Institute of Paper Science and Technology
Atlanta, Georgia

SLIDE MATERIAL

To The

CHEMICAL RECOVERY

RESEARCH REVIEW COMMITTEE

March 24 & 25, 1994

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSION STATEMENT

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and
- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and
- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

CHEMICAL RECOVERY

1994 ANNUAL SPRING RESEARCH REVIEW

S L I D E   M A T E R I A L

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KRAFT RECOVERY BOILER MODELING

Annual Program Review and PAC Meeting March 24, 1994

OVERALL RESEARCH PROGRAM OBJECTIVES

- Develop a Computer-based Model that Describes the Operation of a Kraft Recovery Boiler
- Use the Model to Increase Understanding
- Allow Optimization of New and Installed Units

FUNDING

- U.S. Dept. of Energy
- IPST Member Companies
  (Dues Funded)
- AFPA (API)
- Canadian Sources for UBC effort

RECOVERY BOILER MODELING PRINCIPAL COLLABORATORS

- IPST
- UBC
- OSU
- TMGrace

ASSOCIATED COLLABORATORS

- Abo Akademi (Hupa)
- Univ. of Toronto (Tran)
- Boiler Vendors
- Weyerhaeuser (physical model validation)
- PAPRICAN
- STFI

Contracts via JR & GP

RECOVERY BOILER MODELING PRESENTATIONS

- Introduction
- Black Liquor Combustion (Frederick, OSU)
- NOx: Formation and Depletion (Martin/Thompson, IPST)
- Status of CFD Model (Matys, UBC)
- Char Bed Model (Horton, IPST)
- Recovery Boiler Model Applications (Grace/Horton)

prepared delivered

The Evolution of Fuel Nitrogen During Black Liquor Pyrolysis

Denise Martin

Nitrogen Oxides

- Nitric Oxide — NO
- Nitrogen Dioxide — NO_2
- Nitrous Oxide — N_2O

NO_x Formation Mechanisms

- Thermal NO
- Prompt NO
- Fuel NO

Thermal NO

- Oxidation of Atmospheric Molecular Nitrogen

  $O + N_2 \leftrightarrow NO + N$

  $N + O_2 \leftrightarrow NO + O$

  $N + OH \leftrightarrow NO + H$

- Requires High Temperatures for the Reactions to Proceed

Zeldovich, J.: Acta Pysiochimica U.R.S.S., 21(4):577-628 (1946)

Prompt NO

Reaction of Hydrocarbon Fragments with Molecular Nitrogen

$$CH + N_2 \rightarrow HCN + N$$

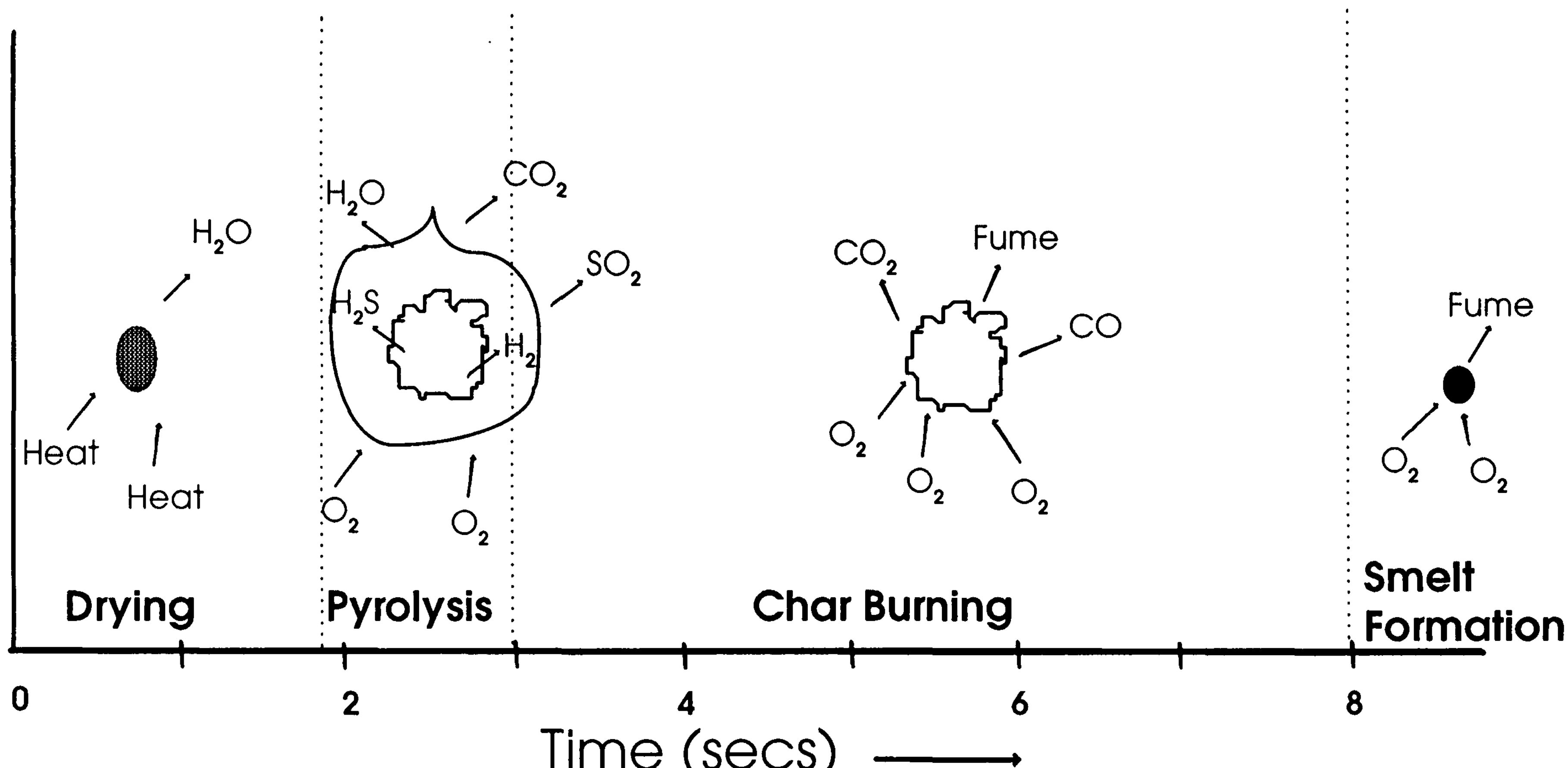
$$CH_2 + N_2 \rightarrow HCN + NH$$

Fuel NO

Oxidation of the Nitrogen in the Fuel

$$\text{Fuel-N} \rightarrow HCN \rightarrow NH_i \rightarrow NO \text{ or } N_2$$

Black Liqour Combustion



NO_x from Kraft Recovery Boiler Operations

- Reported Emissions from 0 -155 ppm NO_x
- Controversy Over Effects of Solids Levels
- Black Liquors contain 0.1 % N
- 20 % Conversion Could Represent the Majority of the NO_x Emissions

Sources of Nitrogen in Black Liquor

- Nitrogen in Wood
  - Lignin, protein amino acids
  - Nonproteinaceous nitrogen compounds, free amino acids, ureids, alkaloids, and inorganic nitrogen
- Nitrogen Containing Additives

Current Understanding

- NO Emissions Dependent on:
  - Fuel Nitrogen Content
  - Oxygen Availability
- Chemical and Physical Nature of the Nitrogen Determine Intermediates
- Fuel NO Weakly Dependent on Temperature

Areas of Uncertainty

- Heating Rate Effects on Nitrogen Volatilization
- Nitrogen Structures in Black Liquor
- Effects of Liquor Composition
  - Inorganics
  - Available Oxygen

Thesis Objectives

"The primary objective is to determine the effects of

- pyrolysis temperature,
- heating rate,
- black liquor solids level and
- the structure of the major black liquor nitrogen compounds

on the evolution of NO_x precursors during black liquor pyrolysis."

Experimental Approach

Phase I -- Evaluation of the Nitrogen in the Black Liquor.

Phase II -- Evaluation of Gaseous Nitrogen Species During Pyrolysis of Black Liquor.

Phase III -- Model the Nitrogen Release During Pyrolysis.

Phase I Results

- Nitrogen Content

Liquor Type	% N
Pine	0.06
Pine/Birch	0.07
Eucalyptus	0.09
Southern Pine I	0.06
Southern Pine II	0.06

Nitrogen Structures--Southern Pine I

- Nitrate (NO_3^-)
- Protein (NH_3)
    - Glutamic Acid
    - Proline*
    - Aspartic Acid
    - Cystine
    - Valine
    - Leucine

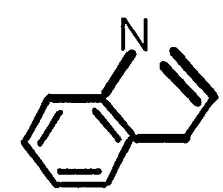
Nitrogen Structures -- Southern Pine II

Nitrate (NO_3^-)

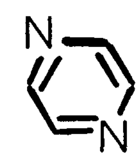
Glutamic Acid (NH_3)

5- and 6- Membered Rings

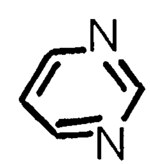
Indole



Pyrazine



Pyrimidine



Points to Note

- Black Liquor has a Very Low Fuel Nitrogen Content
- Nitrogen Structures Present as Amine, Heterocyclic Nitrogen, and Nitrate
- Variations are Liquor Specific

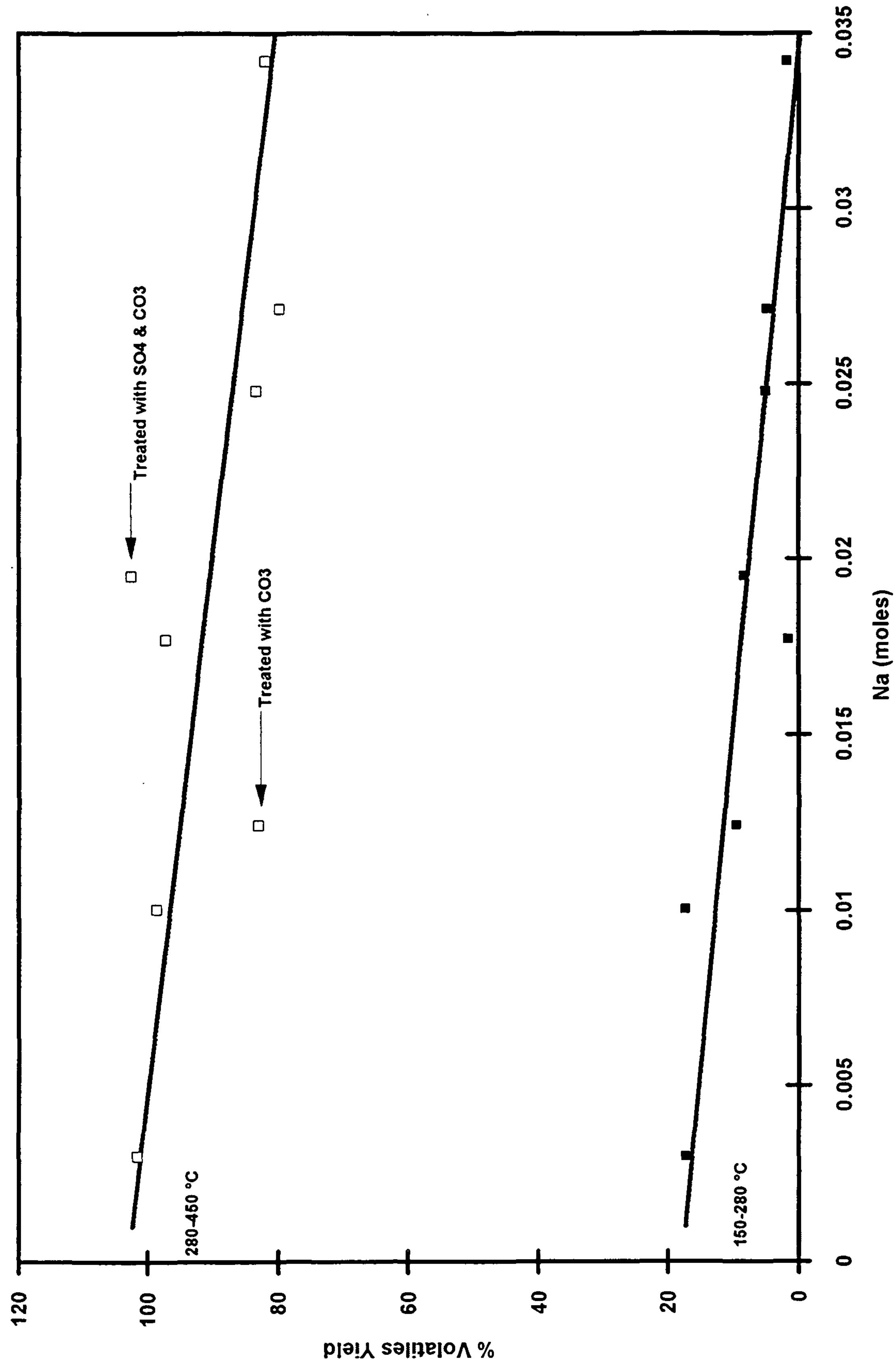
Phase II Results

- Inorganic Composition:
  - Effects Nature of the Decomposition of Model Fuel Nitrogen Compounds

Pyrolysis--Model System

- Parameters Evaluated
- Inorganic Composition
- Organic Nitrogen

- Onset Temperature
- Volatiles Yield

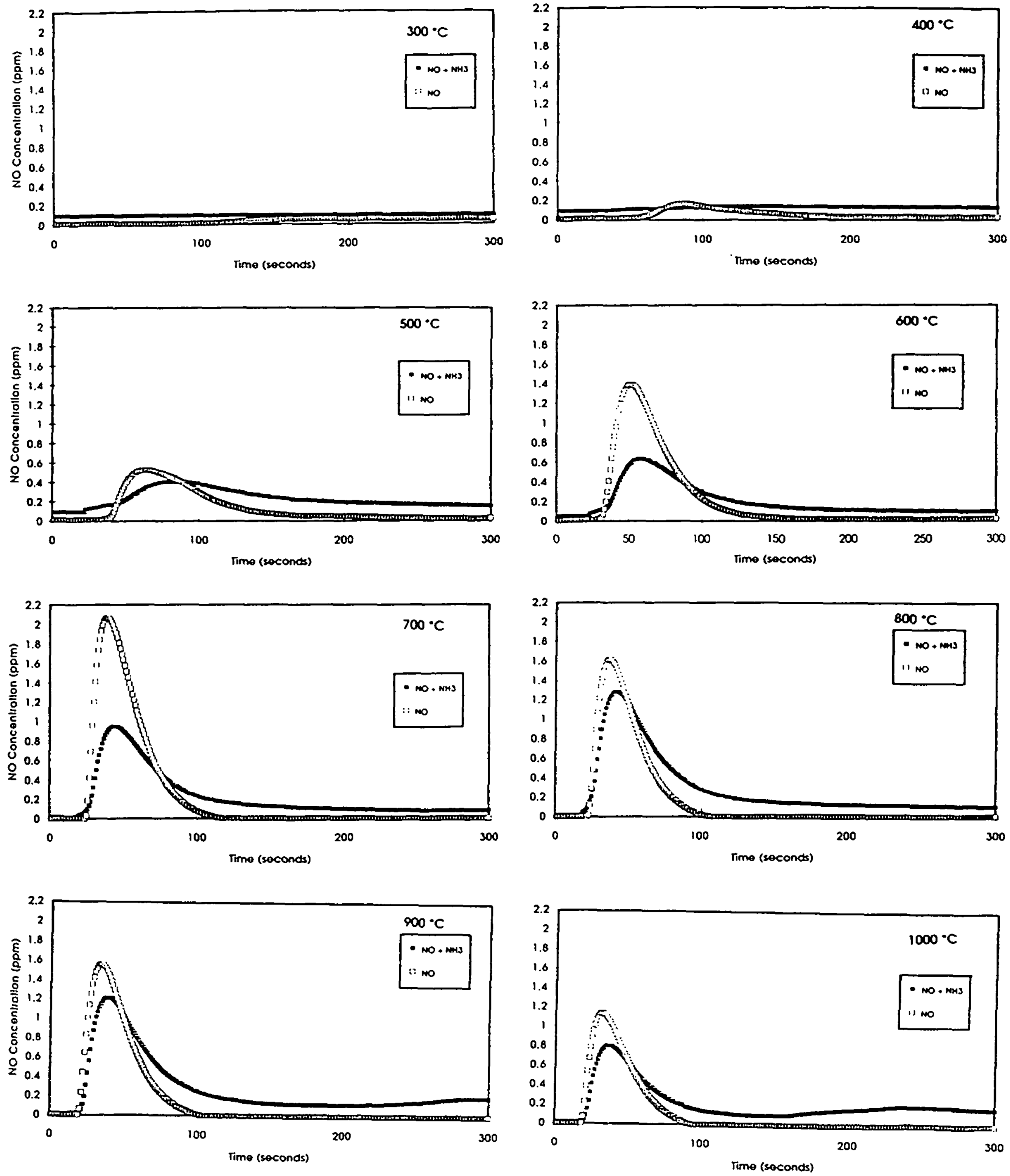

% Volatiles Yield
120
100
80
60
40
20
0
Na (moles)
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
Treated with SO4 & CO3
Treated with CO3
280-450 °C
150-280 °C

Points to Note

- Increased Na Decreases Volatiles Yield
- Increased Na Increases Decomposition Onset Temperature

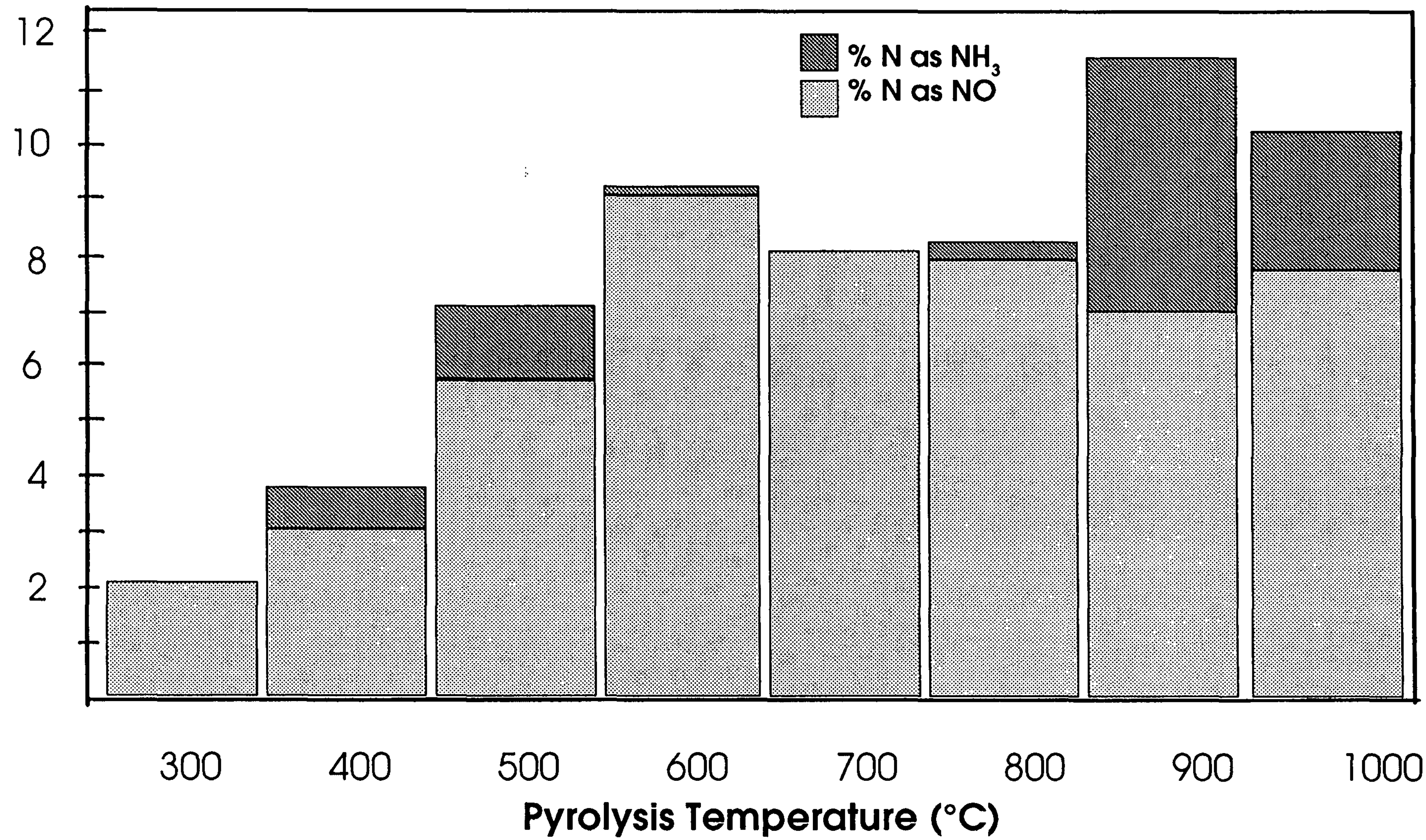
Pyrolysis--Kraft Black Liquor

- Parameters Evaluated
  - Final Temperature
  - Volatile Nitrogen Yield as NO and NH_3
  - Char Nitrogen


300 °C
400 °C
500 °C
600 °C
700 °C
800 °C
900 °C
1000 °C
NO + NH3
NO
NO Concentration (ppm)
Time (seconds)

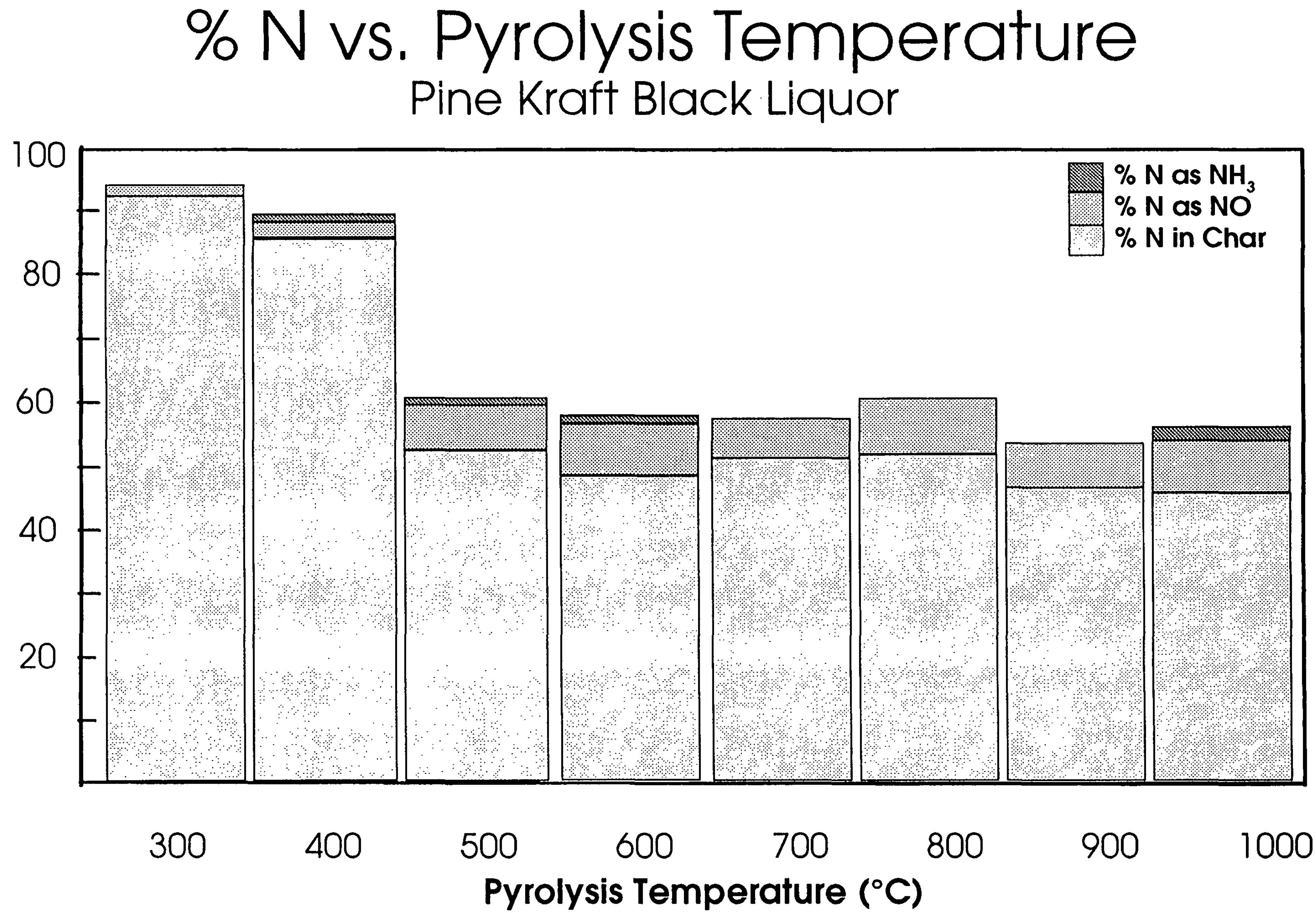
Volatilized Nitrogen

Pine Kraft Black Liquor



Points to Note

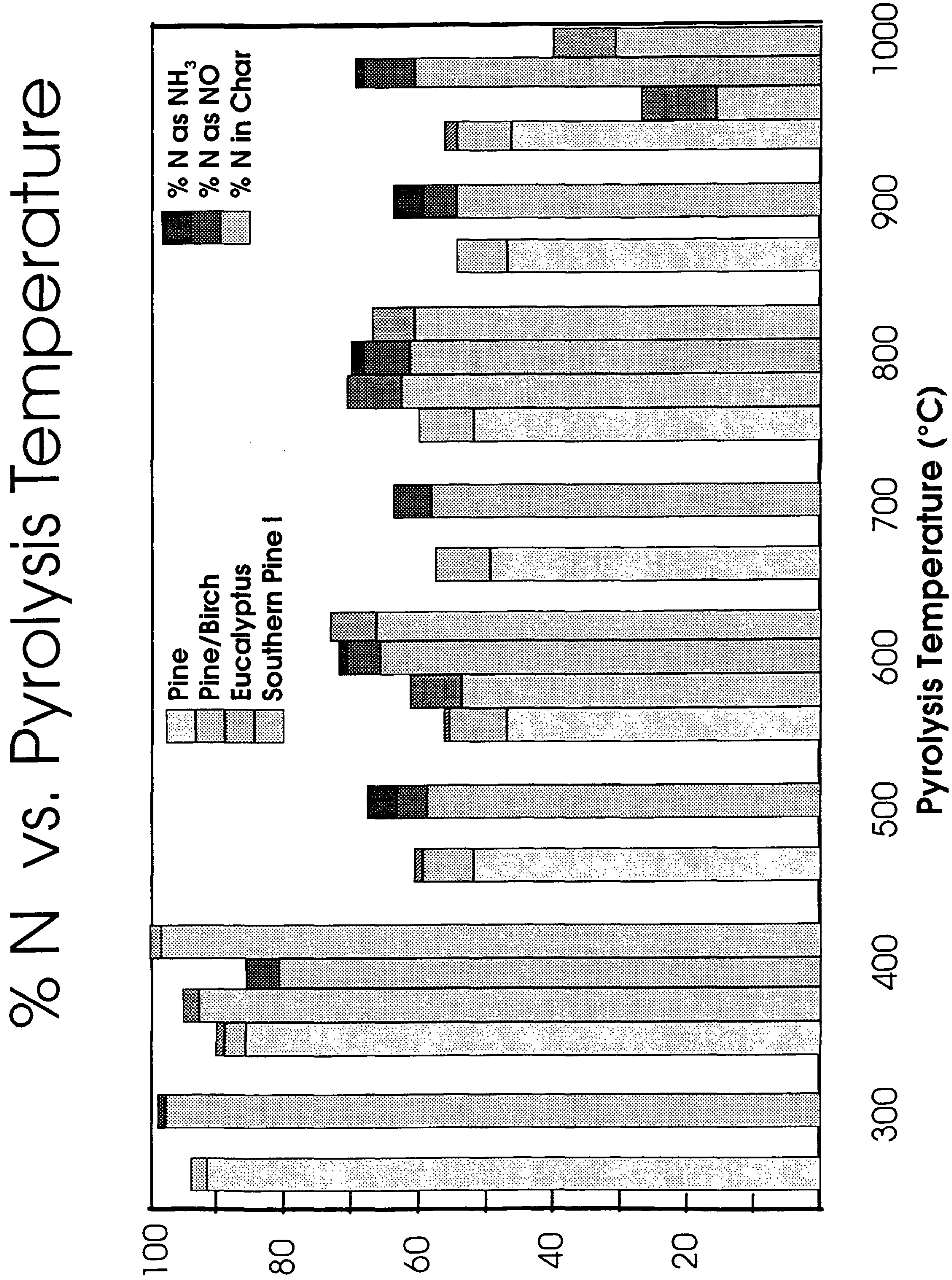
- Majority of NO Released by 500-600 °C
- Primary Species to be released was NO



% N vs. Pyrolysis Temperature
Pine Kraft Black Liquor
100
80
60
40
20
% N as NH_3
% N as NO
% N in Char
300
400
500
600
700
800
900
1000
Pyrolysis Temperature (°C)

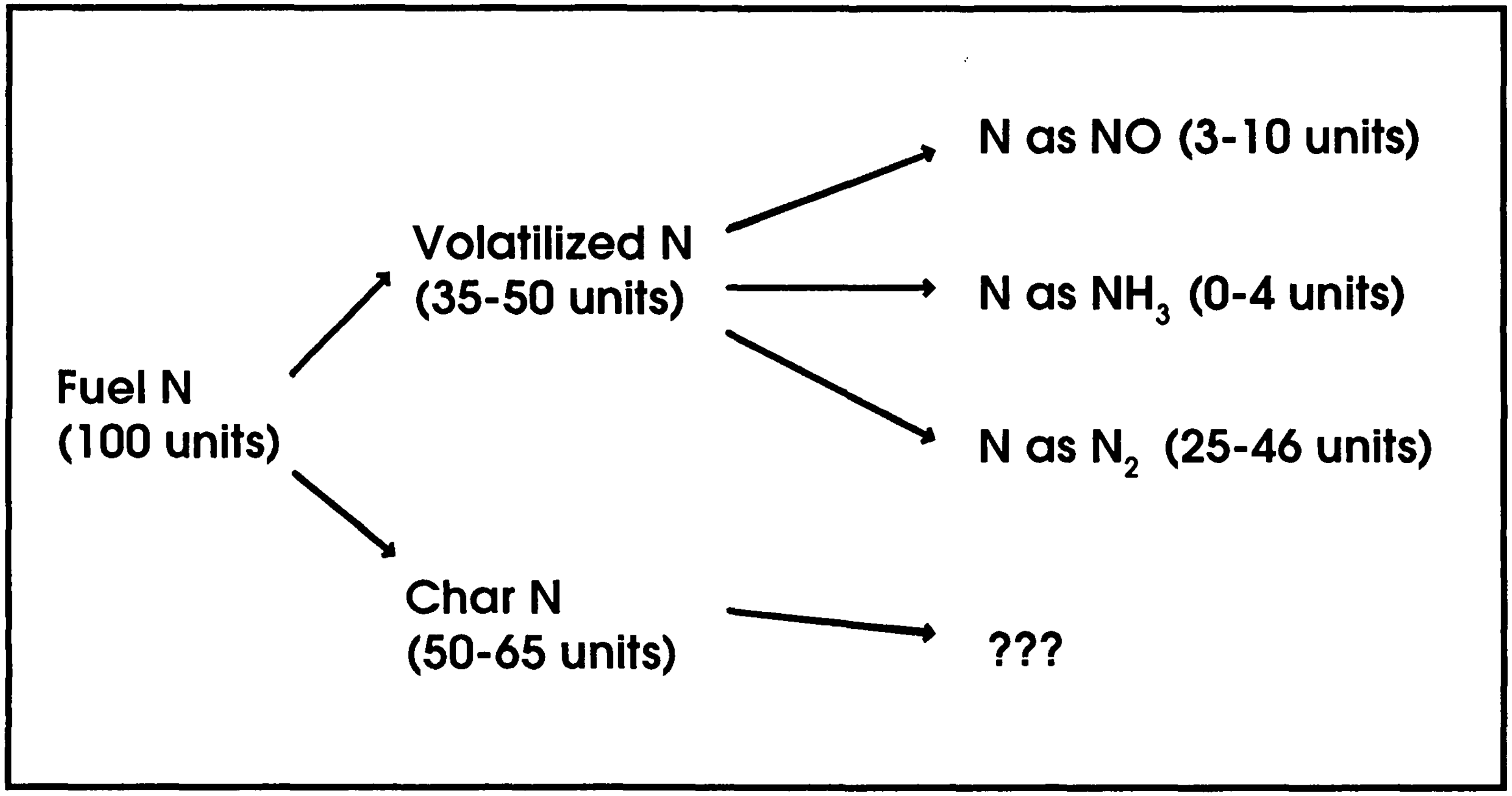
Point to Note

- Majority of the Volatilized Nitrogen Released by 500 °C



% N vs. Pyrolysis Temperature
Pine
Pine/Birch
Eucalyptus
Southern Pine I
% N as NH_3
% N as NO
% N in Char
100
80
60
40
20
300
400
500
600
700
800
900
1000
Pyrolysis Temperature (°C)

Fuel Nitrogen Pathway



Summary of Results to Date

- Nitrogen content in Liquor < 0.1 %
- Nitrogen both Organic and Inorganic
- Inorganic Composition Does Effect the Pyrolysis of Model Fuel Nitrogen Compounds
- Volatilized Nitrogen Released by 500 °C
- Volatilized Nitrogen Primarily as NO During Inert Pyrolysis of Black Liquor
- Discrepancy with NO and NH3 Content in Pyrolytic Gases

Work in SPR
@ lower heating rates.

Thesis Work Remaining

Phase II

- Effects of:
  - Heating Rate
  - Nitrogen Structures
  - Black Liquor Solids Levels
  - Inorganic Composition
- Black Liquor and Model Systems

Thesis Work Remaining

Phase III

- Modeling
  - Mechanistic
  - Kinetic

Depletion of NO_x in a Kraft Recovery Furnace

The Institute of Paper Science and Technology

Atlanta, GA

Laura M. Thompson (student)
H. Jeff Empie (advisor)

Emissions Modeling

Total NO = NO Formed - NO Depleted

Depletion of NO_x

Homogeneous Gas Phase Reactions

Heterogeneous Reactions

Char, Soot

Smelt, Fume

Potential Reactions with Smelt and Fume are
Unique to Recovery Furnaces

Thesis Objective

Determine the mechanism and rate of depletion of NO by reaction with smelt and fume species.

Fume Chemistry (Blackwell and King)

Formation of Na_2CO_3

(1) $Na_2O + CO_2 \longrightarrow Na_2CO_3$

(2) $2Na + CO_2 + O_2 \longrightarrow Na_2CO_3$

(3) $2NaOH + CO_2 \longrightarrow Na_2CO3 + H_2O$

Formation of Na_2SO_4

(1) $Na_2O + SO_2 + 1/2\ O_2 \longrightarrow Na_2SO_4$

(2) $2Na + 2CO_2 + SO_2 \longrightarrow Na_2SO_4 + 2CO$

(3) $Na_2CO_3 + SO_2 + 1/2\ O_2 \longrightarrow Na_2SO_4 + CO_2$

(4) $Na_2CO_3 + SO_3 \longrightarrow Na_2SO_4 + CO_2$

Proposed Fume Chemistry (Thompson)

Formation of $NaNO_3$

(1) $Na + NO + O_2 \longrightarrow NaNO_3$

(2) $Na + NO_2 + 1/2\,O_2 \longrightarrow NaNO_3$

(3) $Na_2O + 2NO + 3/2\,O_2 \longrightarrow 2NaNO_3$

(4) $Na + 3NO \longrightarrow NaNO_3 + N_2$

(5) $Na_2CO_3 + 2\,NO + 3/2\,O_2 \longrightarrow 2NaNO_3 + CO_2$

Thermodynamics of Fume Reactions

Negative Standard Free Energies

Data Extrapolated for $NaNO_3$

Does Not Imply Anything About Kinetics

NO_x Sorbent Processes

Sorbent	Process	Product
Na_2CO_3	Fluidized Bed	$NaNO_3$
$NaHCO_3$	In-Duct Injection	$NaNO_3$
Mixed Oxides (Na_2O)	Development	$NaNO_3$

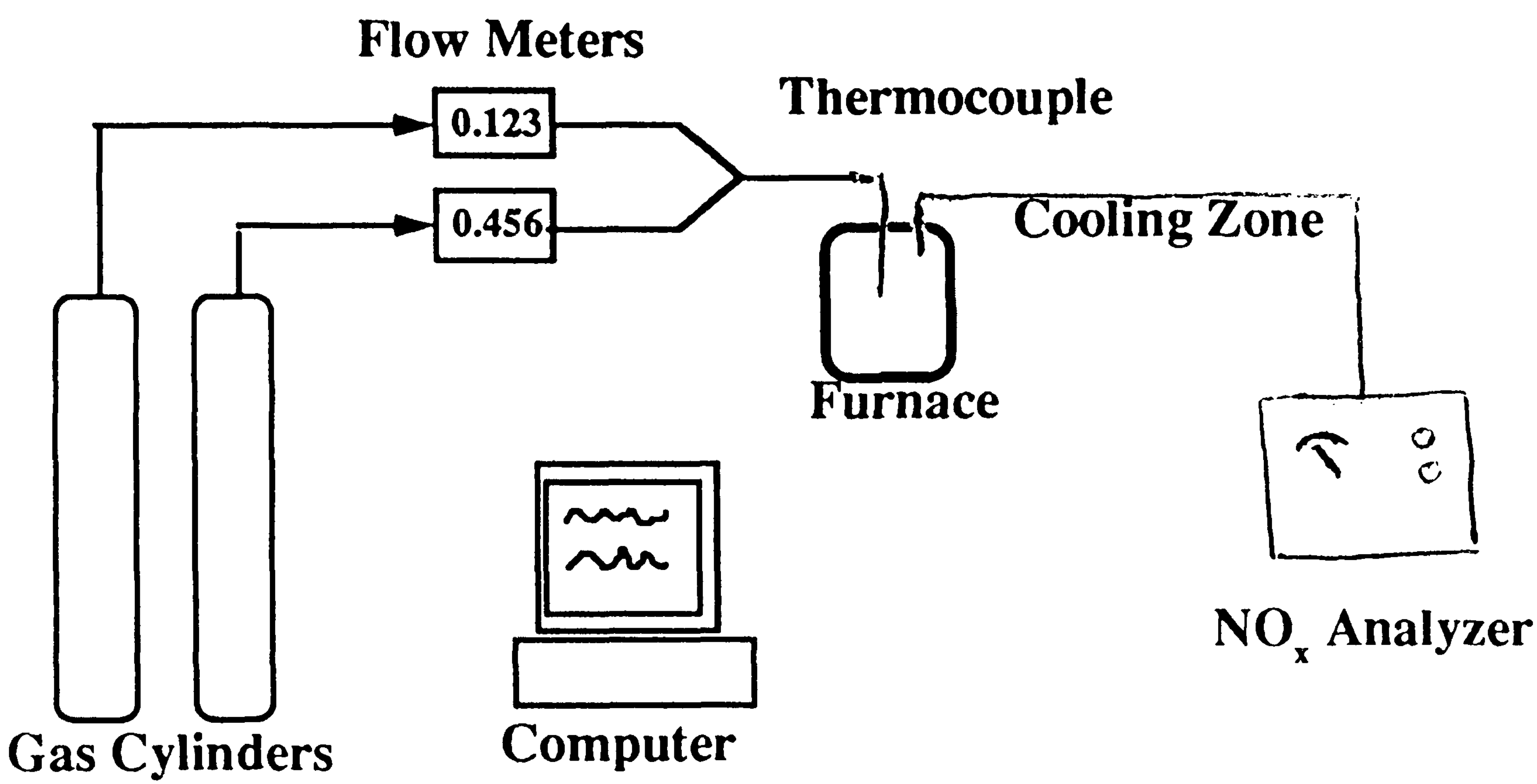
(All use Na to scrub NO and form $NaNO_3$)

Experimental Approach

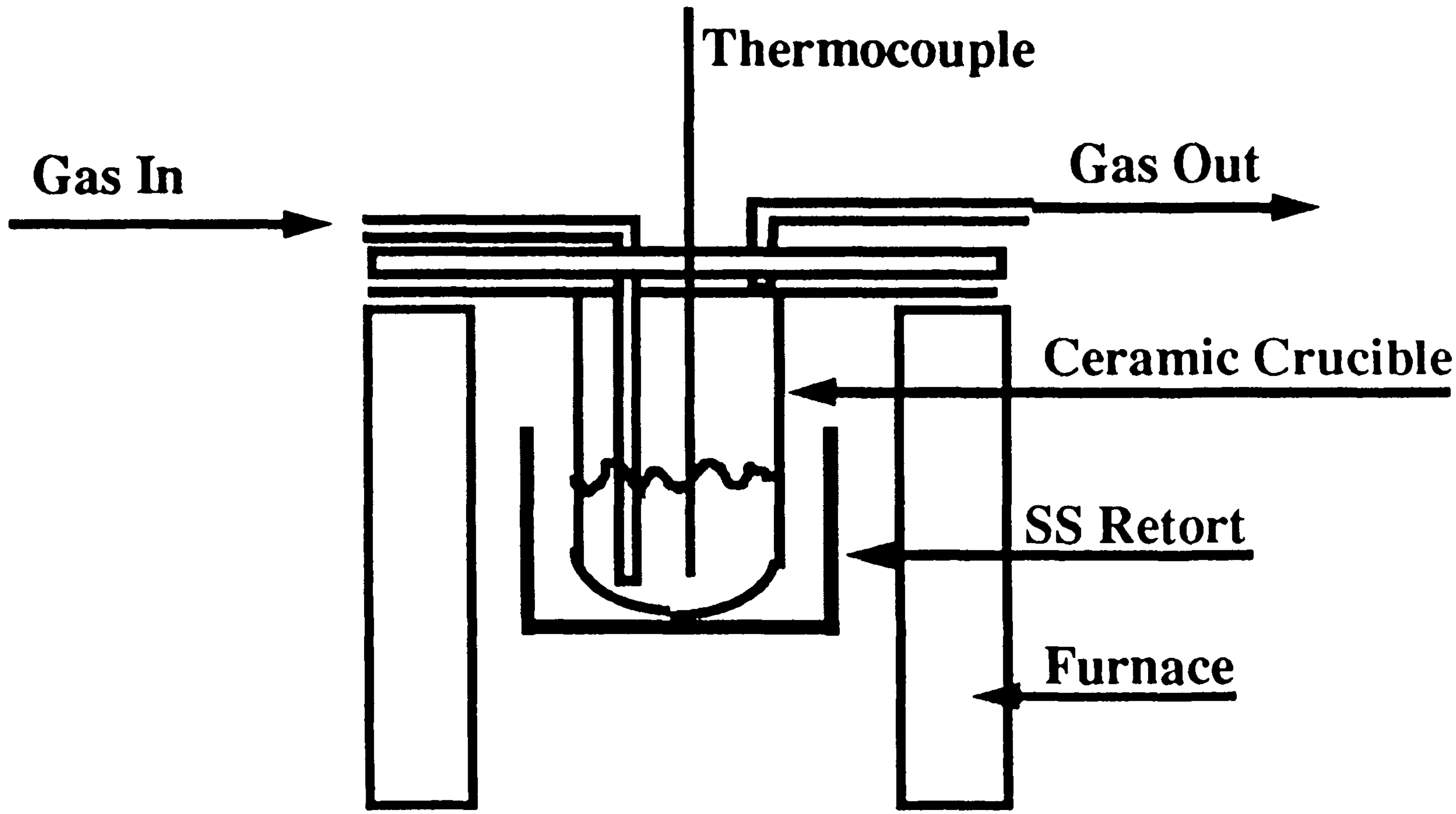
Determine Effect of Following Variables:

- Temperature
- Flow Rate of Gas
- Concentration of NO
- Mass or Surface Area of Na
- Composition of Salt Mixture
- Gas Phase Composition

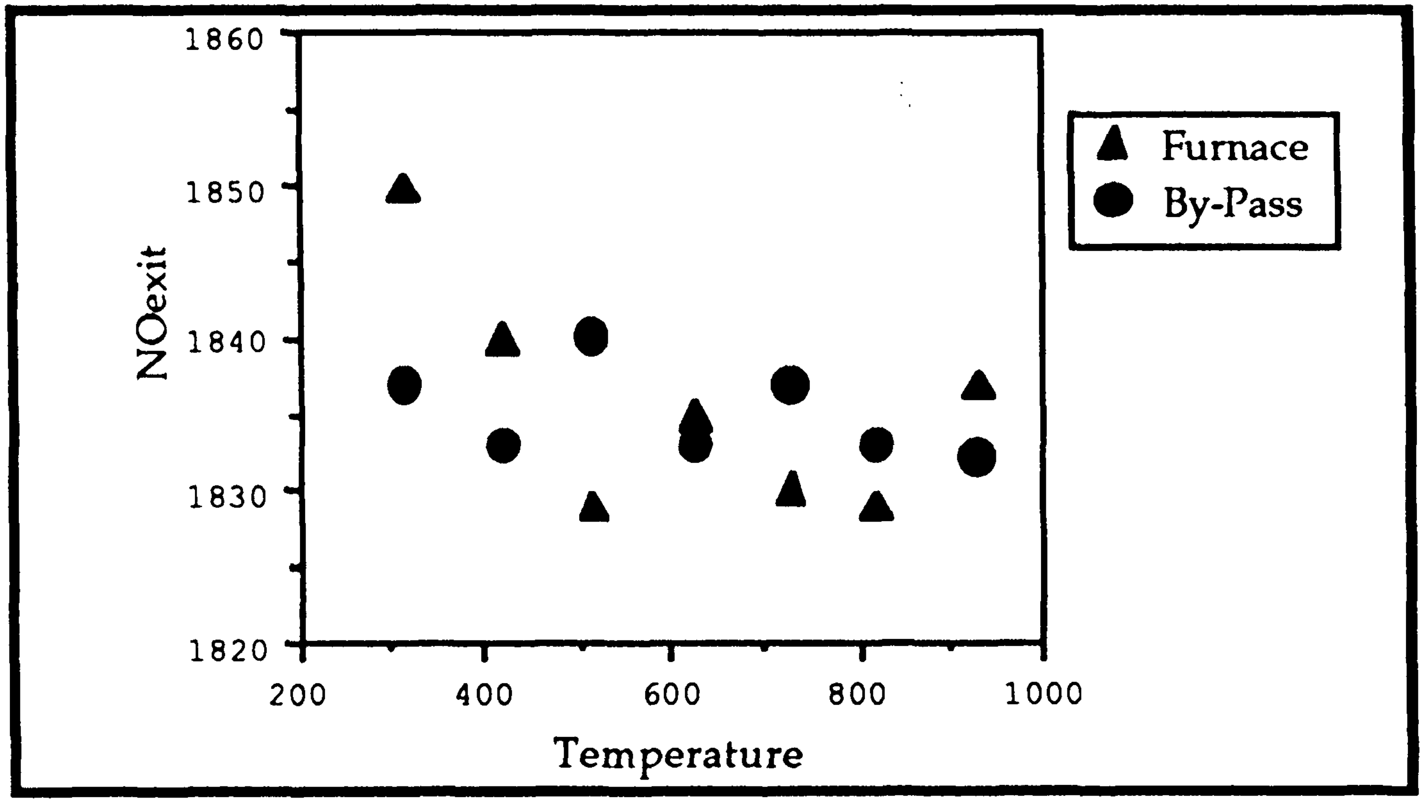
Experimental Apparatus



Furnace/Reaction Vessel

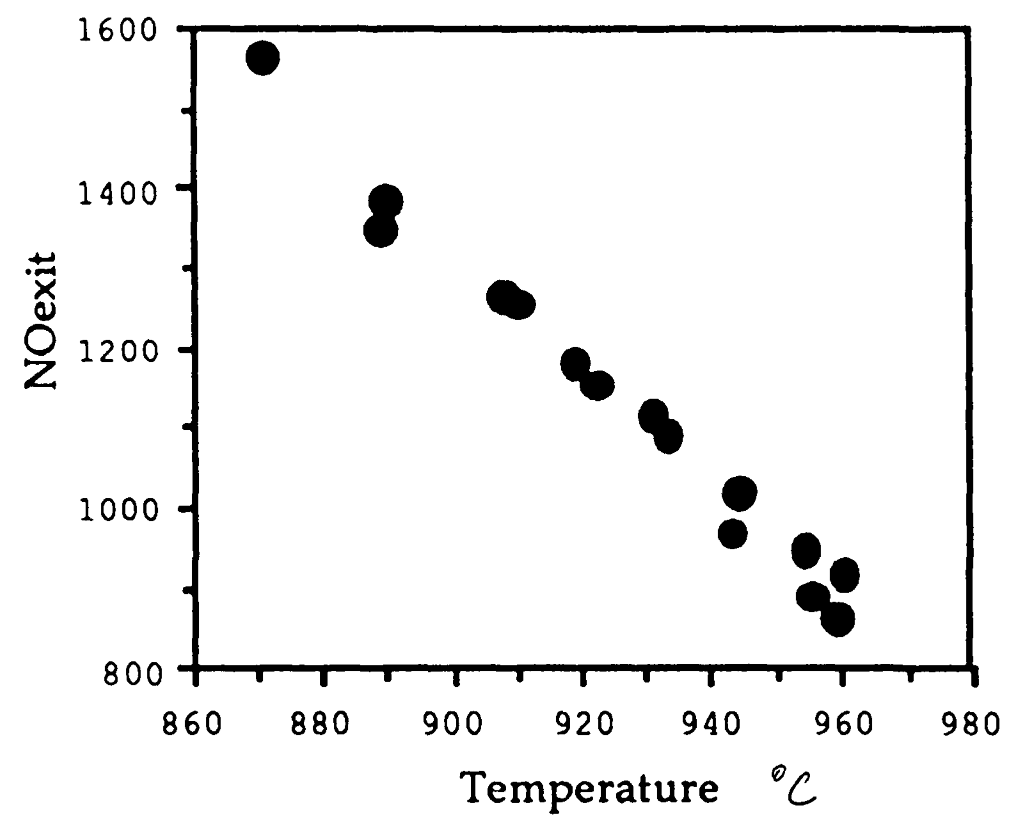


Baseline Check : No Salts in System



No Detectable Reaction Due To System Components

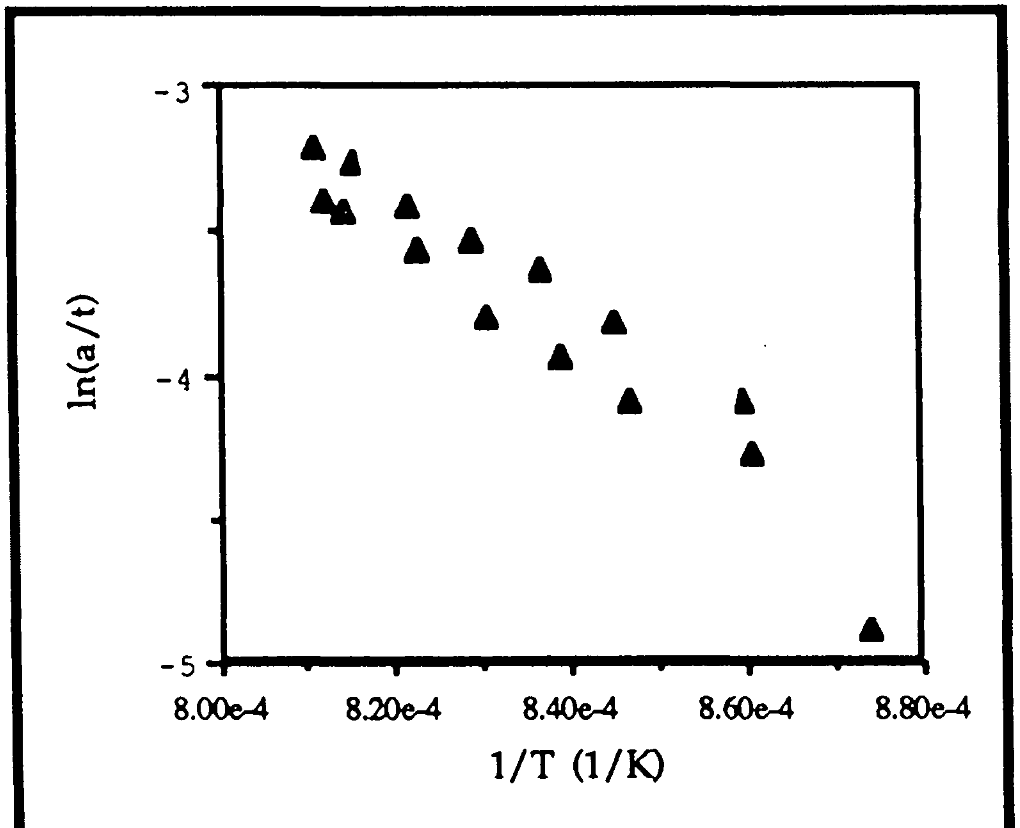
NO Depletion by Reaction with Molten Sodium Carbonate



20-70% decomposition

NO Depletion by Reaction with Molten Sodium Carbonate

(Assuming First Order Kinetics)



Slope = -Ea/R

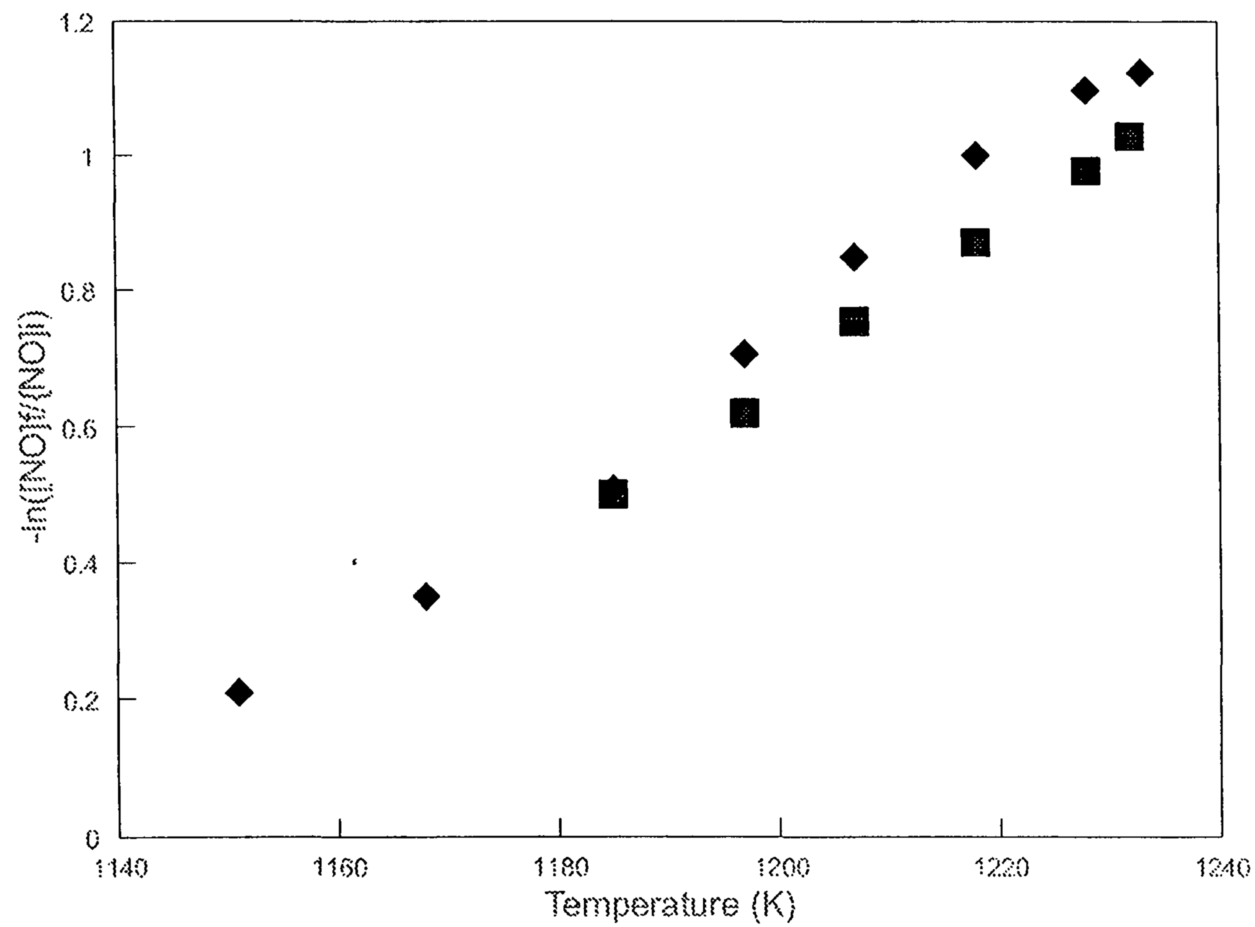
Regression Analysis
First Order Kinetics

Experiment	24	27	34	28	29	33
Mass of Na_2CO_3	35.0	35.0	35.0	17.5	17.5	17.5
R Squared	.8561	.9297	.9440	.9487	9305	9026
Slope: - Ea/R	-36115	-36635	-29244	-17276	-16163	-21538

Average Ea 282.7 kJ 152.4 kJ

(Change in Ea by Factor of 2 Implies Mass Transfer Limited)

NO Depletion by Reaction with Molten Sodium Carbonate (Assuming Mass Transfer Limited)



Solubility of NO in Molten Sodium Carbonate

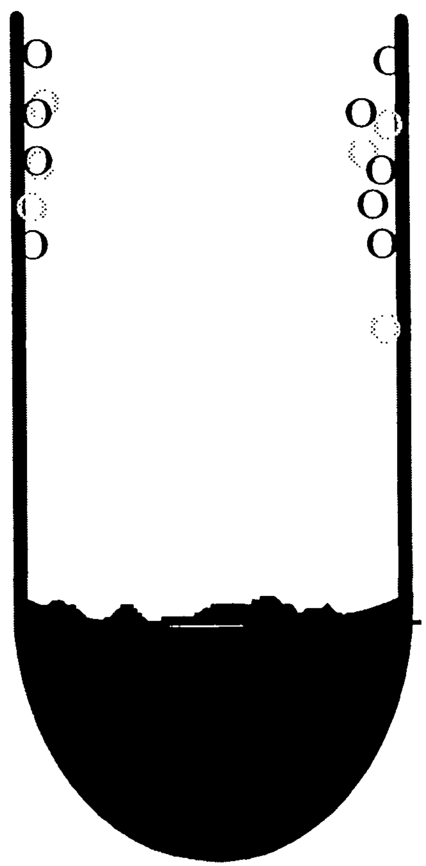
Solubility Increases with Temperature

Predict Hk According to Uhlig-Blander Theroy

Hk = 9.4 E-7 mol/cc atm at 1000 C

Solubility can not account for loss of NO.
Salt would be saturated in less than 10 seconds.

Nitrogen Analysis of Reacted Sodium Carbonate



Sample	N-Content
Dust	80 ppm
Melt	-ND-

Mass balance predicts
6000 ppm N in Salt
(If all N ends up in Salt)

Nitrogen Balance

In = NO (known)

Out = NO (measured)

+ N in Salt (measured)

+ N in Gas Products (??)

Summary/Conclusions

- NO formed primarily by fuel NO mechanism
- Emission is less than expected conversion
- NO/Sodium reactions are unique to recovery furnaces
- Sorbent processes support reaction mechanism
- Nitrate found in industrial smelt samples

Summary / Conclusions

- 20-70 % Depletion of NO observed for NO in contact with sodium carbonate over T = 860 - 960 C
- Depletion appears to be mass transfer limited
- Depletion can not be accounted for by solubility *actually a reaction*
- Analysis of salt indicates NO is being converted to gaseous reaction products

KRAFT RECOVERY BOILER CHAR BED MODELING

R. R. Horton

Institute of Paper Science & Technology

March 24, 1994

PERSONNEL

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- Pekka Siiskonen
  (Visiting Scientist, Tampella)
- Tom Grace
- Steve Lien
- Lisa Swango MS student
- Bob Horton

IMPORTANCE OF THE CHAR BED

- Shape will Influence Gas Flow
- Reduction Efficiency
- Effect on Emissions
- Effect on Temperature Field
- Safety

FEATURES OF A BED MODEL

- Bed Temperature
  - Surface
  - Internal
- Chemical Reactions
  - Surface Chemistry
    - Mass Transfer Coefficients
    - Kinetics
  - Internal Chemistry

FEATURES OF A BED MODEL

- Shape Prediction
  - Material Balance
  - Bulk Movement
    - Impact of Air Jets
    - Smelt Flow
- Entrainment
- Fume Generation
- Wall Mass

INPUTS TO THE BED SUBMODEL

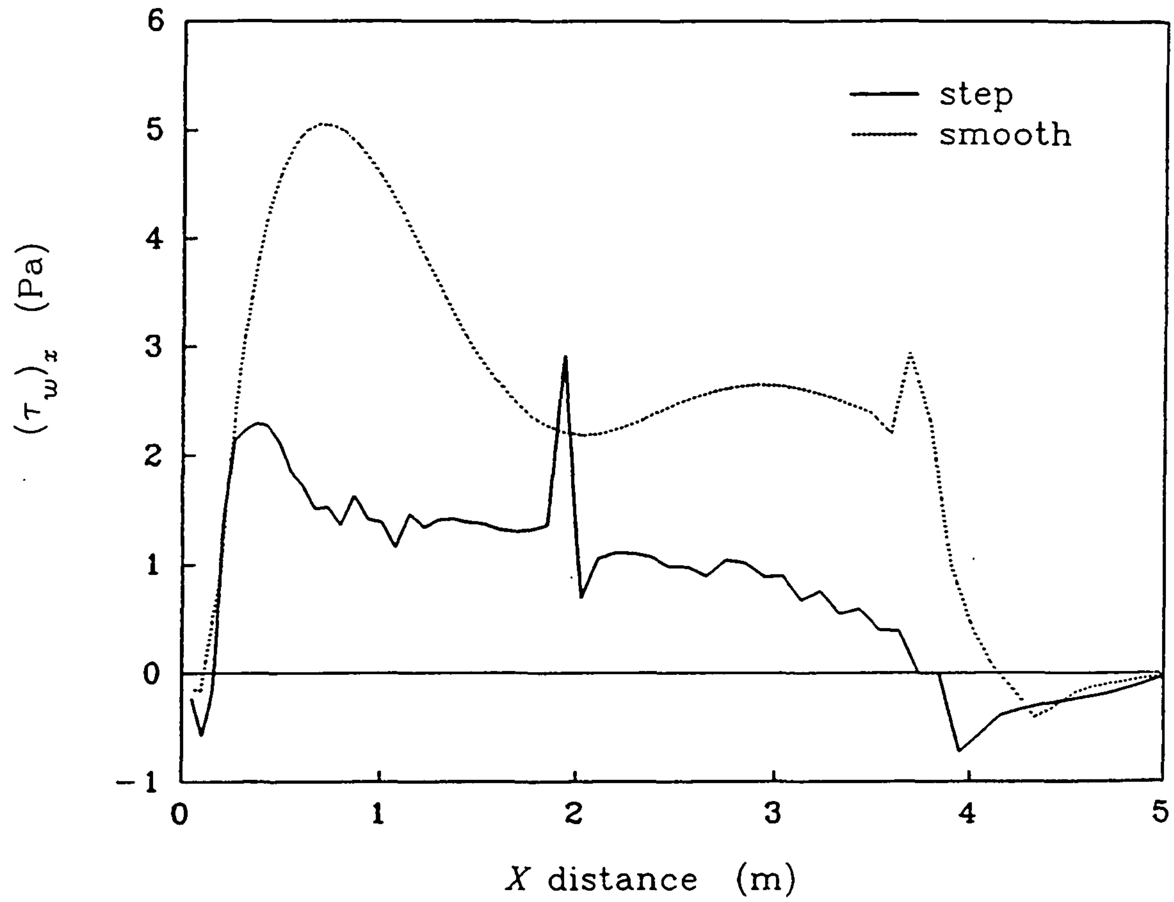
- CFD
  - Gas Velocities near Surface
  - Gas Concentrations
  - Heat Transfer
- Inflight Black Liquor Combustion
  - Rates of Mass to Surface
  - Composition

OUTPUTS FROM BED MODEL

- Shape
- Reaction By-products
- Energy Sinks/Sources
- Surface Temperature
- Entrainment
- Fume

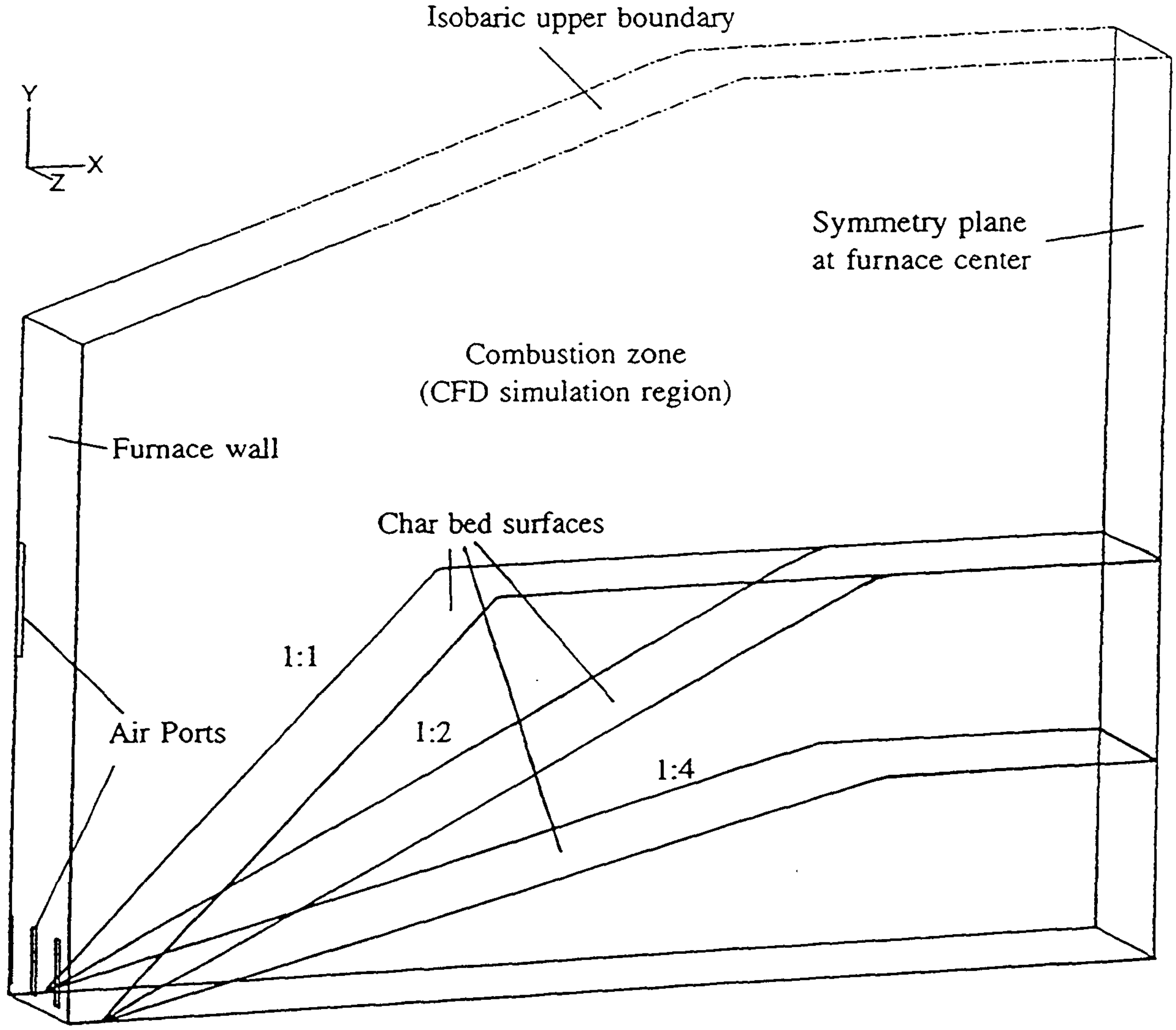
CHAR BED MODELING RESULTS

- Cartesian vs. BFC right angles body fitted coordinate curved surfaces
- Simplified Geometries and Shapes
- Quarter Furnace
- Finite Element vs. Finite Difference unstructured grid
- Chemistry being Added

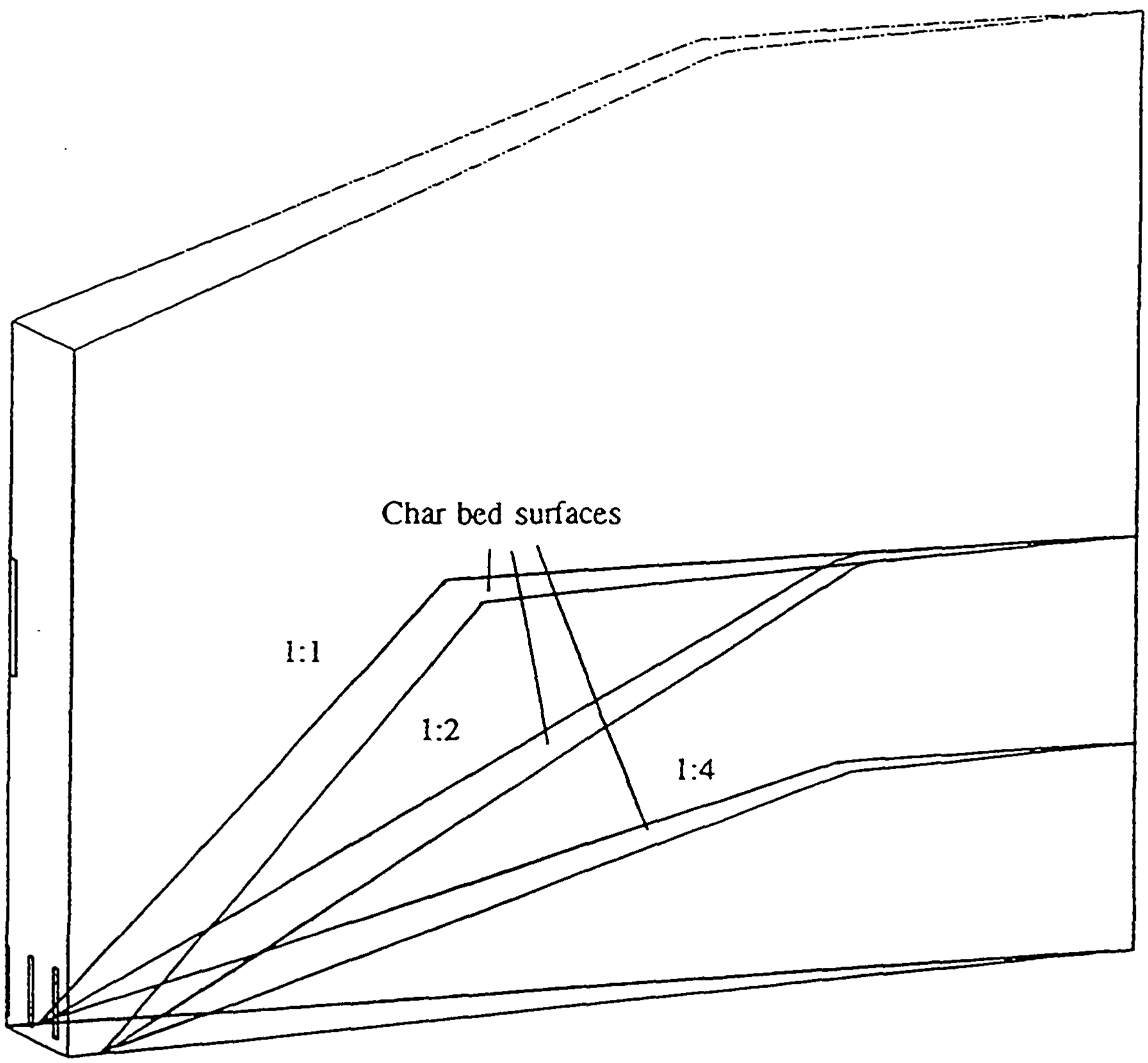


Comparison of shear stress distributions on step and smooth beds for nonisothermal cases.

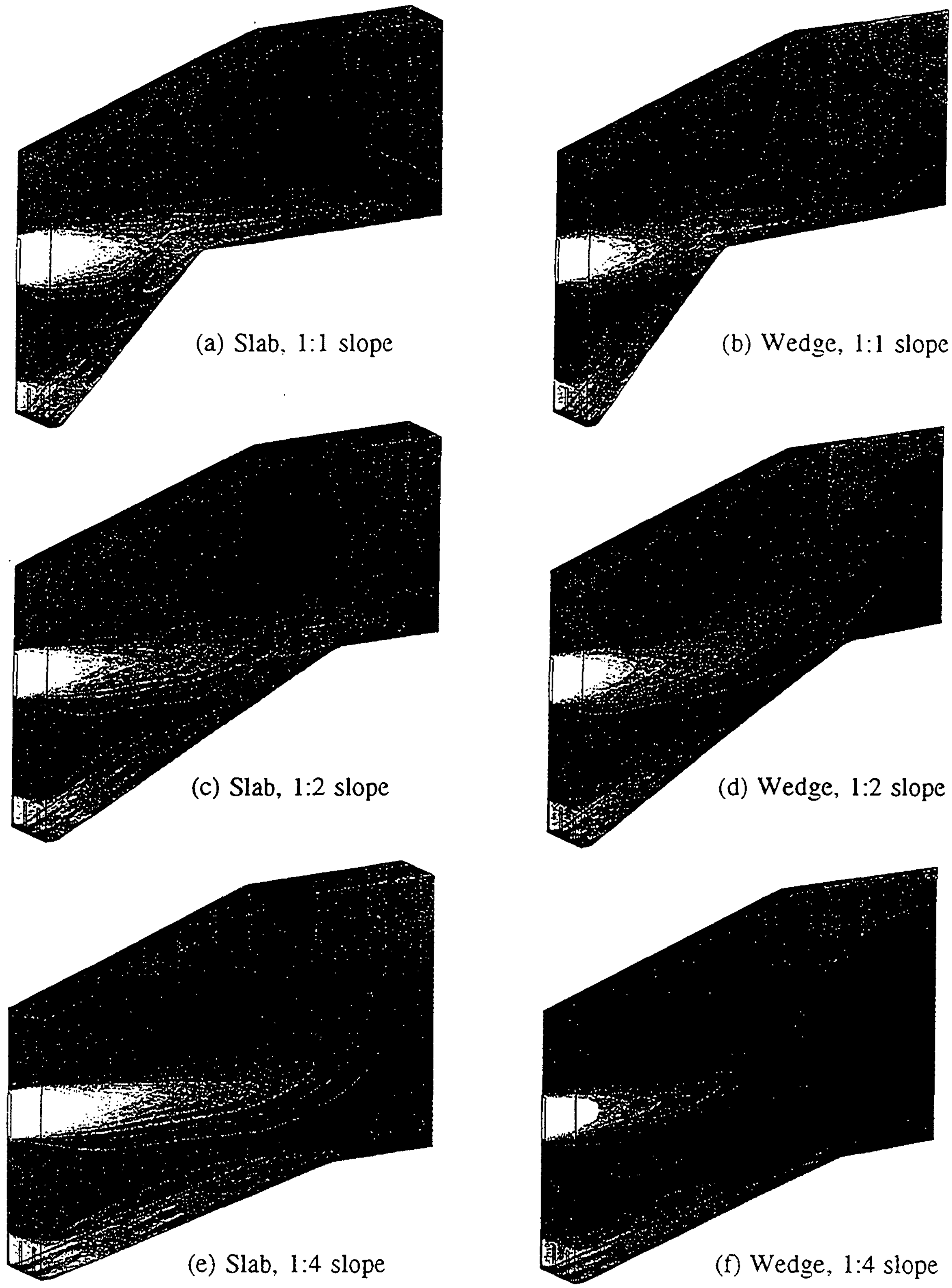
Velocity predictions are the same between
Cart. & BFC.



Geometries of slab char bed models with 1:1, 1:2, and 1:4 slopes.

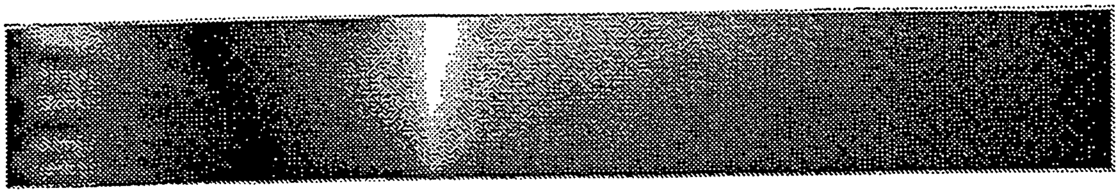


Geometries of wedge char bed models with 1:1, 1:2, and 1:4 slopes.

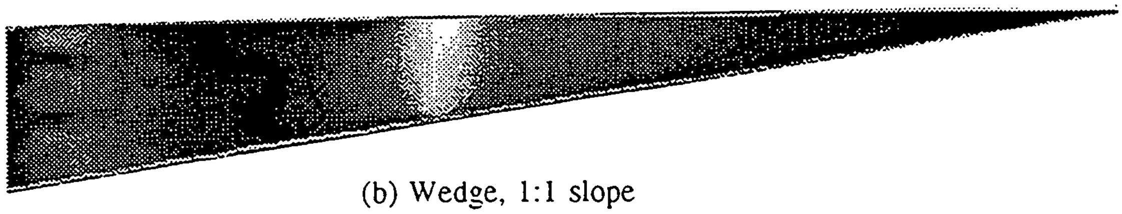


Flow patterns on boundary surfaces in different models.
Gray scale = 0 - 80 m/s (dark - bright).

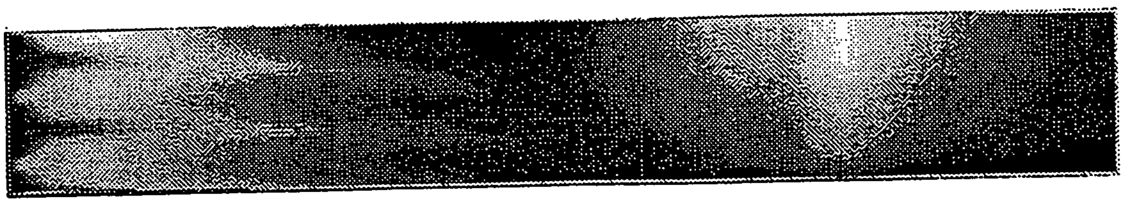
Mass Transfer coeff



(a) Slab, 1:1 slope

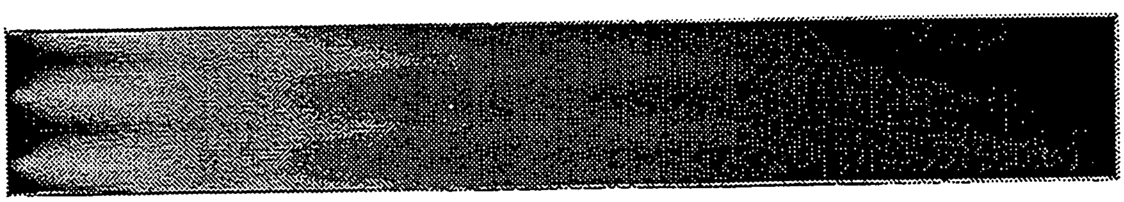


(b) Wedge, 1:1 slope



(c) Slab, 1:2 slope

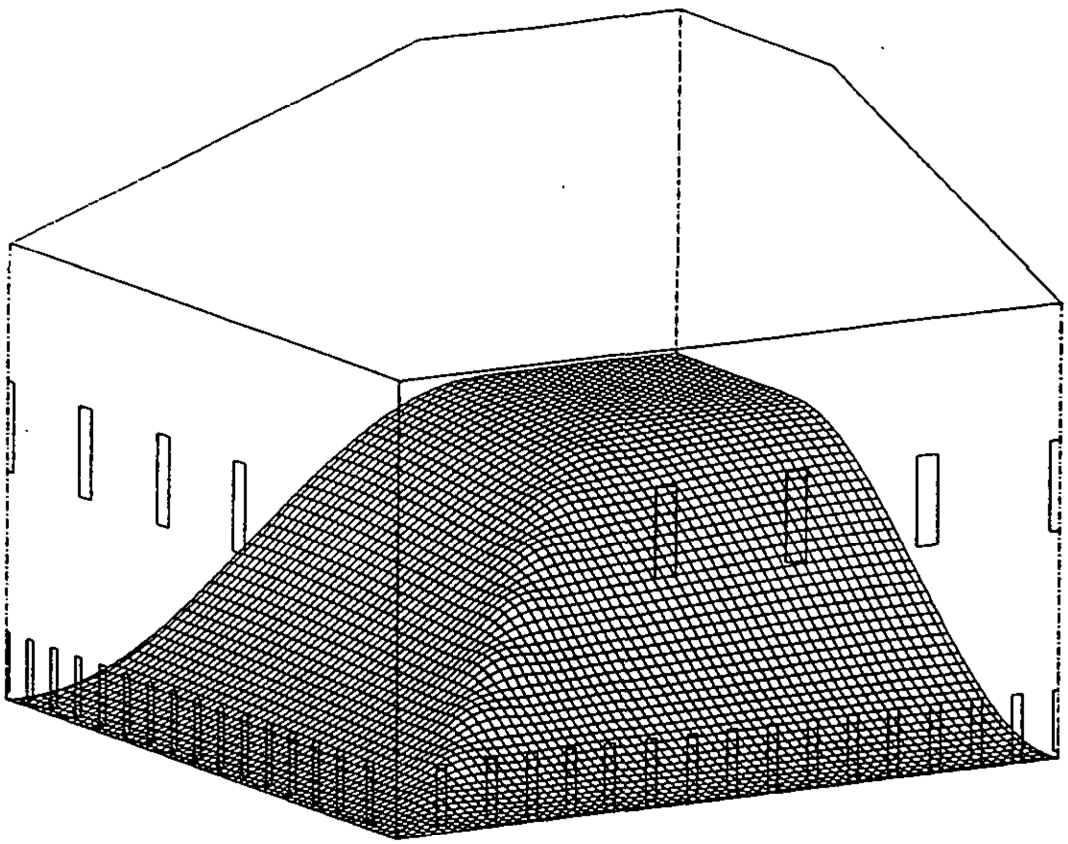
(d) Wedge, 1:2 slope



(e) Slab, 1:4 slope

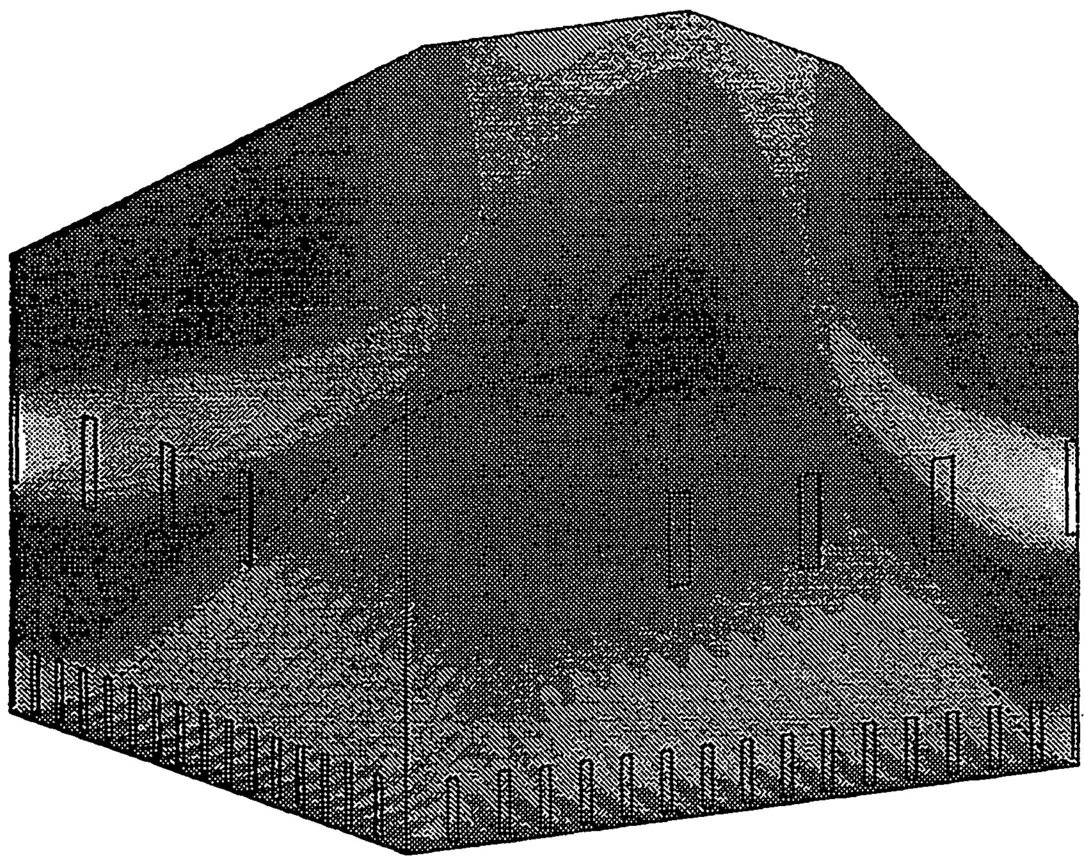
(f) Wedge, 1:4 slope

Plan views of shear stress distribution patterns on the char bed surfaces.
Gray scale = 0 - 4.04 Pa (dark - bright) for (a) and (b).
Gray scale = 0 - 1.45 Pa for (c), (d), (e), and (f).

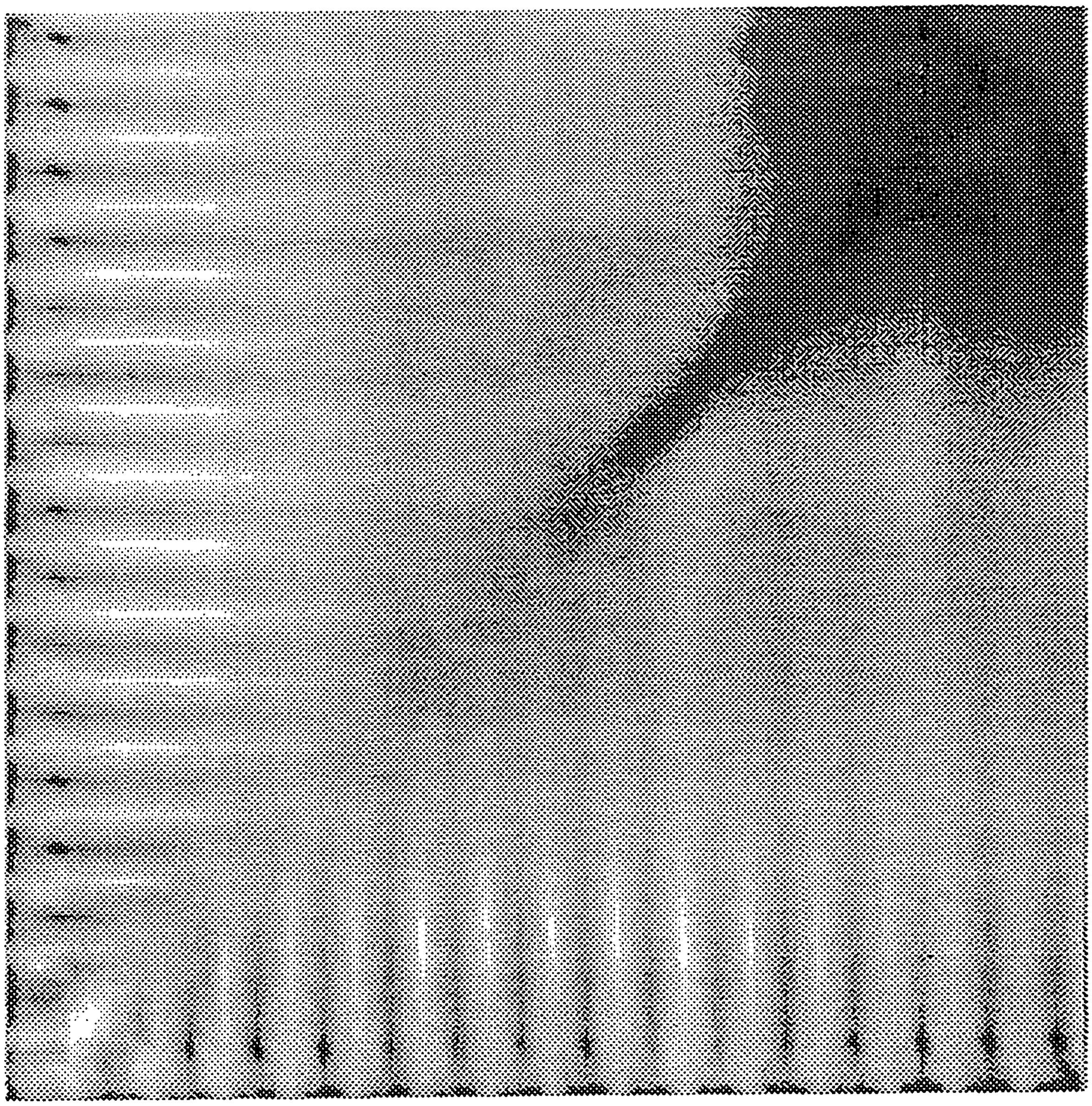


Geometry of the CFD char bed model.

1/4 simulated
with BFC



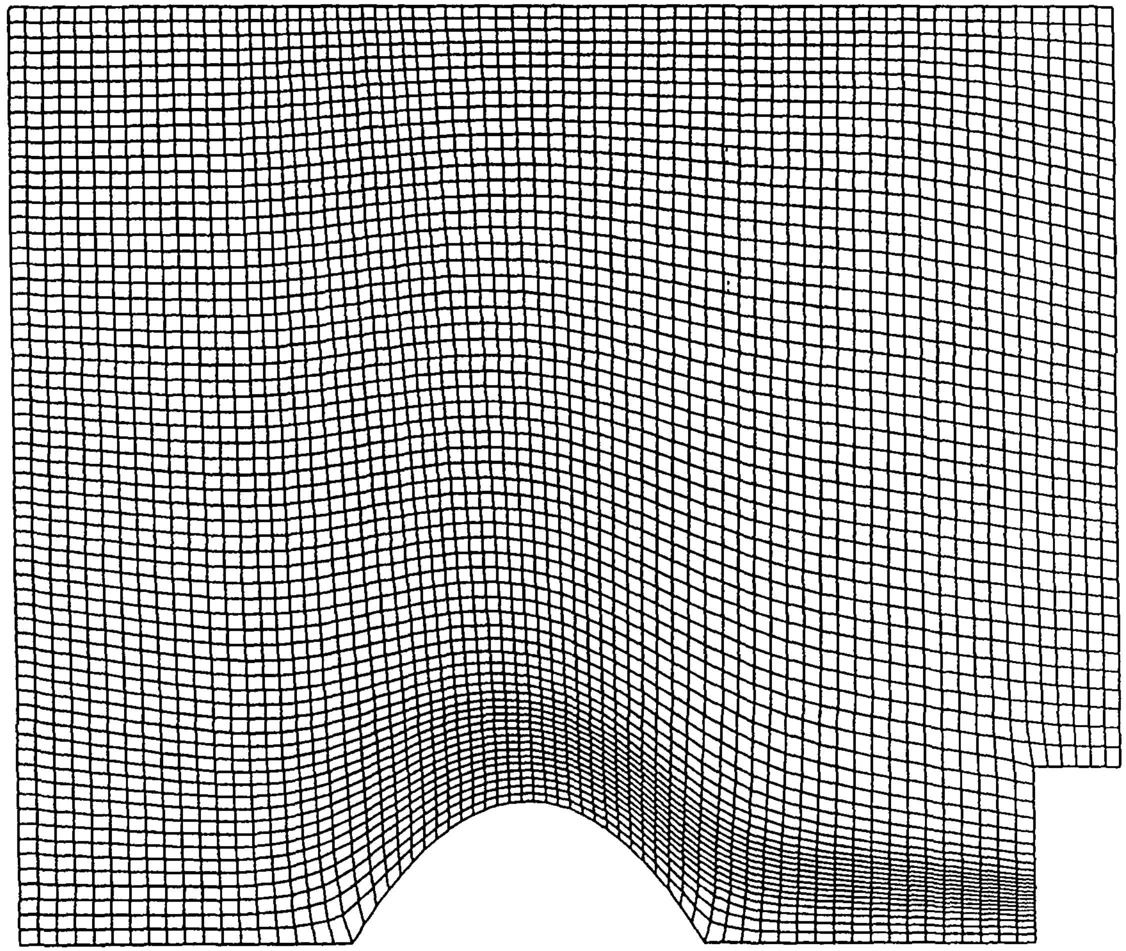
Velocity distributions on the symmetry planes and near the char bed surface.
Gray scale = 0 - 80 m/s (dark - bright).



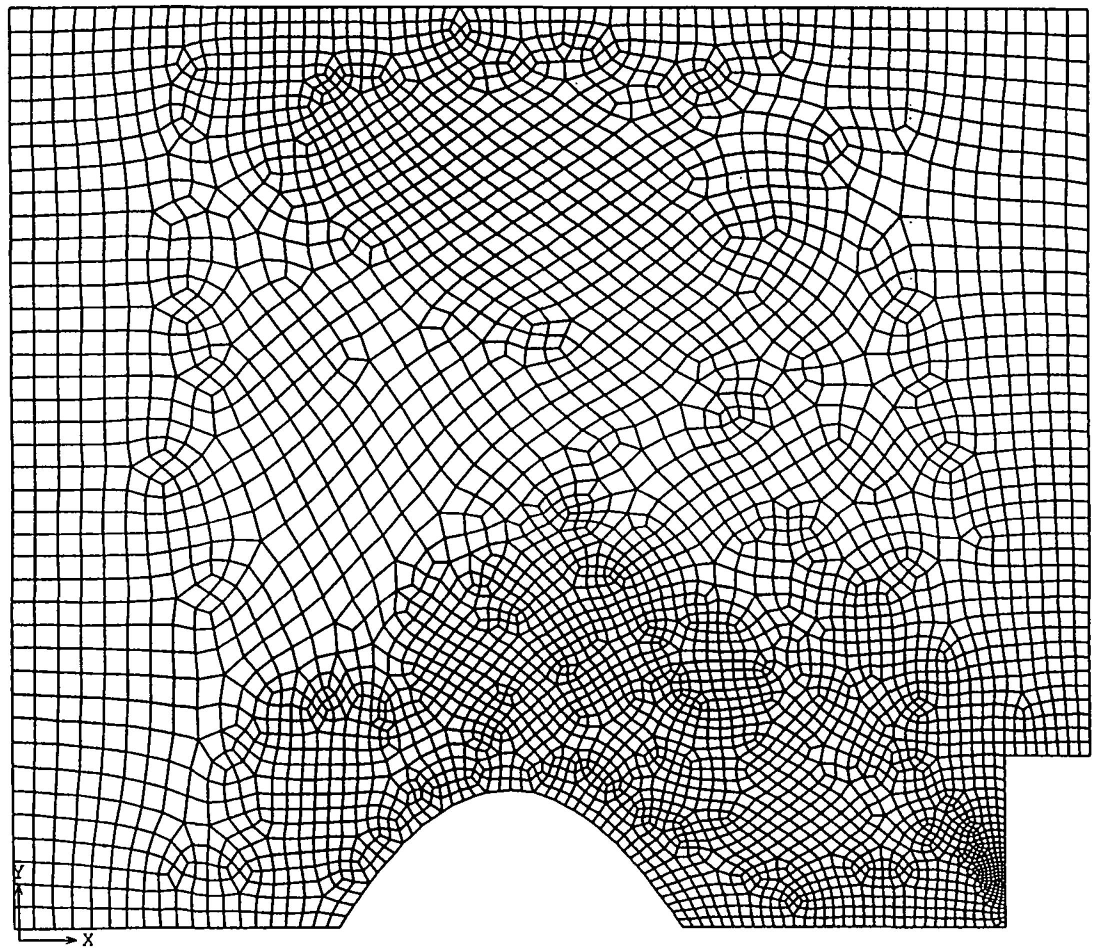
Distribution of mass transfer coefficient on the char bed surface.
Gray scale = 0.01 - 0.16 m/s (dark - bright).

FINITE ELEMENT VS. FINITE DIFFERENCE

- **FIDAP vs. FLUENT codes**
- **Inherent Grid Structure Differences**
- **Predictions were Identical**
- **Solver Speed and Memory are Trade-offs**



BFC Finite Difference Grid for a Char Bed Reactor



Finite Element Grid for a Char Bed Reactor

CHAR BED COMBUSTION ALOGORITHM

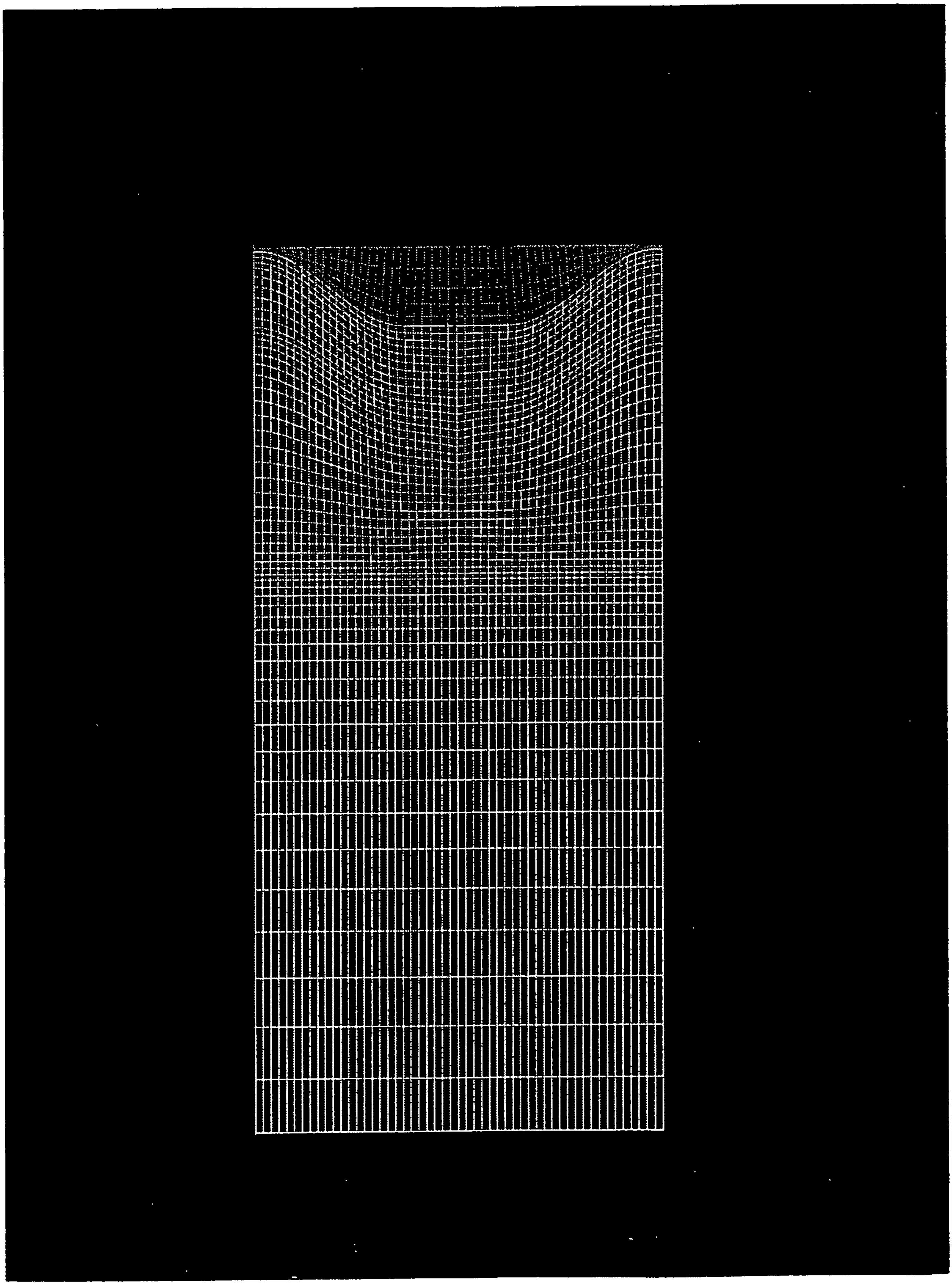
- From CFD Calculations of Gas Phase:
  Shear Stress, Velocity, Composition, Temperature
- From Inflight Black Liquor Combustion:
  Mass, Composition, Location of Material to Bed
- Calculate a Mass Transfer Coefficient
- Predict Mass Transfer Limited Rates
- Predict Kinetically Limited Rates
- Predict Overall Rates for each Cell
- Adjust Boundary Locations
- Exchange Mass and Energy with CFD Portion

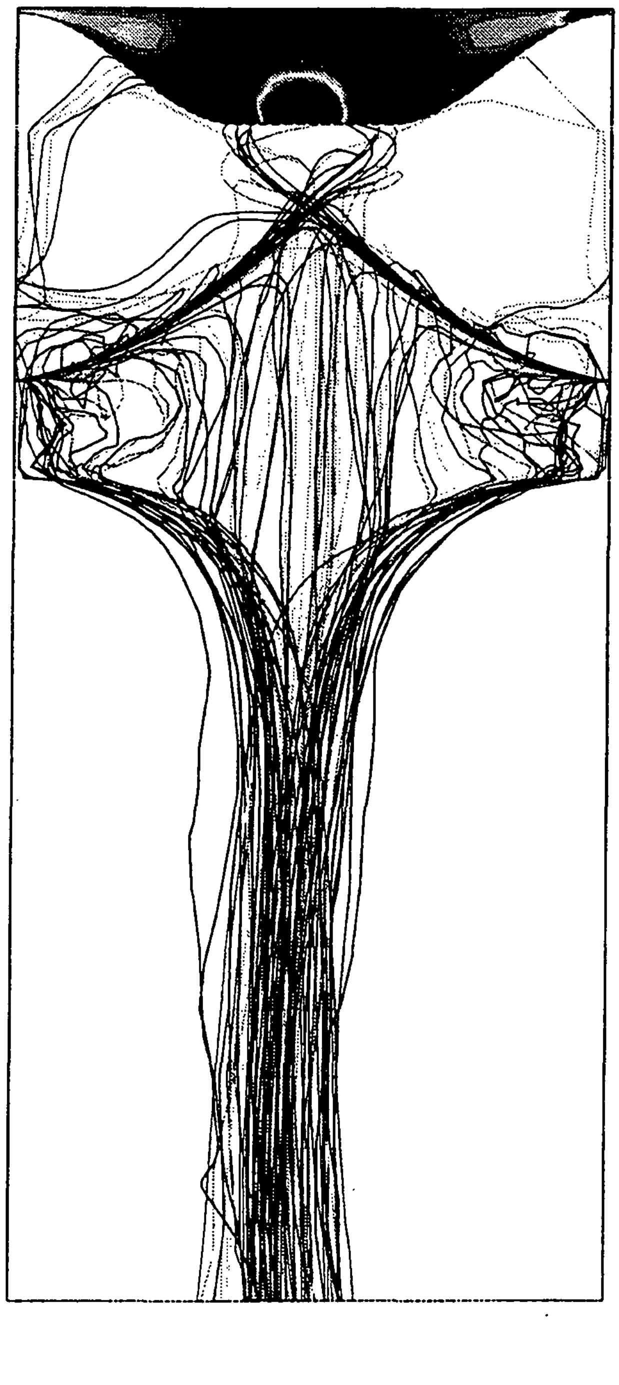
FEATURES OF THE INITIAL CHAR BED MODEL

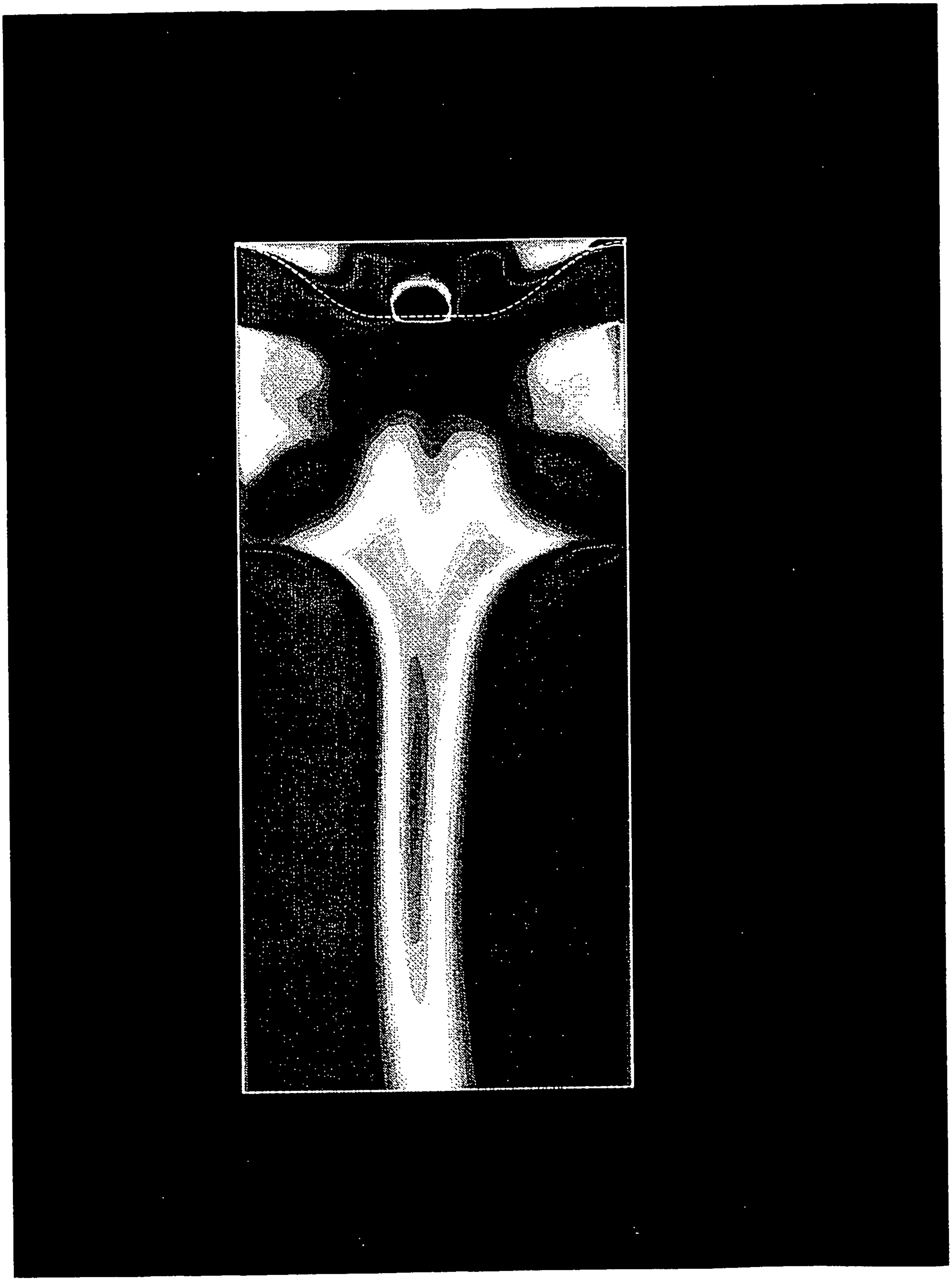
- Fully Three Dimensional
  - Active Surface Region
  - "Conducting Wall" Cells for Interior
  - Conformable Grid Mapping
- Rough Shape via Material Balance
- Full Char Combustion Chemistry
- Evaporation and Pyrolysis

PRELIMINARY RESULTS WITH BED MODEL

- 2-D Case with Inflight Combustion and Flow
- Consider Only Char Reactions
- Mass Transfer Coefficients from CFD (Flat Surface)







REMAINING ISSUES

- **Characterization of Surface**
  - **Flat Surface, Hemispheres, or Individual**
- **Simultaneous Reactions**
  - **Evaporation/Pyrolysis**
  - **Char Combustion/Gasification**
- **Do Combustion Model Parameters Change If a Particle Impacts a Surface?**

EXTENDED CHAR BED MODEL

- Entrainment
- Shape via Impaction
- Contibution to Fume
- Rigorous Wall Model

Key Issues in Recovery Boiler Modeling

1. How will the model/results be used
2. Is there a need for generic results ?
3. Model development technical requirements
4. Fundamental black liquor information needs
5. Model simplification - "cost-effectiveness"
6. Model validation
7. Code ownership, availability, accessibility

How Will The Model Be Used:

Paper Companies:

Most interest at the corporate level, in engineering, R&D, and technical service.

- troubleshooting problems with particular boilers
- optimizing boilers
- checking recommendations and designs of the boiler manufacturers

General knowledge of recovery boiler behavior would be useful in the mills if it were properly distilled and transferred to the mill level.

Paper companies benefit from increased knowledge by boiler manufacturers

Boiler Manufacturers:

- access fundamental black liquor combustion information to upgrade their in-house models
- obtain submodels for incorporation in their own codes
- interact with other model developers to keep abreast of problems, approaches, etc.
- evaluate methods of simplifying models
- access general knowledge about recovery boilers developed on the project
- take advantage of the validation of the DOE models to increase confidence in their own in-house models
- run cross-checks of their in-house models against the DOE project global model.

Generic Results - "DOE Deliverables"

Two different ways that the recovery boiler models can be used.

1. A particular recovery boiler can be modeled and sufficient simulations run to solve one or more problems on this boiler. This would be done on a contract basis and the results known only to the parties involved.

2. Recovery boilers could be modeled generically to determine the effects of different types of variables on furnace performance. The modeled boilers may or may not correspond to any particular real boilers. These simulations would be done within the scope of the project and the results made generally available as part of the project.

The second approach was behind the "DOE Deliverables" which aimed at

a. evaluation of air entry arrangements and developing criteria for air entry

b. evaluation of the effects of liquor sprays on furnace combustion and bed buildup - develop criteria for liquor sprays

c. evaluation of the effect of liquor parameters on combustion in the furnace

d. determine relationship between firing practices and wall heat fluxes

Possible Generic Applications of Modelling

1. Evaluate the effects of flow increases associated with higher furnace loads on carryover and the ability to counter these effects by using coarser sprays.

2. Evaluate the effect of drop size on reduction efficiency. Determine the amount of reduction that takes place in flight.

3. Develop a means for handling liquor spray - gas flow pattern coupling.
   a. are there "pairs" - specific spray and gas flow patterns that go together ? why ?
   b. given a certain flow pattern, what spray pattern should be used ?

4. Use cold flow to evaluate the effect of air entry arrangements
   a. characterization of flow patterns
      - relative stability
      - nature of pattern in vertical velocity
      - mixing or turbulence intensity distribution
      - horizontal-plane velocity characterization
   b. determine limited set of air-entry variables
   c. determine patterns as f(air entry-variables)

5. Determine the effect of flow patterns on black liquor combustion
   a. characterize the combustion
      - carryover
      - quantity of fuel delivered to bed and walls
      - vertical distribution of fuel release
      - horizontal-plane distribution of fuel release
   b. systematic determination of the effects of flow <u>pattern</u> on combustion for several, carefully-defined spray conditions

6. Determine the extent that cold flow patterns can be usefully used in combustion simulations.
   a. evaluate the effects of sources/sinks on flow patterns
      - evaporation
      - local temperature variations
      - mole changes associated with combustion
      - liquor spray momentum transfer
   b. evaluate the effect of temperature and oxygen fields on combustion

7. Rationale for the evolving firing practice of increasing the proportion of air above the liquor guns.
   a. what happens when the air is moved up ?
      - flow pattern changes
      - effect on combustion
   b. why is this good or bad ?
   c. is a large bed a necessary element in this firing approach ?

8. Evaluate the effects of air temperature
   a. cold tertiary vs hot tertiary
   b. effects of air temperature on flow pattern - Thwing-Newby
   c. effects of air temperature on temperature field and on combustion rates

9. Determine how increased furnace load affects combustion patterns in the furnace and thus wall heat absorption patterns and furnace exit gas temperature.

10. Determine the extent that changes in firing practices can influence heat absorption patterns in the furnace.

11. Determine the extent that flow and/or combustion instabilities can influence heat flux variations to the walls.

12. Can oxygen enrichment give increased capacity through lower gas velocities ?
   a. how/where should oxygen be put in
   b. are there adverse effects of using oxygen

13. Definition of conditions that can produce stable vortices in the lower furnace.
   a. is circulation good, bad, or indifferent and what does it depend on ?
      - does the level that circulation is introduced at make a difference
      - how important is shear at the primary air level
      - do interlaced tertiaries help or hinder
   b. can certain bed shapes "lock in" a vortex ?
   c. do vortices form when changing from one flow pattern to another, e.g. in response to macroscopic air flow changes ?

14. Evaluate the effects of draft on black liquor combustion
   a. effects on cold flow pattern
      - infiltration air
      - distortion of air entry velocities
   b. effects on oxygen concentration field
      - extent infiltration air contributes to burning
      - relation to excess O_2 in flue gas

15. Determine the effect of furnace depth-width ratio (for the same cross-section) on black liquor combustion.
   a. define certain constraints on liquor spray and air distribution combinations
   b. look at jet penetration, flow patterns in cold flow
   c. use full model to handle effect of greater heat transfer are per cross-section

Model Development Technical Requirements:

Technical needs to complete the development of the recovery boiler model(s).

- completion of the global recovery furnace model
- models of the convection section of the boiler dealing with deposition and plugging.

The latter is the biggest remaining effort.

Researchers attempting to define these requirements and to put together a draft work statement.

Fundamental Black Liquor Information:

End-users meeting felt that this was a very important part of the DOE recovery boiler modeling program

Most of the information needed for the global furnace model will be available at the end of this 4th year of the project and the remaining is well underway.

Considerable additional fundamental information on particle deposition rates, adhesion, deposit strength development, and removal needs to be developed.

Jim Frederick at Oregon State has a program partially underway that can supply this information.

Honghi Tran of the University of Toronto is also part of that team and brings considerable expertise on deposit strength and sootblowing.

That work needs to be incorporated into this program if the convective section modeling is to be accomplished.

Model Simplification - "Cost-Effectiveness"

The need is to get reliable answers to questions about recovery boilers using models that are simpler to use and which take less time to produce results.

The global models being developed are large, require a huge amount of computation, and it is difficult to assess quantitatively what the model output means, or even whats better or worse.

One objective of any continuing effort should be to evaluate how effectively "fixed-field" solutions can be used to obtain practical answers to problems.

It is also necessary to develop reasonable ways of condensing and interpreting model output.

This is one area where IPST could make a major contribution to the effort.

Model Validation:

Validation is already part of the model development effort.

Submodels are tested against data as they are developed.

- The isothermal flow model has been validated against water model data of two different recovery boilers and there has also been validation against limited cold flow data in a recovery boiler.

- The black liquor combustion models that are being developed have been validated against single-drop black liquor burning data.

the global furnace model must be validated against field data obtained on actual recovery boilers.

Validation does not require breakthroughs in sensors and measurement technology on recovery boilers. The necessary measurements can be made with existing methods, especially if the measurements need only be made for a limited time.

Validation will have the following key elements:

- definition of critical output variables to be predicted and measured

- development of cause and effect relations between selected operating variables and the critical output variables based on model simulations

- measurements of critical output variables for different values of selected operating variables

- comparison of predicted and measured results.

Paprican has some plans for a model validation program and it would be advantageous to tap into that effort.

Code Ownership, Availability, Accessibility:

There are two things necessary in dealing with these issues in developing a plan for extending the modeling work.

1. Determine what the paper companies (and boiler manufacturers) actually want with respect to the code.
   accessibility - is a US access point essential?
   physical possession of the code in-house?

2. Address upfront all ownership, accessibility and access issues in any contract involved in extending the project

ITEMS REQUIRING DECISION

The final development of a statement of work for an extended modeling effort will require decisions on the following.

1. Should generic modeling be carried out in order to address the practical recovery boiler "deliverables" as a specific part of the project?

2. Should the modeling project be extended to include modeling of the convective part of the boiler?

3. What is actually desired by users with respect to codes ownership and accessibility?

4. What is a reasonable time frame?

BLACK LIQUOR DELIVERY SYSTEMS

(DOE Contract No. FC02-88CE 40839)

by

Jeff Empie

Steve Lien

Don Sachs

Richard Rumsey

for

IPST Project Advisory Committee

Institute of Paper Science and Technology

Atlanta, Georgia

March 25, 1994

GOAL

Increase recovery boiler efficiency and capacity through improved black liquor spraying technology

OBJECTIVE

Develop new and improved black liquor spraying nozzles that give the operator some capability to control droplet size and size distribution

BENEFITS

* Increased thermal efficiency

  - Increase fired solids by 5%
  - Reduce flue gas temperature by 25 ^{0}F
  - Reduce carbon in smelt by 0.5%
  - Reduce sootblowing steam by 0.5%

  - Potential is 500,000 BTU/adt

  - Industry value is $90MM/yr

* Increased process productivity

  - Recovery boiler debottlenecking
  - Reduce shutdown frequency due to plugging

* Improved equipment design potential

* Improved process control potential

DOE FUNDING

		$M
Initial Allocation (thru 9/92)		1,250
Fifth Year Extension (thru 9/93)		160
Sixth Year Extension (thru 9/94)		153
	TOTAL	1,563

TECHNICAL APPROACH

* Video tapes of black liquor sprays from commercial nozzles

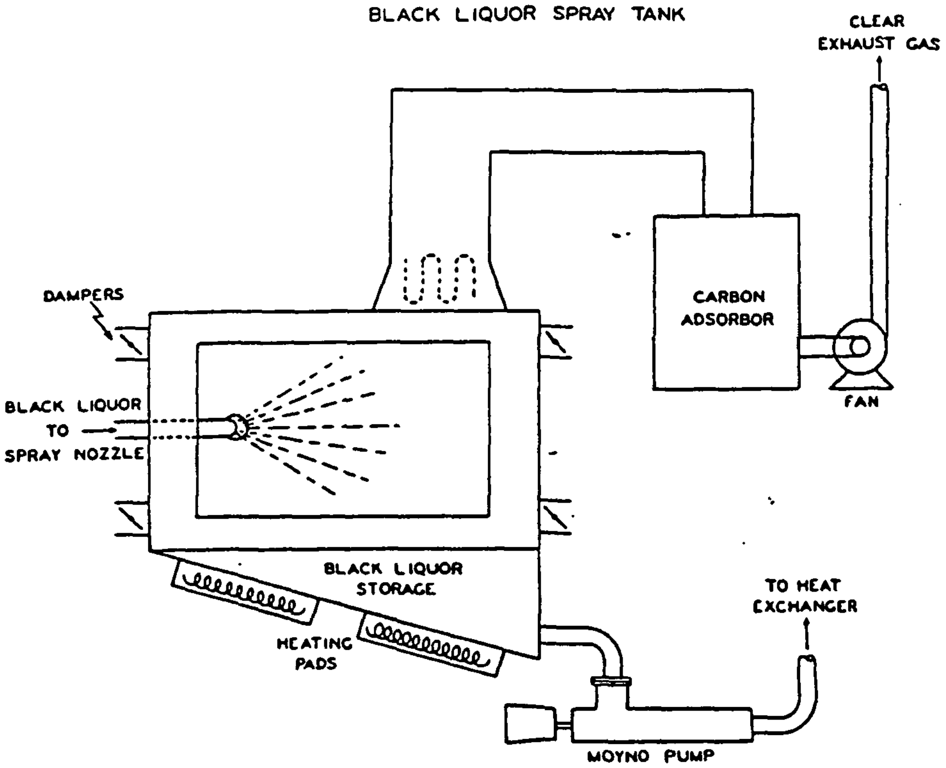
* Image analysis of videos to give droplet size distribution

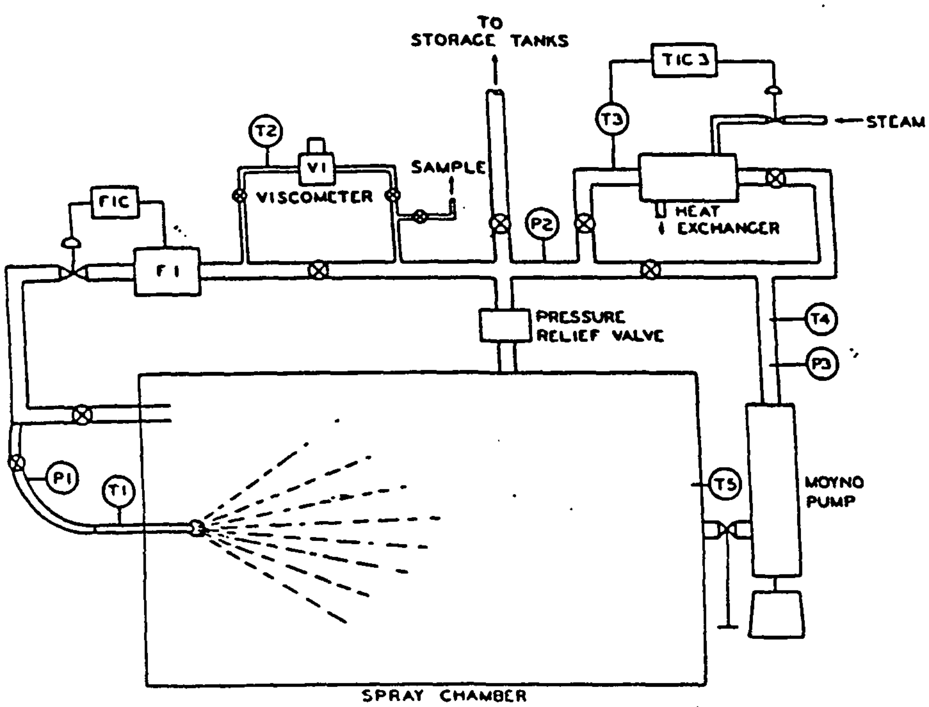
* Range of experimental conditions with black liquors from several mills using different pulping conditions

PROGRAM PHASES

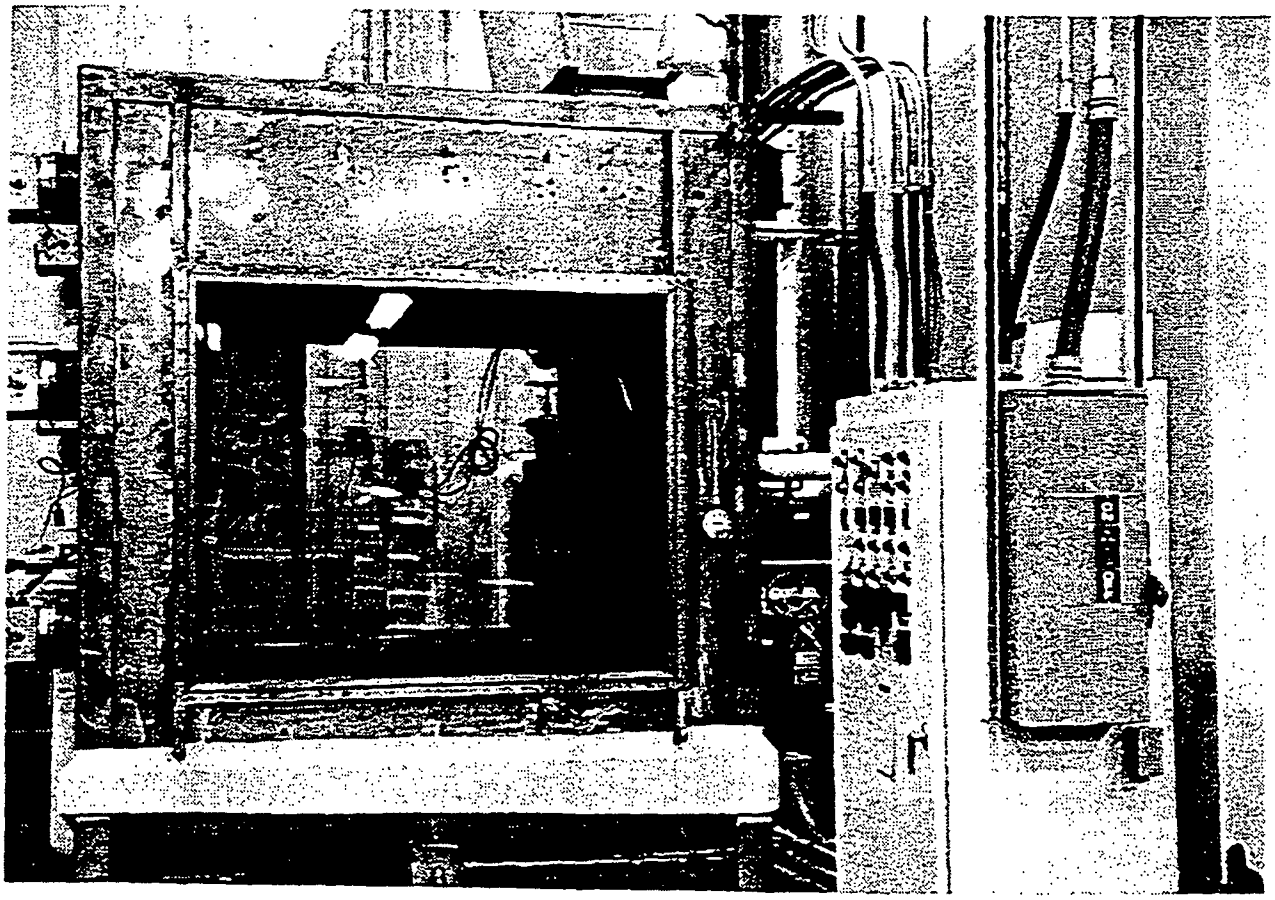
* Equipment design and construction, and methods development
* Characterization of nozzles currently in use
* Characterization of other commercial spraying systems
* Investigation of commercially viable improvements
* Exploratory study of alternative delivery systems

BLACK LIQUOR SPRAY TANK





Black Liquor Spraying Facility at IPST



PREVIOUS RESULTS

* Drop size data obtained for three commercial nozzles for range of operating conditions and variety of liquors.

* Square Root-Normal Distribution most effective.

* Median drop diameter correlated with operating parameters and physical properties.

* Drop size independent of liquor type at same viscosity. Most important parameters are nozzle type and diameter, liquor pressure, temperature, and viscosity.

* Alternative commercial nozzles no improvement.

* Modifications to present commercial nozzles not effective.

* Weak temperature effect up to a transition temperature. Above this, sharp decrease in drop size of more than 20%. Related to flashing phenomena.

* Fluid mechanics controls drop size. Balance of viscous, momentum, and surface tension forces. Need independently-controlled force to change distribution

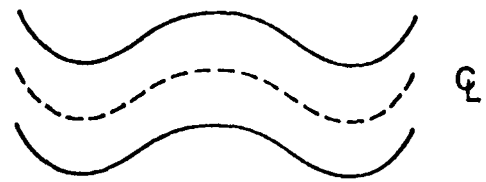
NOVEL NOZZLE CONCEPTS

* Vibratory Assist
  - potential for narrower size distribution
  - pulsating flow mode
  - interrupted flow mode

* Dielectrophoresis
  - potential for skewed distribution
  - uses non-uniform field around spray sheet to promote coalescence
  - weak effect requires high voltage and no current

VIBRATORY ASSIST

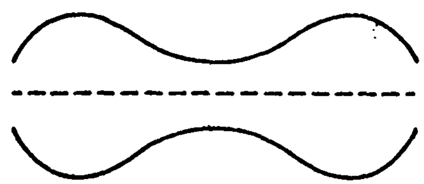
Sinuous Wave Generation – Wave-like Disturbances to Upper and Lower Surfaces of the Sheet Are in Phase



– Vibration in Direction Normal to Plane of the Sheet

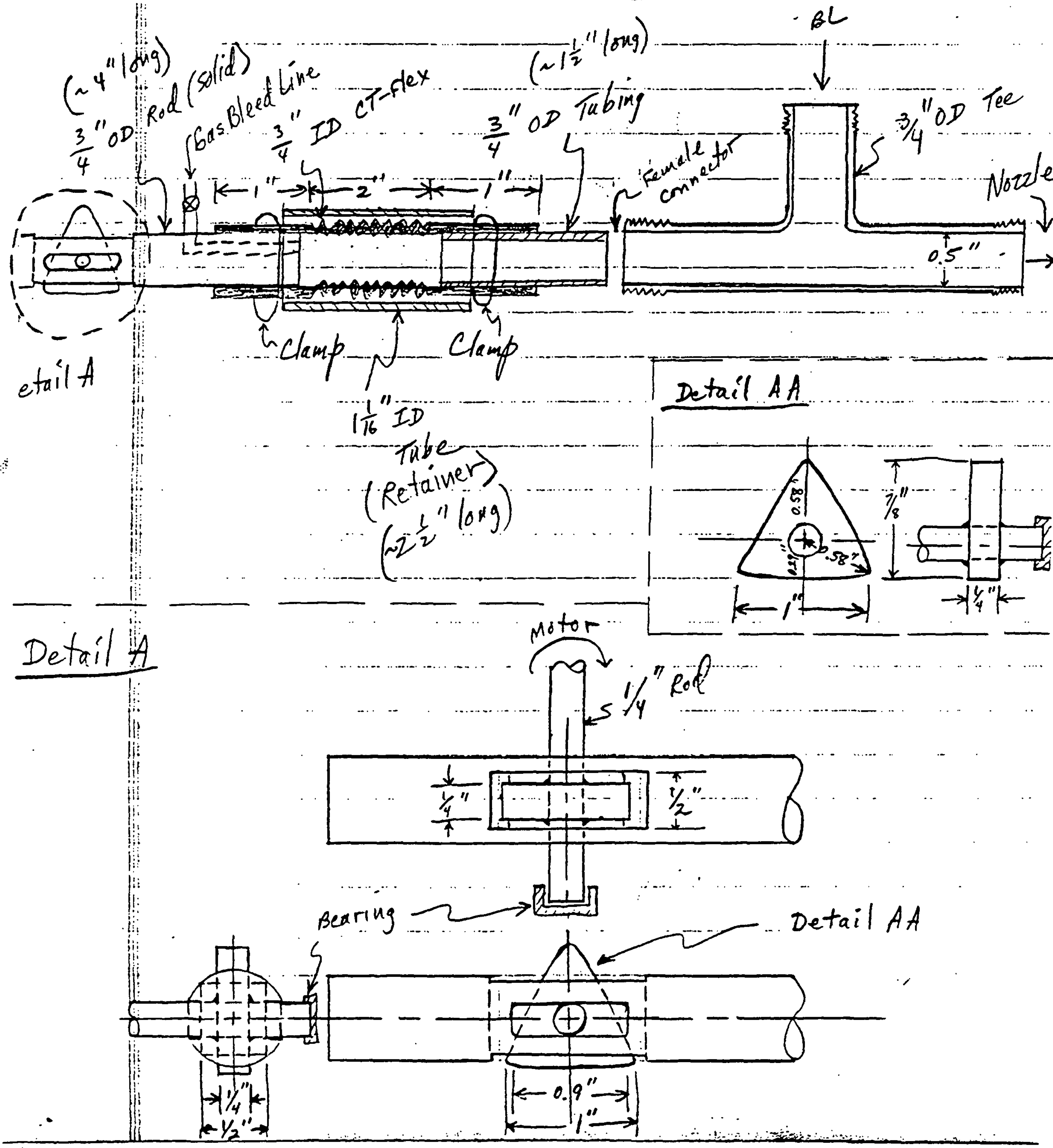
VIBRATORY ASSIST

Dilational Wave Generation – Wave-like Disturbances to Upper and Lower Surfaces of the Sheet Are Out of Phase



– Vibration in Direction of Liquor Flow (i.e. pulsation of Liquor flow)

VIBRATOR ASSEMBLY
(with CT-Flex Tubing)



EARLY RESULTS

* Vibratory Assist - Pulsating Flow

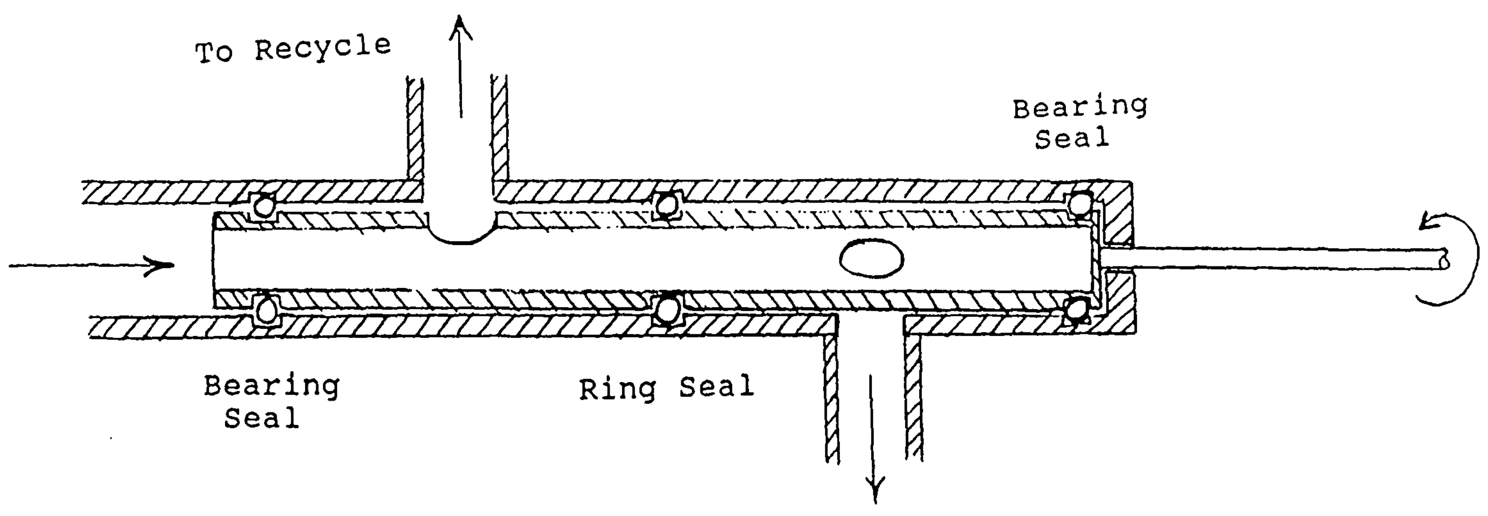
  - +/- 20% flow variation

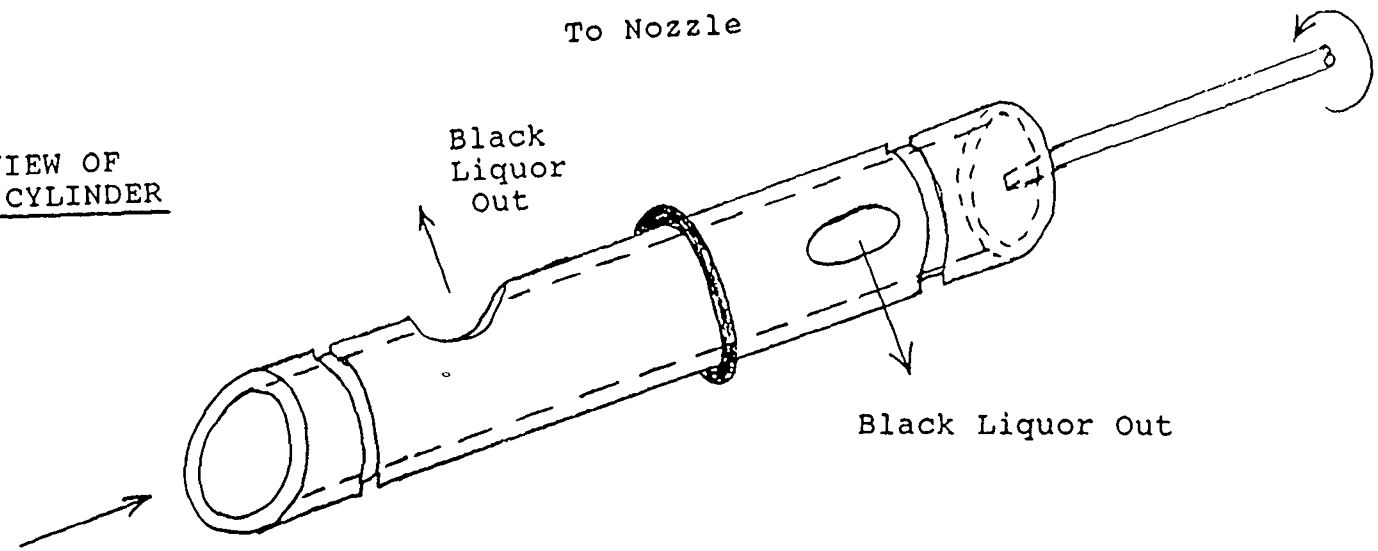
  - frequencies up to 150 Hz

  - no change in median drop size or size distribution

AXIAL VIBRATORY ASSIST

(INTERRUPTED FLOW MODE 1)

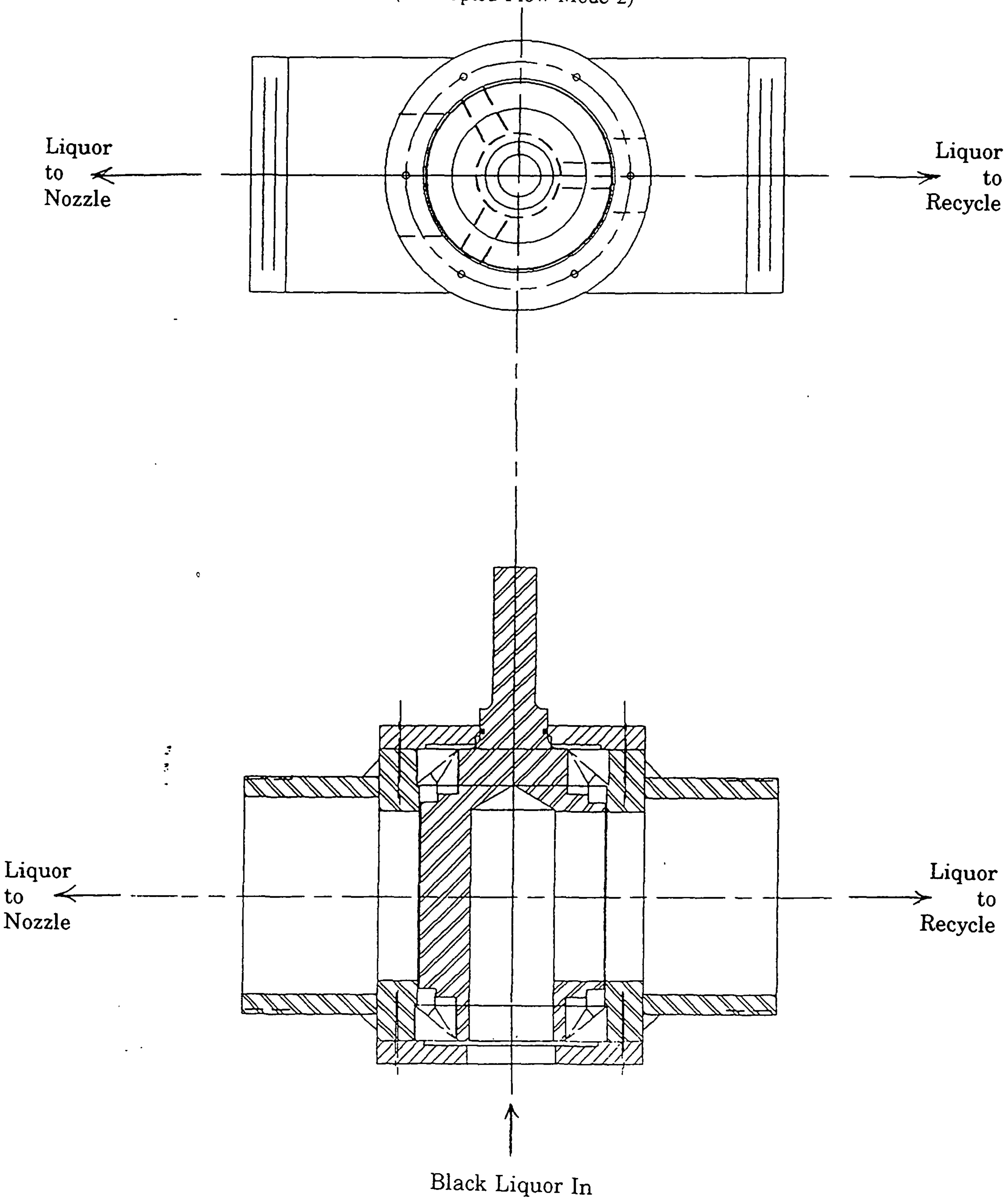




PLAN VIEW OF ROTATING CYLINDER

AXIAL VIBRATORY ASSIST

(Interrupted Flow Mode 2)



Early Results (cont'd)

* Vibratory Assist - Interrupted Flow
    - frequencies up to 270 Hz
    - mechanically reliable
    - distribution narrows weakly as frequency increases
    - indication of harmonic frequency at 230 Hz (?)

Vibratory Assist Results

(SS V-jet 11/65)

Run	Solids(%)	μ (cP)	Freq. (Hz)	D_m (mm)	δ_m	dδ/df
70	49	120	10-32	3.19	0.197	-0.000557
72	56	120	30-96	2.45	0.179	-0.000078
75	56	120	120-270	2.90	0.175	-0.000063
72	56	230	40-96	3.23	0.200	-0.00037

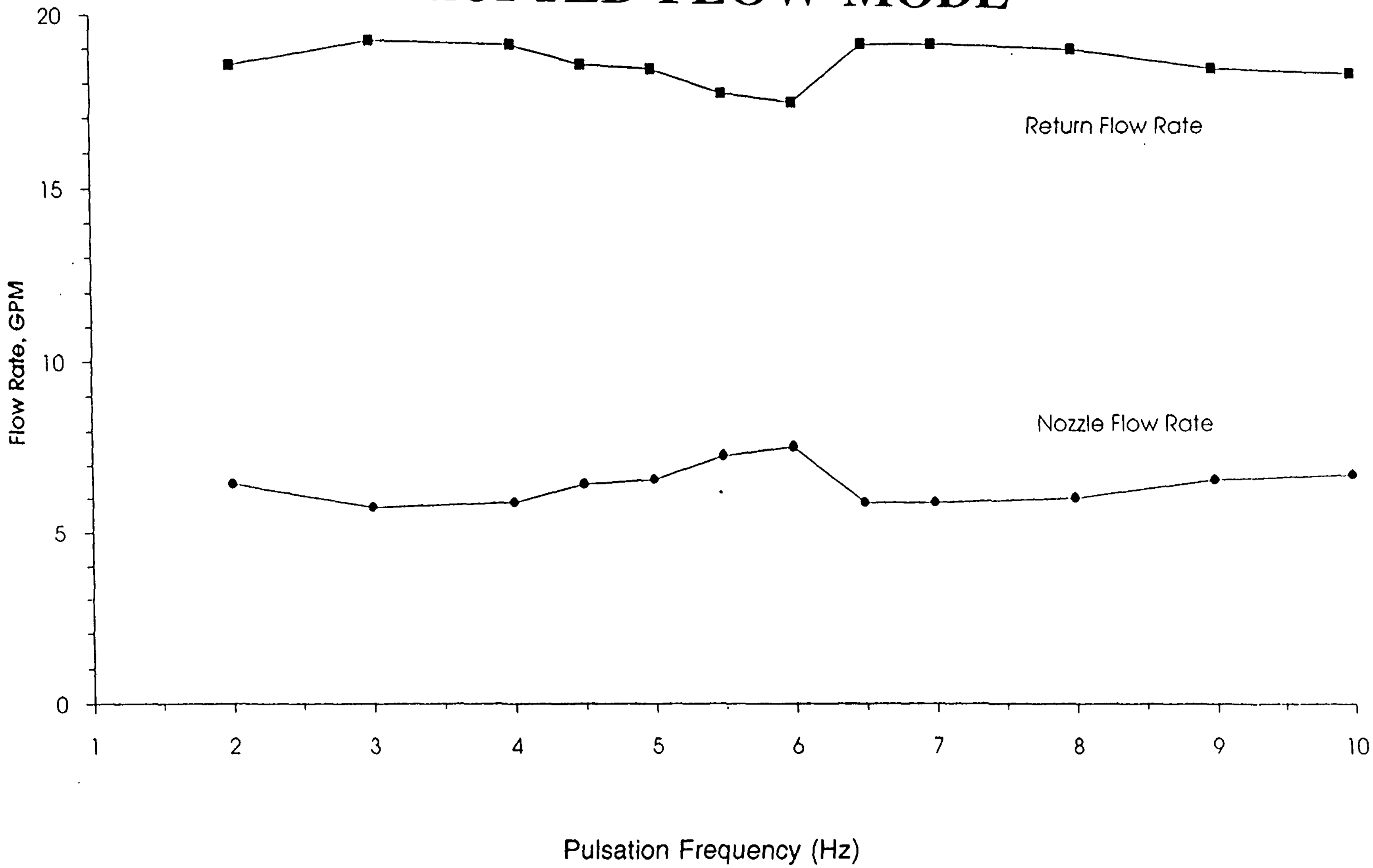
μ = Liquor viscosity

D_m = Mass median drop diameter

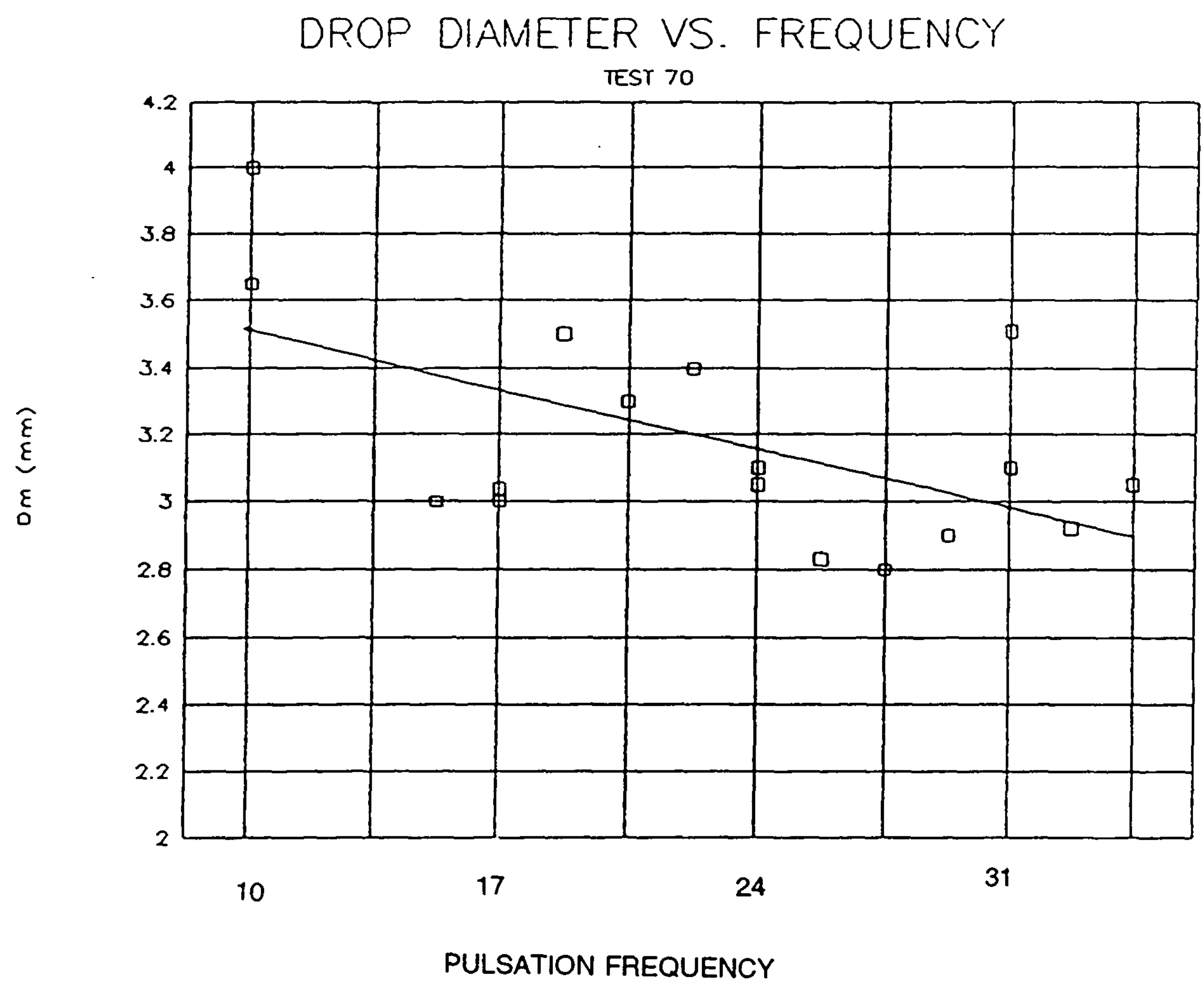
$\delta = S/\sqrt{D_m}$

δ_m = Mean δ

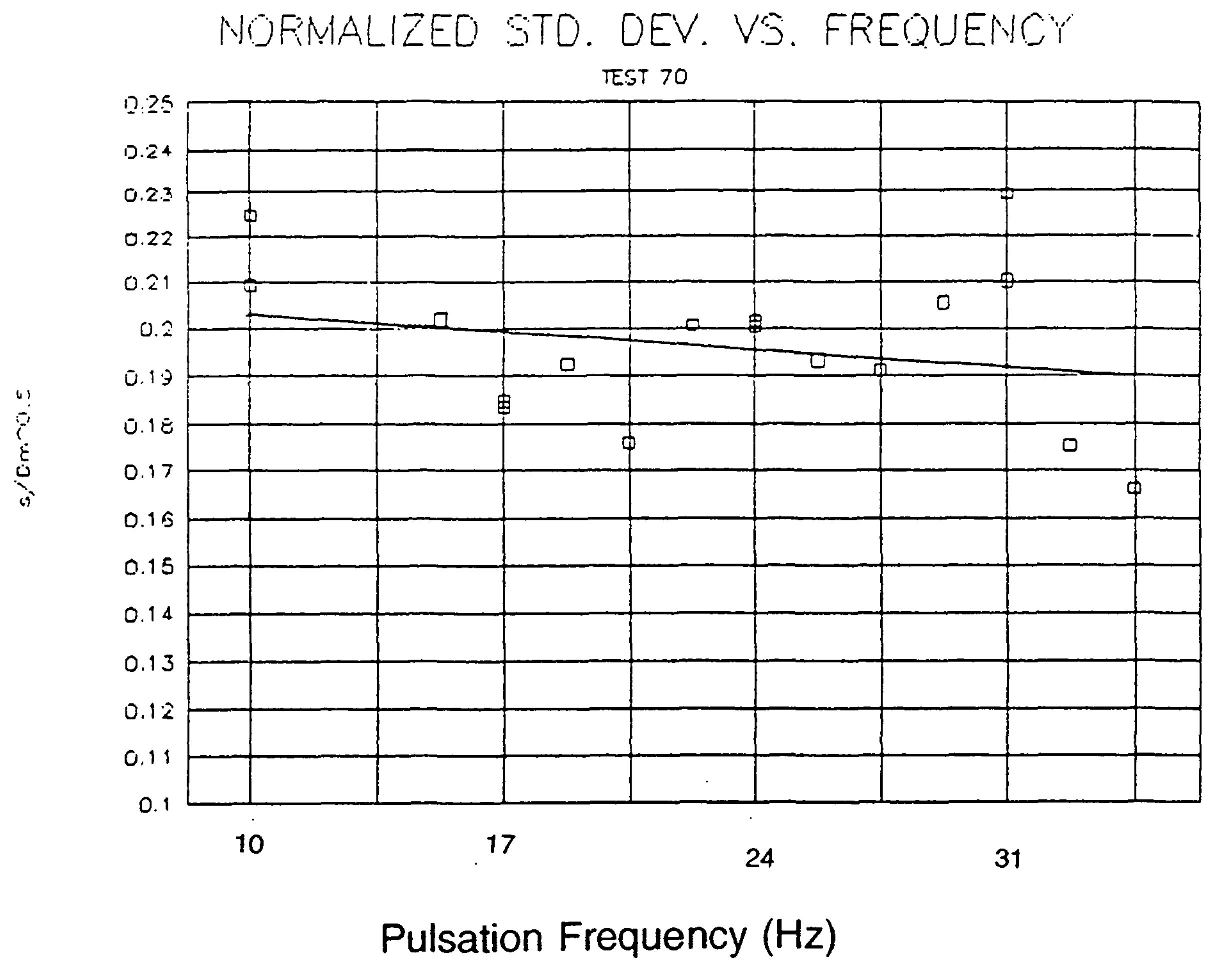
BLACK LIQUOR FLOW DISTRIBUTION WITH INTERRUPTED FLOW MODE



Test 70 - 92°F
- 51% Solids
- 120 cP
- f = 10 - 32 Hz

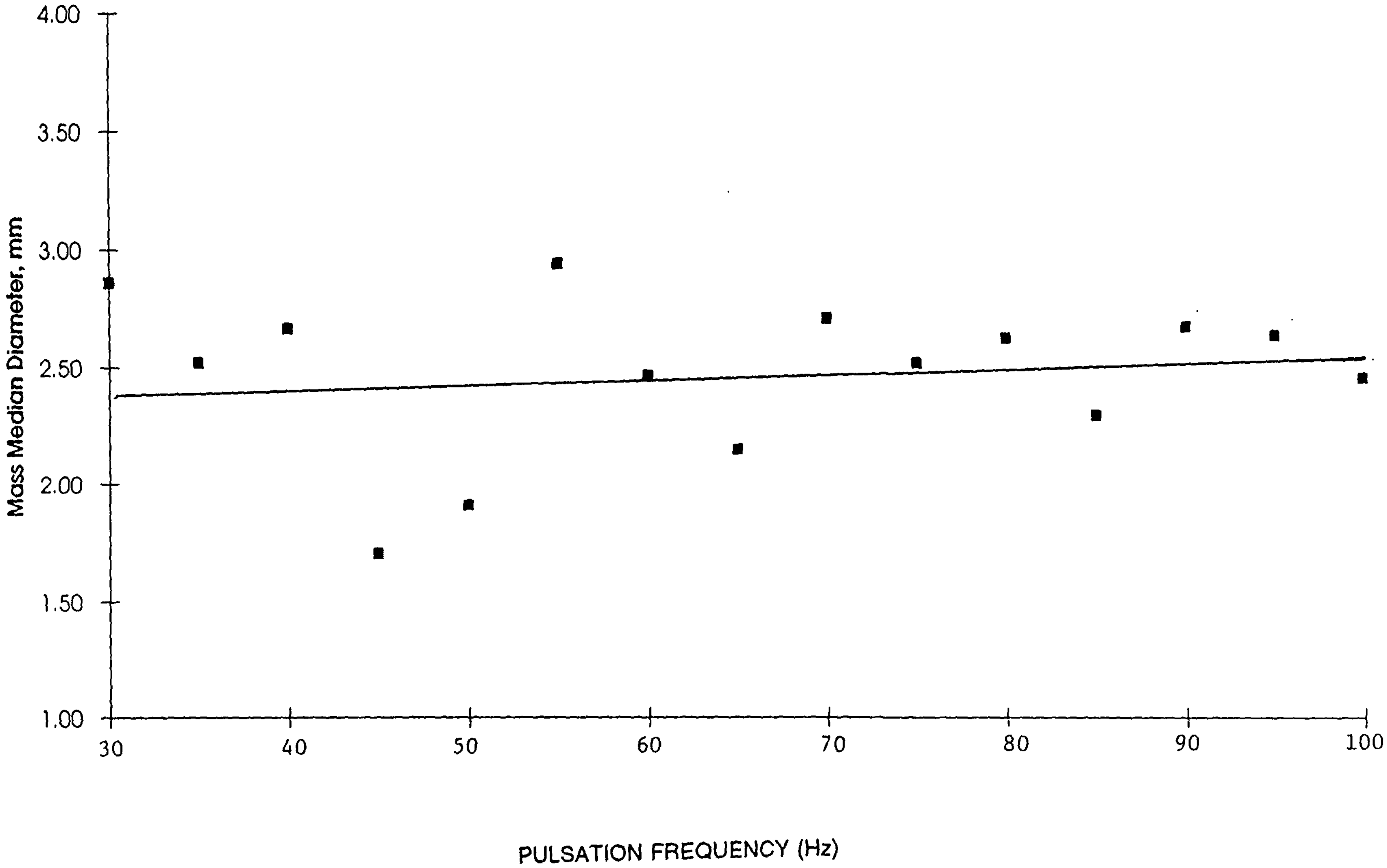


$$D_m = 3.77 - 0.0262\, f$$

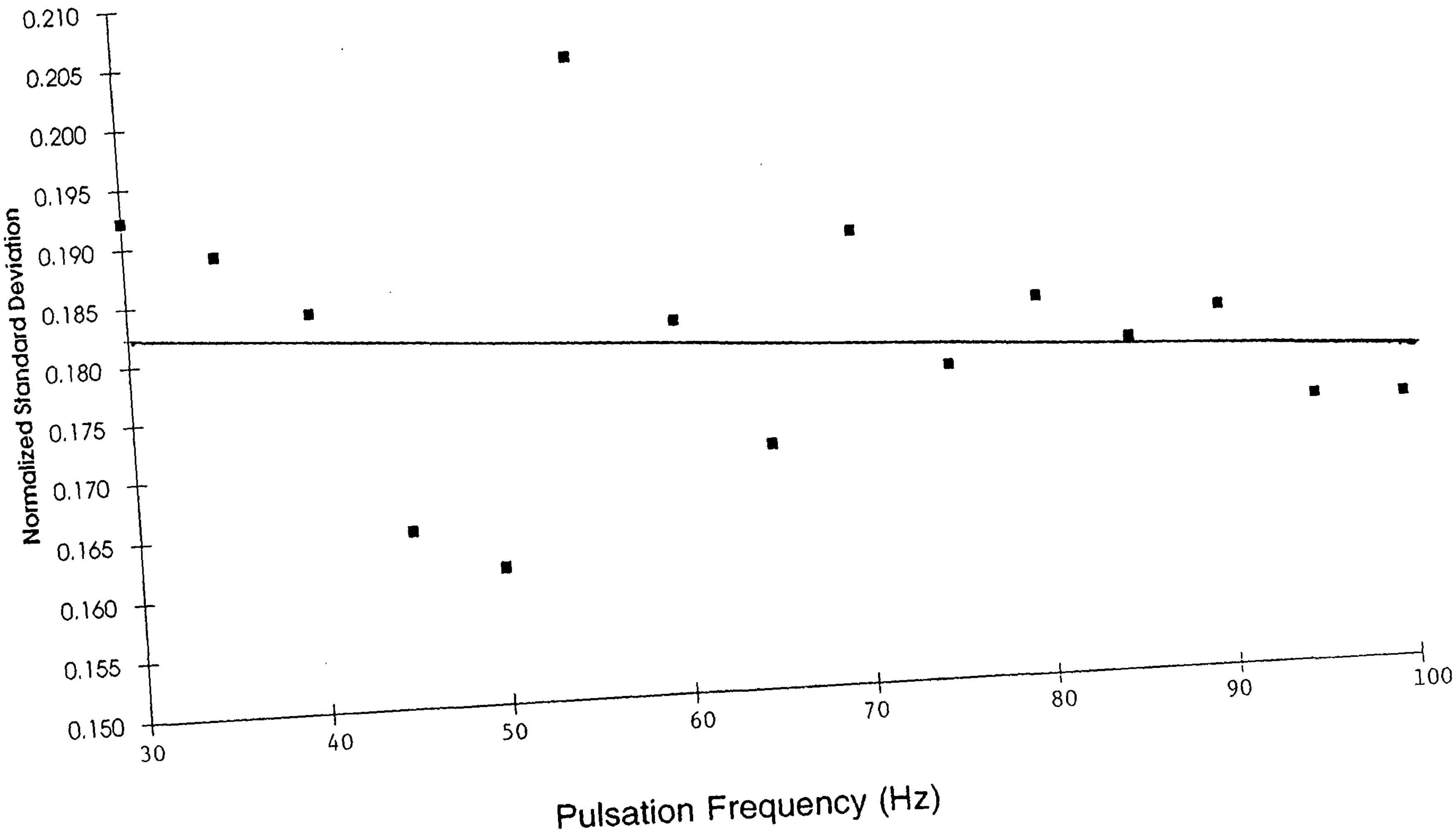


$$S/\sqrt{D_m} = 0.209 - 0.000557f$$

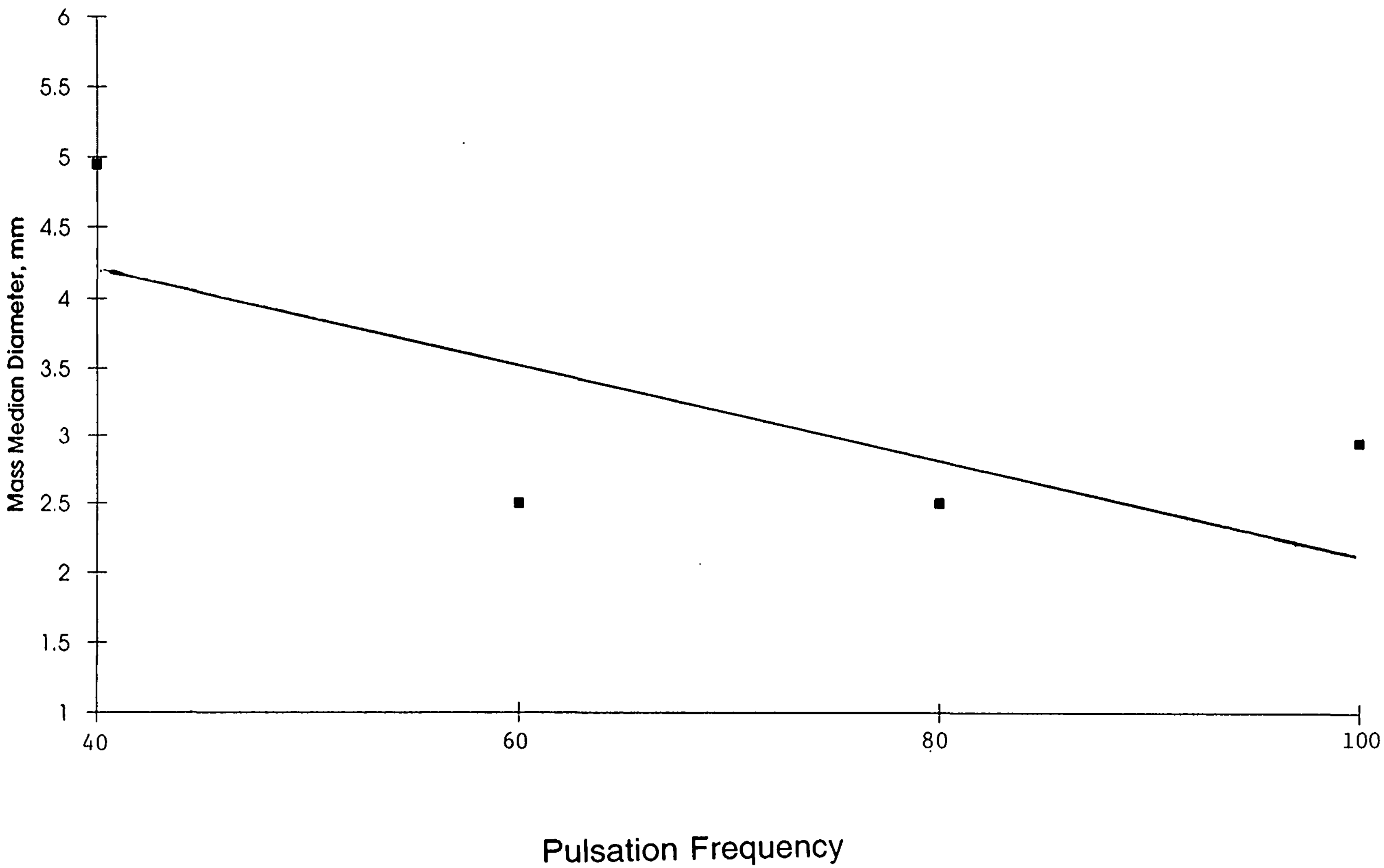
DROP DIAMETER VS. FREQUENCY - TEST 72 (LOW VISCOSITY)



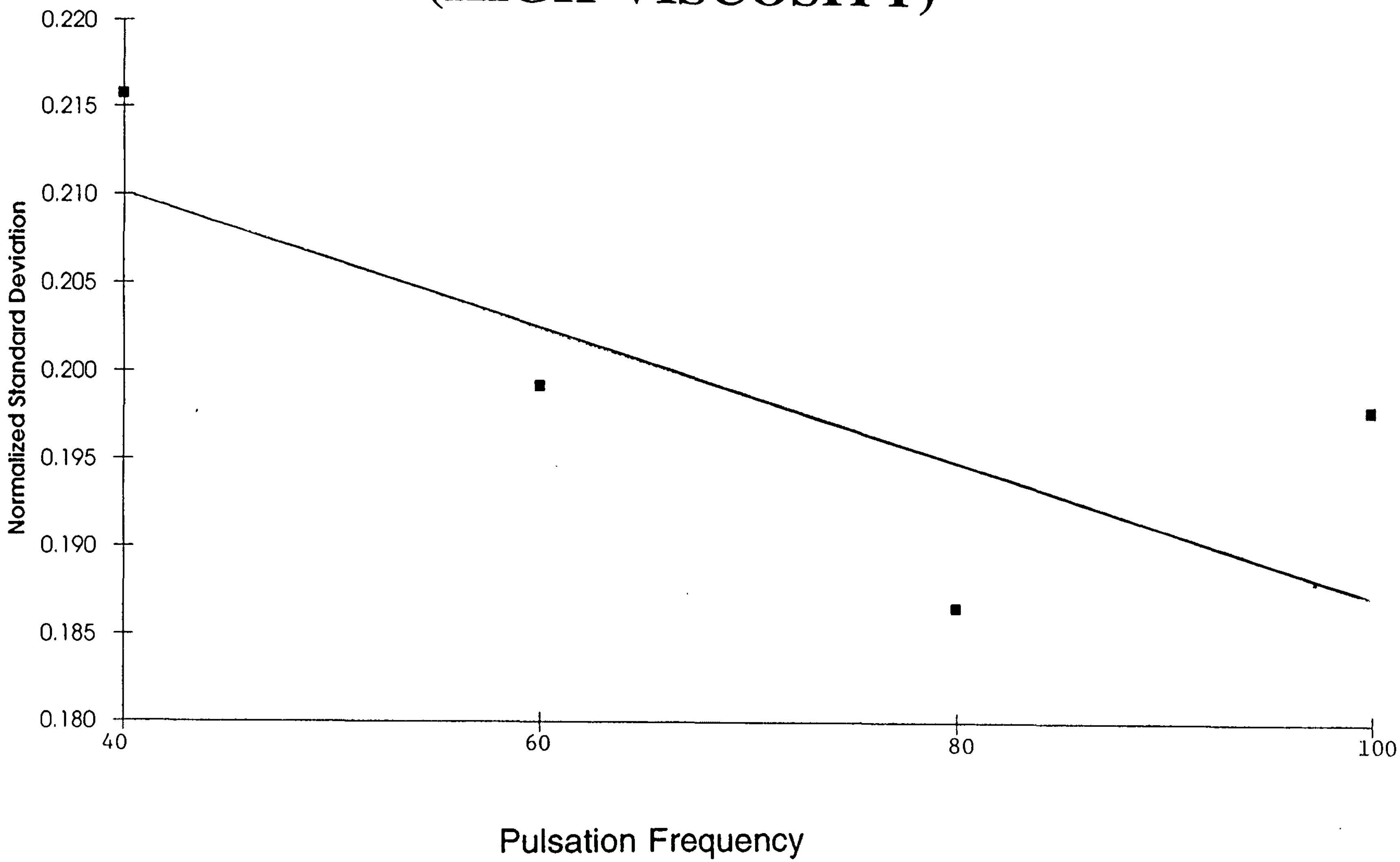
NORMALIZED STANDARD DEVIATION VS. FREQUENCY - TEST 72 (LOW VISCOSITY)



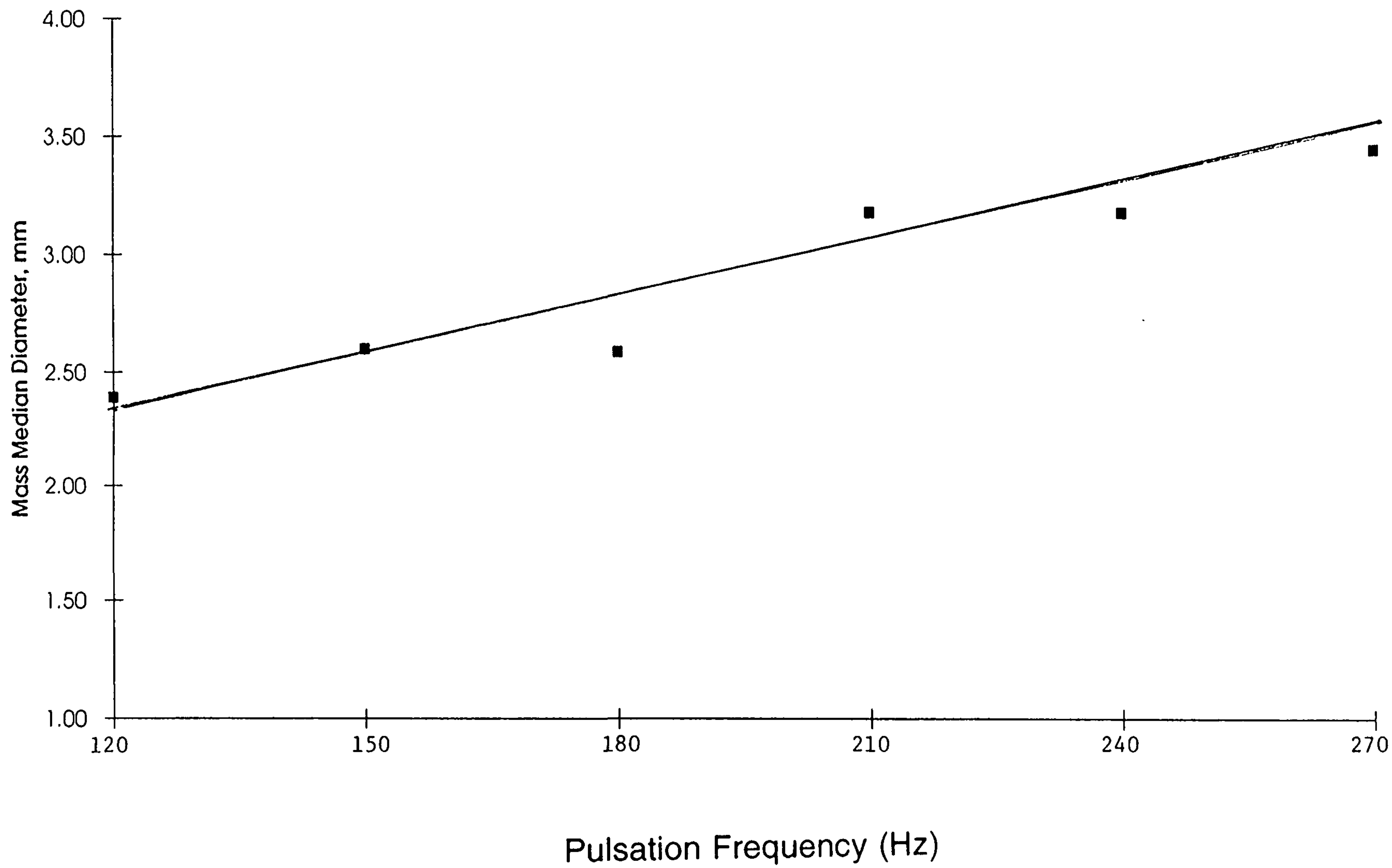
DROP DIAMETER VS. FREQUENCY - TEST 72 (HIGH VISCOSITY)



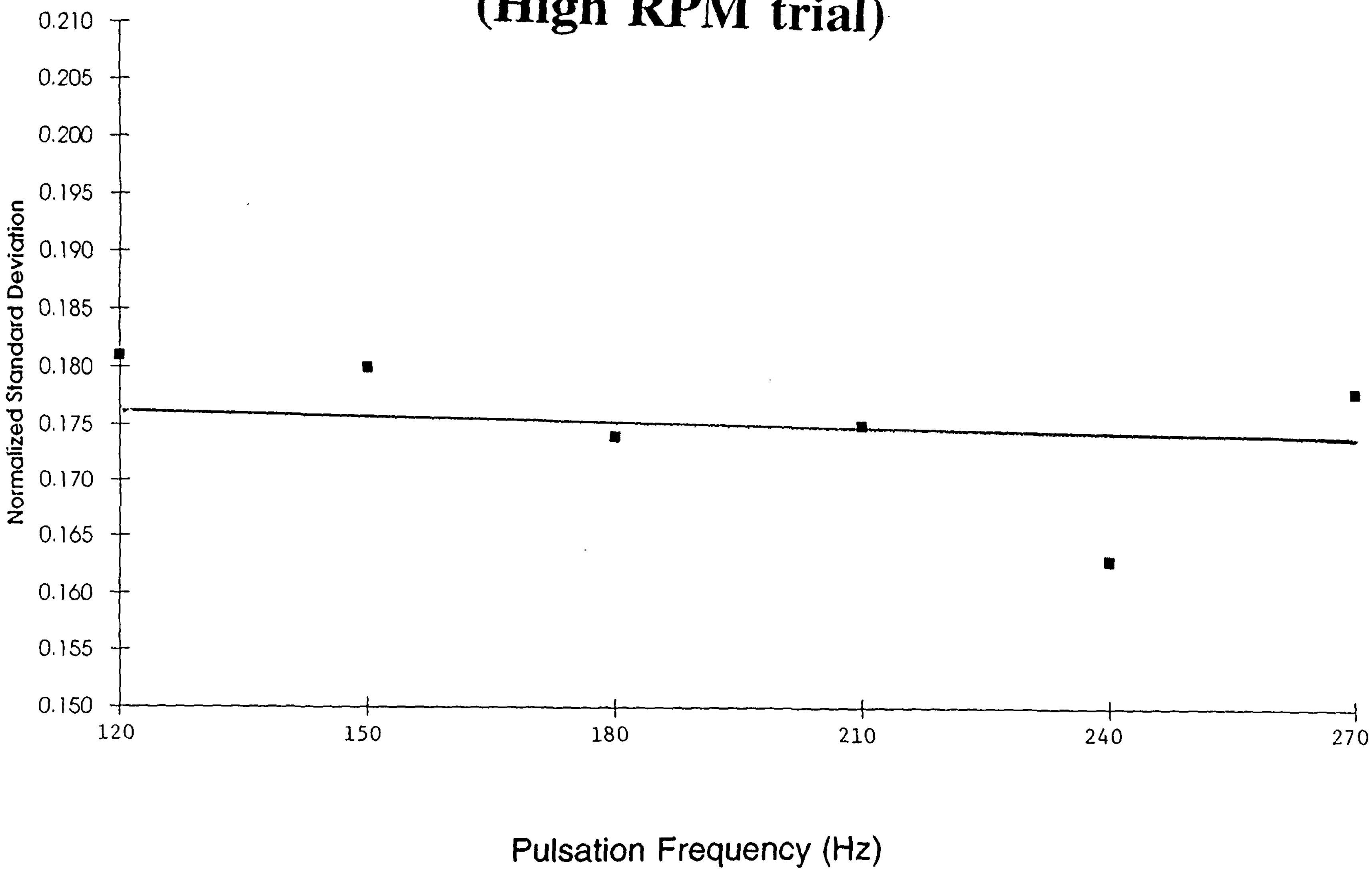
NORMALIZED STANDARD DEVIATION VS. FREQUENCY (HIGH VISCOSITY)



DROP DIAMETER VS. FREQUENCY
(High RPM trial)

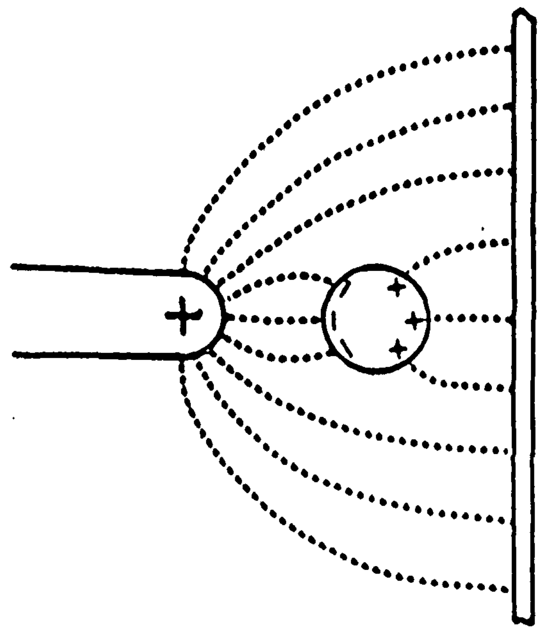


NORMALIZED STANDARD DEVIATION VS. FREQUENCY (High RPM trial)



Dielectrophoresis

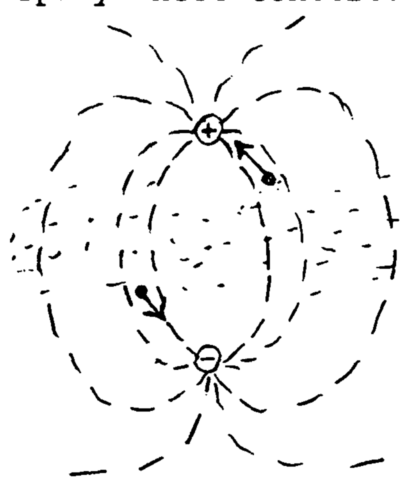
- *Movement of an uncharged particle in a non-uniform field*
- *Dipole induced on particle by the field*
- *Force on dipole towards higher field for both polarities of field*



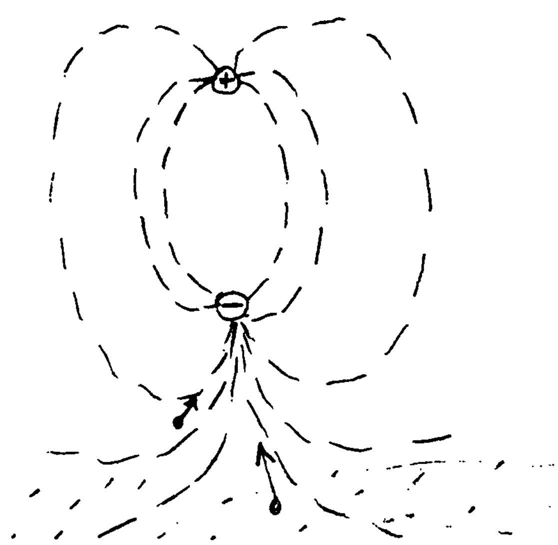
Force on a dipole in a non-uniform field. The negative end of the particle is in a higher field and therefore experiences a higher force than the positive end and there is a net translation towards the higher field.

Spray Sheet - Electrode Configuration

Spray Sheet Centered

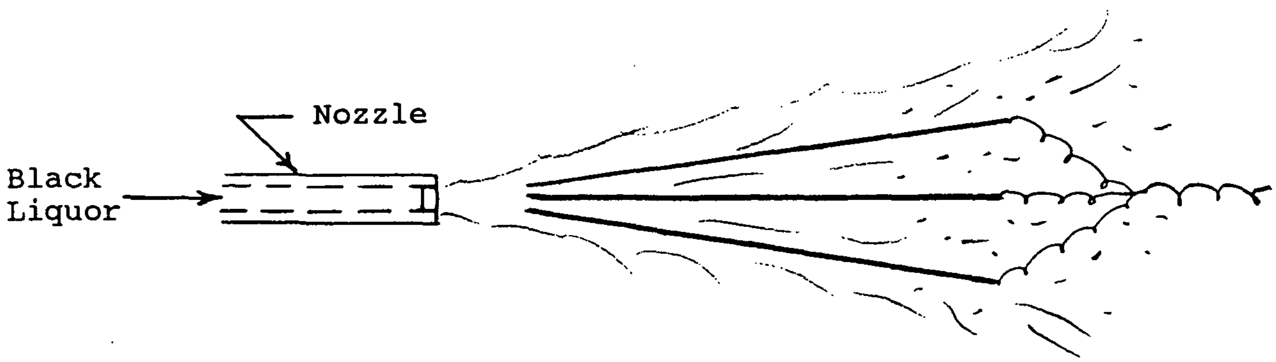


Spray Sheet External

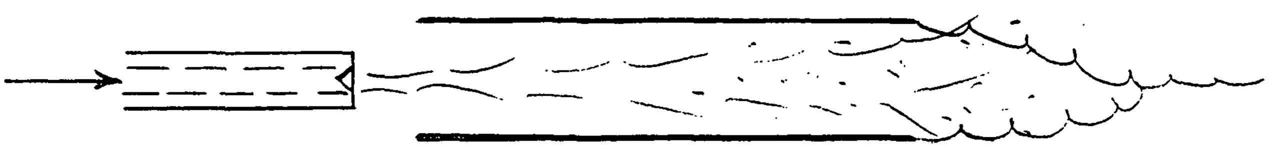


Nopzzle - Electrode Configuration

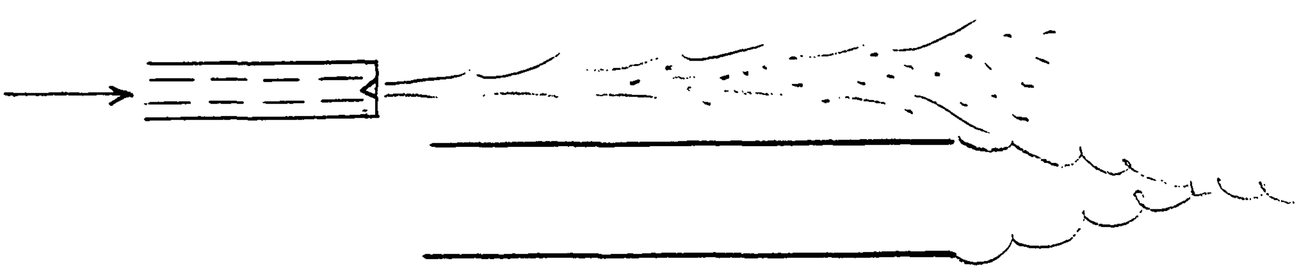
Front View



Side View (Spray Sheet Centered)



Side View (Spray Sheet External)



Coalescence Phenomena

Electrostatic forces have been used to encourage coalescence in emulsions.

Coalescence can occur as particles moving at different velocities collide. Potential for skewing the drop size distribution away from the smaller diameters.

Dielectrophoretic force dependent on particle (droplet) size, difference in dielectric constants for droplet and continuous phase, and the strength of the field and field gradient.

Early Results (cont'd)

* Dielectrophoresis

Test 77
- electrodes (6) encased by PVC
- 48% solids
- 13 gpm
- 130 cP (100 F)
- 0, 3, 5 kV

Runs A - D - Spray sheet centered (+/- 9 inches) between parallel electrodes.

Runs E - G - Spray sheet external to electrodes (9 inches from closer "bank").

No change in spraying characteristics.

Voltages above 5 kV exceeded current limit of high voltage supply.

PRESENT OBJECTIVES

* Develop and test a high frequency vibratory device to induce a pulsed liquor flow in an attempt to reduce the randomness of the liquor sheet break-up process.

* Provided that positive results are obtained with the developmental vibratory assist nozzle, select a host mill for mill scale testing of a vibratory-assisted prototype nozzle for performance comparison with existing nozzles.

* Using existing commercial nozzles, collect extensive drop size data at temperatures above the transition point.

* Obtain drop size data for a range of nozzle diameters under standard spraying conditions using conventional nozzles.

Closed-Cycle Mill Project

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Previous IPST Closed-Cycle Mill Work

- ➡ Paper mill water conservation study-1981
- ➡ Bibliographic Series #293, issued 1985
  - comprehensive literature, 2157 citations
- ➡ Paper machine closure simulation research
- ➡ Alternative pulping and bleaching research
- ➡ Recovery boiler corrosion research
- ➡ Student research-process review, modeling

Non-Process Elements (NPE's)

- Cl, K
- Fe, Cu, Mn
- Al, Si
- Ca, Mg, P
- Organics
  - volatile & non-volatile
  - soluble & insoluble

NPE Issues

- Environmental impact
- Water consumption
- Product quality
- Energy
- Chemical consumption
- Corrosion and pluggage

Closed-Cycle Mill Project Objectives

- Integrated approach to NPE control
- Identify maximum tolerable NPE levels
- Identify new/improved NPE purge processes
- CCM information dissemination

Integrated Approach to NPE Control

- NPE's enter with wood, water, chemicals
- First-pass effects controllable
- Process is cycle, NPE's can build up
- Buildup avoided by purges, anywhere in mill
- Example, green liquor dregs purge for NPE's

Closed-Cycle Mill Project Tasks

- Update literature compilation
- Summarize process knowledge
- Assess existing/proposed closure schemes
- Research NPE impacts on pulping/bleaching
- Research separation technologies
- Research BL gasification processes

Black Liquor Gasification

- Rapson-Reeve process
  - pitch deposits
  - RB corrosion and pluggage
- Gasification with fuel-gas cleanup
  - removes Cl, carryover
  - reduces fume, SO_2

Closed-Cycle Mill Project Activities

- New project
- Literature search complete
- 1000 additional citations
- Bibliographic series being prepared
- Proposals for additional funding submitted
- Simulation project initiated