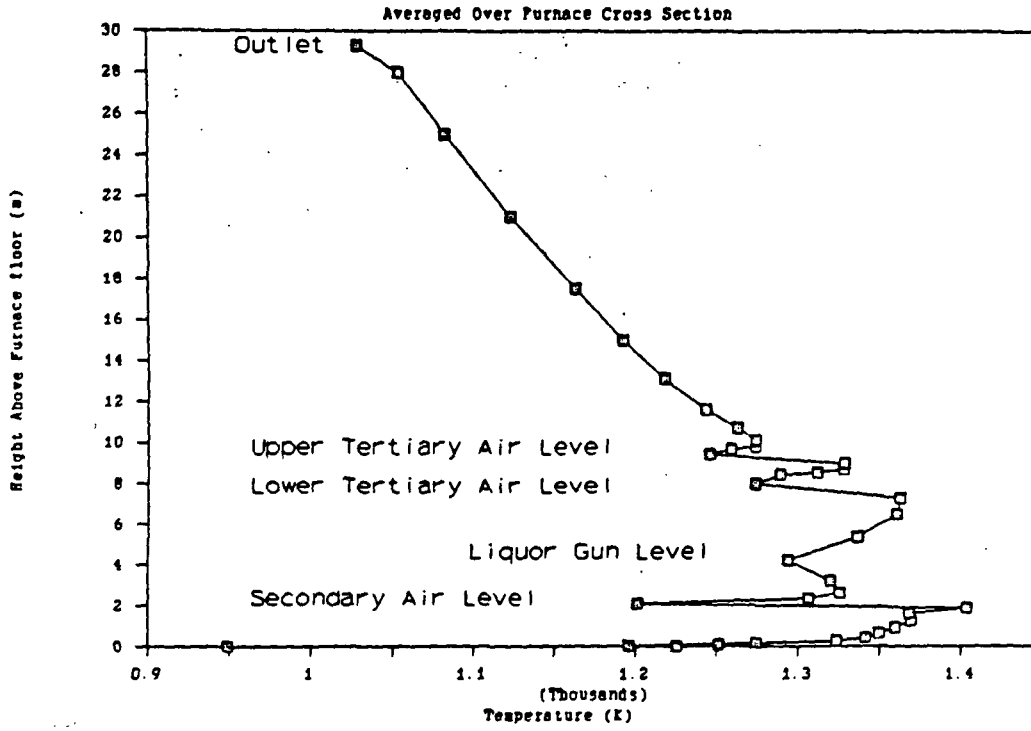


Vertical Slice of Furnace at Centerline



Zoom of Lower Left Corner of Figure 31

Average Temperature vs Height Above Bed



Temperature as a Function of Furnace Height

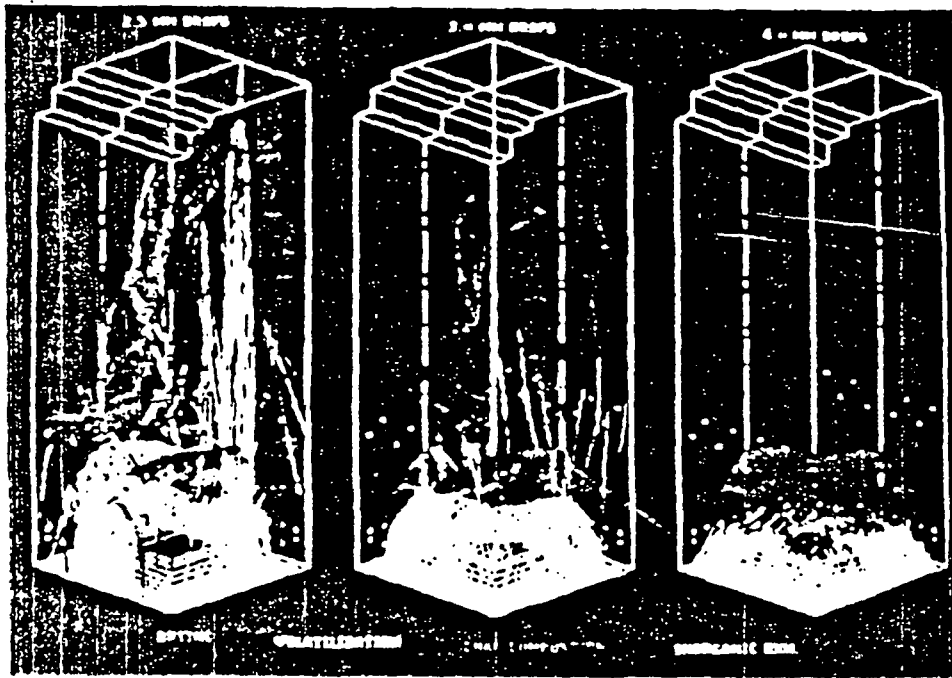


Figure 33. The trajectory and combustion behavior of drops with initial diameters of 2.5, 3.0, and 4.0 mm.

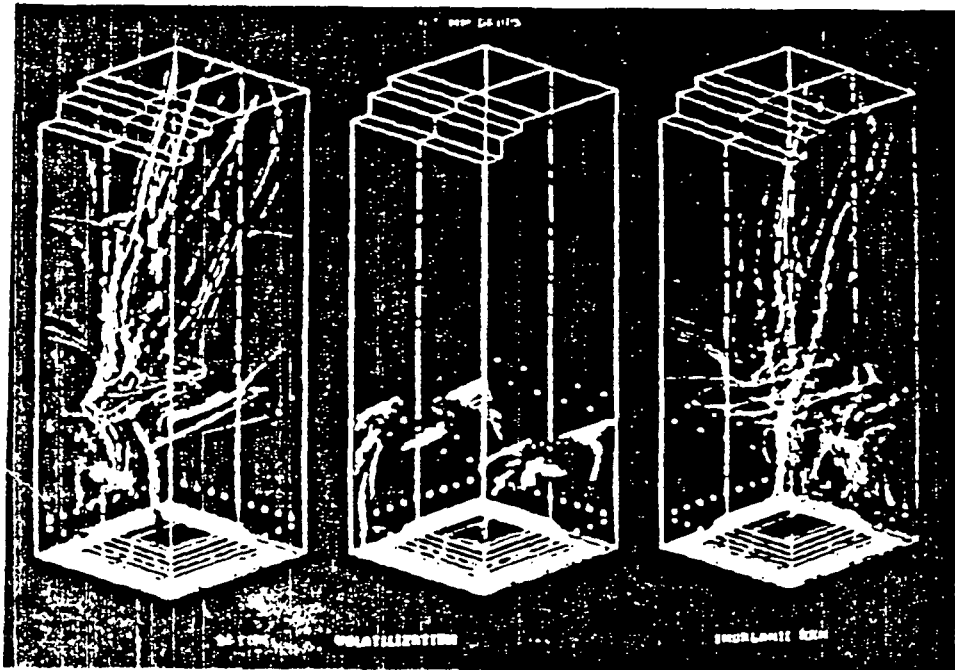


Figure 32. The trajectory and combustion behavior of drops with an initial diameter of 0.5 as a function of the position of the spray nozzles.

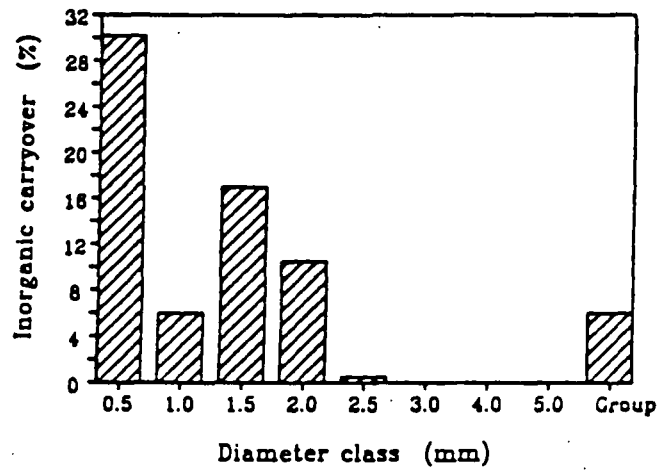
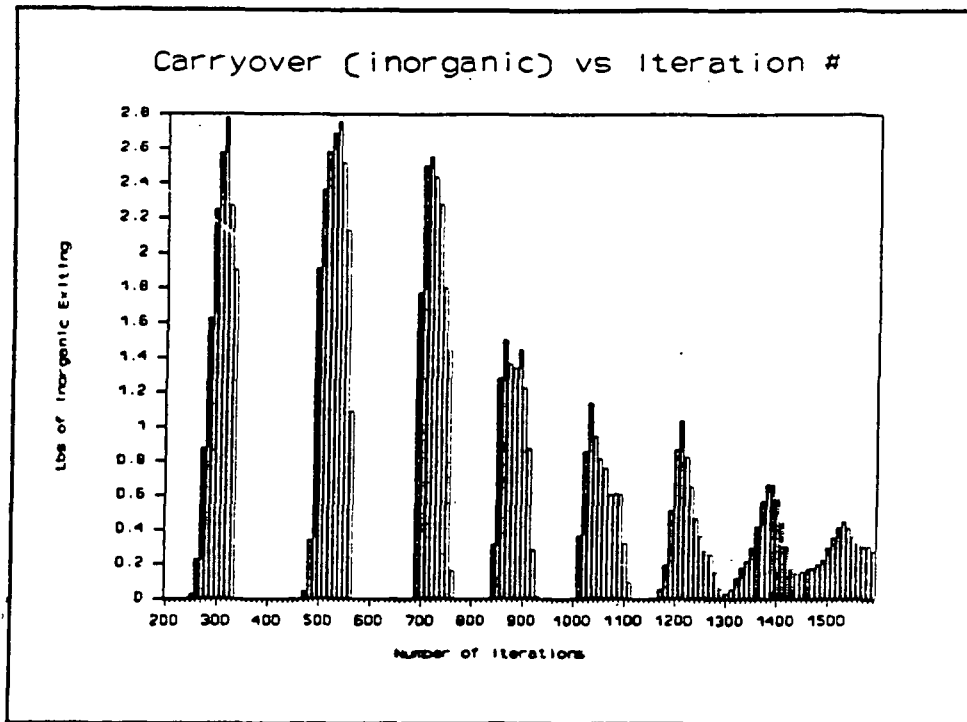


Figure 31. The fraction of inorganics that were carried over as a function of the initial drop diameter.



Inorganic Carryover vs Iteration Number

Needed Model Enhancements

- Remove Plane of Symmetry
- Add Sulfur and Sodium Species
- Increase Resolution (increase max. nodes)
- Increase speed (reduce convergence time)
- Make program more user-friendly

Future Project Directions

- I Short Term Program (1 year)
 - Determine if Practical Convergence is Possible
 - Update Hardware and Software
 - New IBM Workstation (10 x speed and RAM)
 - New version of CFD Code
 - Enhance convergence algorithms
 - Update Combustion Model with Fixed Flow Field
 - DOE Funding

- II Long Term Program (4 years)
 - Functional Model of Kraft Recovery Furnace
 - Model Recovery Furnace in stages
 - Customized, In-house CFD Code
 - Cooperative Effort with UBC and/or Ga Tech
 - Faster Modules:
 - Combustion and Concentration
 - Cold Flows
 - Energy Bal. and Heat Trans.
 - Integrated Model
 - DOE assisted funding
 - Validation and Industrial Testing

Conclusions

Computer simulation of the recovery furnace gives important insights for improved operation.

More work needs to be done to model the recovery furnace with higher resolution and accuracy, but within a more reasonable time scale.

Results

- Only one Base-case Simulation has converged
- High upward flow velocities in a central core region
- Downward flows in some zones near furnace walls
- Temperature is highest in central core
- Central core is not effectively dispersed by tertiary air
- Carry over does not monotonically decrease with drop size