

THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GEORGIA

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

October 17, 1989

The Institute of Paper Science and Technology

Atlanta, Georgia

*Earl Malcolm 855-9708*

THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GEORGIA

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Your advice and suggestions on any of the projects will be most welcome.



October 4, 1989

TO: Members of the Pulping Processes Project Advisory Committee

The next meeting of the Pulping Processes PAC will be held in Atlanta on Tuesday, October 17, 1989. The meeting will convene at 8:00 in the Radisson Inn and Conference Center in Atlanta. Please note that because of space limitations, the PAC meeting will not be held at the IPST facilities. The Radisson is in midtown Atlanta, a short drive from IPST. Please confirm that you will attend this meeting at your earliest convenience.

The following information is enclosed with this letter for you review prior to the upcoming meeting:

- 1) a list of current committee members,
- 2) the agenda for the October meeting (please note the special one (1) day format),
- 3) a table of 1989-1990 dues-funded projects,
- 4) a list of current M.S. and Ph.D. research, and
- 5) status reports for the individual funded projects and related research areas.

Because of move-related activities, the progress reports are somewhat shorter than previous fall PAC reports. The project presentations will also be reduced and we plan to complete the entire meeting within a one day format. As indicated on the agenda, project presentations will be made during the morning and early afternoon, with the committee meeting scheduled for the latter part of the day.

I 75- 2nd St. 104 S turn left.

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TO: Members of the PPPAC

October 4, 1989  
Page 2

Please call me (404 853-9708) or my secretary, Sally Mayo  
(404 853-9695) if you have questions.

See you in ATLANTA!

Sincerely,



Earl W. Malcolm  
Director  
Chemical Sciences Division

EWM/sam  
Enclosures

PULPING PROCESSES PROJECT ADVISORY COMMITTEE

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AGENDA

PULPING PROCESSES PAC MEETING  
October 17, 1989

The Institute Of Paper Science And Technology  
Atlanta, Georgia

Tuesday, October 17, 1989

8:00 a.m. OPENING REMARKS R. Yeske

8:20 RESEARCH OVERVIEW E. Malcolm

8:35 PROJECT PRESENTATIONS

KRAFT CHEMICAL RECOVERY PRESENTATIONS

*Answers to  
Roly Moore*

Fundamental Processes in Alkali Recovery Furnaces (Project 3473-1) J. Empie  
T. Adams

Black Liquor Combustion (DOE supported) (Project 3473-6) K. Nichols

Kraft Black Liquor Delivery Systems (DOE supported) (Project 3657-2)

10:00 BREAK

10:15 CHEMICAL PULPING

Fundamentals of Selectivity in Pulping and Bleaching (Project 3475) D. Dimmel

Sulfur-Free Selective Pulping Process (Project 3661) (DOE) D. Dimmel  
J. Bozell

11:30 LUNCH/TOUR IPST

1:00 p.m. PROJECT PRESENTATIONS (continued)

BLEACHING OF CHEMICAL PULP

*Ron Hise*

Improved Processes for Bleached Pulp (Project 3474) T. McDonough  
H. Ohi

Mechanisms of Dioxin Formation in Pulp Production (API/NCASI supported) (Project 3667) D. Dimmel  
L. Sonnenberg

2:45 HIGH YIELD PULPS

Fundamentals of Brightness Stability  
(Project 3524)

A. Ragauskas

Stong High Yield Fibers (Project 3566)

A. Rudie

3:00 COMMITTEE MEETING

5:30 END OF PULPING PROCESSES PAC

CHEMICAL SCIENCES DIVISION

MEMBER FUNDED PROJECTS

	1989-1990 (\$1,000)
Fundamental Processes in Alkali Recovery Furnaces (3473)	280
Computer Model of Recovery Furnace (3605)	80
Improved Process for Bleached Pulp (3474)	250
Fundamentals of Selectivity in Pulping and Bleaching (3475)	120
Fundamentals of Brightness Stability (3524)	155*
Strong Intact, High Yield Fibers (3566)	50*
High Brightness Mechanical Pulps (proposed)	120
Development of Analytical Techniques (3477)	15
Exploratory Research (3534)	60
	<hr/>
Total	\$1,130

\*new goals may require budget revision

A 190  
MASTERS  
INDEPENDENT STUDY

<u>Student</u>	<u>Topic</u>	<u>Advisor</u>
Connor	Effects of particle orientation on the fluid mechanics of coatings.	Lindsay
Ebert	An investigation of the compression/expansion mechanisms of a porous layer in a press nip.	Aidun
Gao	Monitoring the aging of paper nondestructively.	Waterhouse
Huhn	The effects of metal chlorides on corrosion fatigue of suction roll alloys.	Ahlers
Kindler	A kraft recovery furnace model study.	Nichols/Grace
Lang, M.	Development of a clay-organic pitch-control agent.	Stratton
Lang, F.	Construction of a partial genomic library for restriction fragment length polymorphism analysis in sweetgum ( <u>Liquidambar styraciflua L.</u> ).	Dinus
Lee	Kraft char gasification: Determination of gasification rates of char-carbon with CO <sub>2</sub> and H <sub>2</sub> O.	Nichols
Mallat	The effects of acid strength in peroxyacid bleaching of mechanical pulp.	McDonough
Meyer	The determination of volatiles in paper by multiple headspace extraction gas chromatography.	Agarwal
Palokangas	The role of formation in hard nip and soft nip calendering processes.	Waterhouse
Rogers	A study of rewetting in impulse drying using flash x-ray radiography.	Lindsay
Ross	Statistical geometric study of the molecular structure of water.	Etzler

Status Report

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
Schwantes	Alkaline degradation of a polymer supported cellulose model.	Dimmel
Thompson	The concentration of the hydrosulfide ion in the early stages of the kraft cooking process.	Malcolm
Veverka	Dynamic contact line instability and air entrainment in coating systems.	Aidun
von Oepen	Synthesis of an anthraquinone pulping catalyst from lignin.	Dimmel
Wallace	The effects of extraneous substances on the colloid titration technique.	Stratton
Waren	Transport of anthraquinone model compounds in kraft pulping.	Malcolm
Wood	The effect of cold-shocking on cultures of <u>Larix decidua</u> .	Dinus

A490

Ph.D.

## THESES IN PROGRESS

<u>Student</u>	<u>Passed to Thesis Candidacy</u>	<u>Approval</u>	<u>Subject</u>	<u>Committee</u>	<u>Room</u>
Bither	9/10/85	1/27/86	Strength development through internal fibrillation and wet pressing.	Waterhouse, chr. Habeger Stratton	203A
Triantafill- opoulos (Not in residence summer 1986)	6/13/86	1/7/87	Investigation of coating flows via flash x-ray.	Aidun, chr. Lindsay Dr. Shands (Beloit) [adjunct member]	203A
Burns, B.	6/27/86	10/6/86	A kinetic study of medium consistency chlorination.	McDonough, chr. Lindsay Malcolm	168 and 49
Uhlin (Not in residence summer 1986)		5/30/86	The influence of hemicelluloses on the structure of bacterial cellulose.	Atalla, chr. Johnson Conners (Thompson)	K216
Burns, J.	9/23/86	1/7/87	Investigation of the constrained expansion phase of wet pressing.	Lindsay, chr. Conners	251
Bond	4/2/87	5/12/87	A Raman microscopic investigation of the patterns of molecular order in the secondary cell wall of southern pine tracheids.	Atalla, chr. Agarwal Conners Dinus	K113
Rudemiller	6/9/87	7/16/87	A fundamental study of boiling heat transfer mechanisms in impulse drying.	Lindsay, chr. Orloff Aidun	143
McKibben (Not in residence summer 1987)	8/7/87	12/18/87	A numerical and experimental study of a splash-plate type black liquor spray nozzle.	Aidun, chr. (Farrington) Grace Lindsay Halcomb	67

Status Report

<u>Student</u>	<u>Passed to Thesis Candidacy Approval</u>		<u>Subject</u>	<u>Committee</u>	<u>Room</u>
Medvecz (Not in residence summer 1987)	8/7/87	12/4/87	Spectroscopic evaluation of the gas phase above a burning black liquor char bed.	Atalla, chr. Nichols Lindsay	SR17
Miller	9/8/87	10/23/87	Investigation of the role of zeta potential distribution on fines retention.	Stratton, chr. Halcomb Lindsay	219
Verril (Not in residence summer 1987)	12/8/87	3/9/88	Chemical fume formation during kraft black liquor droplet combustion.	Grace, chr. Lindsay Nichols	SR3
Luetzgen (Not in residence summer 1987)	1/18/88	3/18/88	An investigation of the role of mixing conditions during polymeric retention aid addition on the adsorption homogeneity.	Stratton, chr. Etzler Lindsay	1214
Burker (Not in residence summer 1987)	11/19/87	3/29/88	An investigation of the role of the drying strategy in the structure of pigment-adhesive films.	Connors, chr. Etzler Waterhouse	K127
Spielbauer	7/14/88	10/11/88	An examination of the mechanisms controlling the droplet size distribution of a spray.	Aidun, chr.	209
Friese (Not in residence summer 1988)	7/14/88			Stratton, chr.	220

STATUS REPORT  
TO THE

PULPING PROCESSES PROJECT ADVISORY COMMITTEE

October 17, 1989

The Institute of Paper Science and Chemistry  
Atlanta, Georgia

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PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3473-6: FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION  
(DOE FUNDED PROJECT)

PROJECT LEADERS: H. L. Empie, T. M. Grace  
NBS Subcontractor - Dr. A. Macek

IPST GOAL:

Develop fundamental data on black liquor combustion which can be used to enhance energy efficiency and productivity of recovery boilers.

OBJECTIVE:

The three main objectives are:

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

CURRENT FISCAL YEAR BUDGET: \$254,000

PRIOR RESULTS:

The project is divided into 4 phases: Phase 1 - in-flight processes; Phase 2 - char bed processes; Phase 3 - inorganic fume formation processes; Phase 4 - recovery furnace simulation. Progress Reports One and Two have been issued by the Department of Energy. These reports cover all of the work on the project through January 1987. This includes the majority of the work on in-flight processes, which includes data on drying rates, carbon fixation rates, and particle dynamics. Phase 1 was substantially completed at the time of the October, 1987 PAC meeting. Some of that material has been reported in Progress Report Three, which was issued in April, 1989. The Phase 3 report summary is attached, complete copies will be mailed directly to committee members. Copies are also available upon request.

## SUMMARY OF RESULTS SINCE LAST REPORT:

The focus of the DOE black liquor combustion study over the past year was to measure char burning rates in a laboratory system under conditions similar to those found in recovery boilers. In order to extend the study of black liquor combustion beyond the drying and volatiles burning stages which were measured in the flow reactor, the char bed furnace was added to the bottom of the existing reactor. This additional system allowed us to study char burning rates in a realistic burning geometry. The experimental char bed system was devised in such a way that the gas jet from a narrow slot passes horizontally over a small (4 x 8 inch) char bed. The experimental data for the char burning project were collected and analyzed. Among the significant findings are:

1. The char bed reactor has been successfully used to determine char burning rates. Carbon burning flux rates have been measured in the range from 15 to  $110 \times 10^{-6}$  gmol/sec/cm<sup>2</sup>.
2. The char burning rate is a linear function of the bulk oxygen concentration and appears to be a mass transfer limited process. Mass transfer coefficients were calculated and found to be a linear function of the average gas velocity raised to the 0.65 power.
3. Char bed surface temperatures were measured and ranged from 900 to 1150 C. Using the bed temperature profiles, the thickness of the active burning char layer was estimated to be between 3 and 7 cm. thick.
4. The presence of water vapor and carbon dioxide in the gas phase has a significant effect on the char burning rate. CO<sub>2</sub> increased the carbon flux by 23% apparently through the reaction  $\text{CO}_2 + \text{C} = 2\text{CO}$ . H<sub>2</sub>O catalyzed the conversion of CO to CO<sub>2</sub> resulting in a 29% increase in the oxygen flux.
5. The ratio of CO to (CO + CO<sub>2</sub>) was found to vary widely from 0.0 to 0.63. The ratio was dependent on the oxygen level, with O<sub>2</sub> levels of 21% producing CO/(CO + CO<sub>2</sub>) ratios of less than 0.25 rather than the typical 0.4 to 0.6 ratios seen at lower oxygen levels.

Measurement of fume particle size and number density continued using the light scattering technique. As indicated in earlier progress reports, the initial measurements of fume from synthetic smelt yielded no useful or reproducible particle information. Because of these results, each part of the optical system was examined for its sensitivity and function. The stability and restrictions of the software used to perform the Mie calculations were also examined. Some conclusions which resulted were:

1. A reduction of the size of the spatial resolution of the scattered light led to improved data quality, and

2. The angular domains for the receiving systems which yielded the best data were 96-110 degrees and 165-170 degrees with respect to the incident laser beam.

As a result of the first conclusion, the optical receiving systems were rebuilt, so that a diffuser was placed in front of each photomultiplier tube. By using the diffusers and by using the proper angles, a limited amount of reproducible fume data was collected using the synthetic fume generator.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1990:

The DOE black liquor flow reactor system has been completely disassembled and moved to Atlanta. The industrial research area for the reactor in the new Atlanta facility is nearly complete and equipment reinstallation is proceeding presently. The char bed reactor and flow reactor system will take several months before it is operational. Needed are rate data on char burning rates using realistic boiler gas velocities and gas concentrations.

Work on the laser system for the measurement of fume particle size was stopped at the end of July and the equipment has been moved to Atlanta. A post-doctoral appointee will be sought for this project.

A proposal will be written for a recovery boiler velocity probe study to help validate the FLUENT/RFM model.

The work on FT IR monitoring of the gas phase above burning char will continue.

## FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

INTRODUCTION

The focus of the DOE black liquor combustion study over the past year was to measure char burning rates in a laboratory system under conditions similar to those found in recovery boilers. In order to extend the study of black liquor combustion beyond the drying and volatiles burning stages which were measured in the flow reactor, the char bed furnace was added to the bottom of the existing reactor. This additional system allowed us to study char burning rates in a realistic burning geometry. The experimental char bed system was devised in such a way that the gas jet from a narrow slot passes horizontally over a small (4 x 8 inch) char bed. The experimental data for the char burning project were collected and analyzed in three phases.

INITIAL TESTS

The base case data were collected at nine different test conditions with two or three replicates. Tests were performed at three different inlet oxygen concentrations (7, 14 and 21%) and four different gas velocities. Data for the second phase were collected at higher gas jet velocities (all at 14% O<sub>2</sub>), by reducing the width of the slot jet from 0.3 to 0.1 inch, again with 3 replicates.

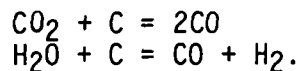
The char burning rate was measured as g-mole of carbon per minute (gmol C/min), calculated directly from the outlet molar gas flow and the CO and CO<sub>2</sub> concentrations. This value was converted to a flux based on the nominal cross sectional area of the char bed. This flux was determined at steady state conditions for each char burn. The following conclusions were drawn from the data collected:

1. The char bed reactor system has been successfully demonstrated to function as a part of the black liquor flow reactor. It has shown the capability to accurately measure char burning rates. Tests have been performed with inlet oxygen concentrations ranging from 7 to 21% and gas flow rates of 100 to 550 slpm.
2. Carbon flux burning rates have been measured in the range of 15 to 110 x 10E<sup>-6</sup> gmol/sec/cm<sup>2</sup>. Oxygen flux rates have ranged from 12 to 87 x 10E<sup>-6</sup> gmol/sec/cm<sup>2</sup>.
3. Burning rates are a linear function of the bulk oxygen concentration. This is consistent with a mass transfer controlled process.

4. Mass transfer coefficients were calculated and found to range from 5 to 40 cm/sec.
5. Gas jet velocities were measured over the char bed. Average velocities over the bed surface ranged from 6 to 33 ft/sec for the test conditions.
6. Mass transfer coefficients were found to be a function of the average gas velocity over the char bed, raised to the 0.65 power. This is similar to theoretical correlations used to predict mass transfer coefficients.
7. Char bed surface temperatures were measured and ranged from 900 to 1150 C. Using the bed temperature profiles, the thickness of the active burning char layer was estimated to be between 3 and 7 cm. thick.
8. The ratio of CO to (CO + CO<sub>2</sub>) was found to vary widely from 0.0 to 0.63. The ratio was dependent on the oxygen level, with O<sub>2</sub> levels of 21% producing CO/(CO+CO<sub>2</sub>) ratios of less than 0.25 rather than the typical 0.4 to 0.6 ratios seen at lower oxygen levels.

#### GASIFICATION REACTIONS

The last of three sets of char burning studies were performed to measure the effect on the char bed burning rates of the addition of carbon dioxide and water vapor to the gas stream over the char bed. Some combustion literature indicates that carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) can contribute to the combustion process through the following gasification reactions:



Since all previous char burning experiments in the DOE flow reactor were done with dry air and nitrogen, this could explain why burning rates are somewhat lower than expected. Significantly higher char bed burning rates have been achieved with the recovery boiler computer model by including these reactions. These tests were performed as a 2 x 2 matrix, using both H<sub>2</sub>O and CO<sub>2</sub> at 0 and 10% levels. Because of the greater uncertainty involved in measuring the difference between the base burning rate and the new rate, five replicates were performed to reduce the experimental error.

#### CONCLUSIONS:

1. The addition of CO<sub>2</sub> at a 10% concentration increases the burning rate, as measured by the carbon flux, by

approximately 25% from  $24.6 \times 10E-6$  to  $30.3 \times 10E-6$  gmol/sec/cm<sup>2</sup>. The average carbon flux measured at the base case of  $24.4 \times 10E-6$  gmol/sec/cm<sup>2</sup> is almost exactly the value measured in previous work at these conditions.

2. The water vapor appears to act as a catalyst for the oxidation of CO to CO<sub>2</sub>. The earlier tests had indicated that the CO comprised from 10 to 63% of the carbon gases. For the tests with 14% O<sub>2</sub> this ratio of CO/(CO+CO<sub>2</sub>) was about 55%. Almost the same ratio (50%) was also measured in this set of tests when no H<sub>2</sub>O or CO<sub>2</sub> was added. When H<sub>2</sub>O is added to the inlet gas the ratio of CO to CO + CO<sub>2</sub> changes dramatically; almost all of the carbon comes off as carbon dioxide. With 10% H<sub>2</sub>O the amount of CO was less than 1%.
3. Both of the factors (CO<sub>2</sub> and H<sub>2</sub>O) increase the oxygen mass transfer rate over the base case, by 23% for CO<sub>2</sub> and by 29% for H<sub>2</sub>O. There is no interaction effect between the two factors. For a given carbon flux rate from the char bed, a change in the ratio of CO/(CO+CO<sub>2</sub>) will mean a change in the net oxygen flux required to the char bed. For the runs where water vapor was added, the oxygen flux and the carbon fluxes are equal, since all of the carbon is converted to CO<sub>2</sub>. For the other test conditions with no water, the oxygen flux is less than the carbon flux.

#### FUTURE WORK

There are several differences between the burning conditions in the char bed reactor and an actual recovery furnace. First the surface of a real char bed consists of partially pyrolyzed char, and possibly partially dried black liquor. The volatiles and the water vapor evolved from this material can have a significant influence on the char burning rate. A second related point is that in a recovery furnace the surface of the char bed is continuously replenished from above. In the laboratory system the completely pyrolyzed char is replaced from below. Overall the basic mass transfer controlled char burning processes should be similar. However, further experimental work should be carried out to study the effect of partially pyrolyzed material on the overall char burning rates.

Differences in oxygen concentrations and gas velocities between the experimental system and a real recovery boiler may also be important. The burning rates were measured with oxygen concentrations of up to 21%. In a boiler the oxygen level will vary from 21% at the air ports to near 0%. Similarly the gas velocity will cover a wide range in a recovery boiler up to 140 ft/sec near the air port. The highest velocity used in the laboratory system was 33 ft/sec. Application of the char burning rates will require additional information on realistic boiler gas velocities and gas concentrations.

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3474: IMPROVED PROCESS FOR BLEACHED PULP

PROJECT LEADER: T. J. McDonough

IPST GOAL:

To improve the process of production of bleached chemical pulp.

OBJECTIVE:

Define pulping and bleaching technology that will decrease or eliminate the need for chlorine in the bleaching sequence.

CURRENT FISCAL YEAR BUDGET: \$150,000

PRIOR RESULTS:

Results obtained since the inception of this project are summarized in the September 6, 1988 Status Report. Results obtained since then, but prior to the Spring, 1989 meeting of the Pulping Processes Project Advisory Committee may be briefly summarized as follows. Please note that results from our collaborative work with NCASI/API are included in the summaries.

Bleaching Effluent Control

Earlier studies of the combined effects of several process changes on dioxins formation were supplemented by an experiment in which a control CEDED sequence was preceded by solvent extraction of the unbleached pulp. 2378-TCDD production was so low that no effect of the extraction could be seen; 2378-TCDF formation was reduced by two-thirds. Additional information on the effect of solvent extraction is given below.

Studies of the significance of unchlorinated dioxin and furan (DBD and DBF) as precursors for chlorinated dioxins were initiated. The early experiments incorporated carryover of black liquor into the chlorination stage and gave equivocal results. Repetition of these experiments without carryover has since given significant and reproducible results, as described below.

Studies of the source of DBD and DBF were also initiated, to determine if they are present in wood and whether they are formed or destroyed during pulping.

Pulps were prepared according to both conventional and low-chlorine strategies for physical properties evaluation, with the aim of better understanding the strength losses that resulted from the low-chlorine sequences. The low-chlorine sequence gave an unbleached pulp of kappa

number 20 and viscosity 24, the latter figure dropping to 12 after an oxygen stage and three stages of bleaching. The conventional sequence gave kappa 33 and a viscosity after three stages of bleaching of 22. The physical properties of both pulp types have since been characterized at various points in the sequence.

### Bleaching

Methylation was shown to retard oxygen delignification of nitrogen dioxide treated and untreated kraft pulps by the same amount. This observation shows that nitro group activated cleavage of ether linkages is not an important component of the mechanism by which nitrogen dioxide pretreatment accelerates oxygen bleaching.

### Pulping

In a student research project (K. Biasca, Ph.D.), a flow-through pulping system and lignin concentration detector were constructed and procedures for determining delignification rates were refined. The system was used to perform a series of experiments aimed at determining the rate law governing delignification during the early stages of alkaline sulfite anthraquinone (ASAQ) pulping.

#### RECENT RESULTS:

Results obtained since the Spring, 1989 meeting of the Pulping Processes Project Advisory Committee meeting may be summarized as follows:

### Bleaching Effluent Control

#### Collaboration with NCASI/API

Replicated bleaching experiments were performed on thoroughly washed pulps to determine whether direct chlorination of DBD and DBF is solely responsible for the TCDD and TCDF formed during bleaching and to gain insight into other formation mechanisms. Solvent-extracted, control and precursor-spiked pulps were bleached and analyzed.

Spiking the unbleached pulp with DBD and DBF sharply increased TCDD/F formation, confirming earlier reports that these precursors were important sources of chlorinated dioxins and furans. On the other hand, substantial amounts of both TCDD and TCDF were formed even after virtually complete removal of DBD and DBF from the brownstock prior to bleaching. The fingerprints of the chlorinated furans formed from the solvent extracted pulps were significantly different from those formed from the spiked ones. These observations indicate that nonextractable precursors, different from DBD and DBF, are present in the pulp; there is apparently an important TCDD/F formation mechanism in addition to direct precursor chlorination.

Dioxins were observed to accompany the chlorinated pulp almost to the

exclusion of the chlorination effluent. Dioxins emerging from the caustic extraction stage were found predominantly in the filtrate. The total amounts of most isomers emerging from the extraction stage, in particular the 2378's, were equal to or slightly greater than the amounts entering it. The concentrations of certain chlorinated furans, however, increased significantly during caustic extraction. These included the 2368 and 2468 tetrachlorinated isomers, the 12378 pentachlorinated isomers and two other unresolved groups of pentachlorinated isomers.

In other experiments, the ability of chlorine dioxide to destroy dioxin precursors was tested. Chlorinations were conducted in three stages. In the first, chlorine was supplied in an amount equal to 0.12 times the kappa no., to satisfy most of the lignin's immediate chlorine demand. In the second, chlorine dioxide was injected and given the opportunity to react with dioxin precursors. Research at PAPRICAN and elsewhere has indicated that precursors compete poorly with lignin for chlorine and presumably also for chlorine dioxide, making it necessary to satisfy much of the lignin's oxidant demand before adding the chlorine dioxide. In the third stage, more chlorine was added to serve as an indicator of surviving precursors; analysis of the chlorinated pulp was expected to show that detectable levels of chlorinated dioxins were not present if the chlorine dioxide in the second stage had destroyed the precursors. This experiment was repeated with various levels of chlorine applied in the final part of the chlorination. The entire series was repeated with no chlorine dioxide added in the second stage, to provide suitable controls.

The results of these experiments showed that chlorine dioxide failed to destroy the important precursors under these conditions. Furthermore, at a given total charge of molecular chlorine, experiments with chlorine dioxide gave higher levels of dioxins and furans than the experiments in which water was injected into the second stage in place of chlorine dioxide solution. The latter observation suggests that chlorine dioxide either generates precursors or converts them to TCDD/TCDF.

#### Bleaching

Postdoctoral Fellow Hiroshi Ohi has continued our investigation of the mechanism of nitrogen dioxide pretreatment for oxygen bleaching. Among other things, he has shown that aromatic rings containing free phenolic hydroxyl groups are nitrated, that fully etherified rings are nitrated slowly or not at all, and that NO<sub>2</sub> pretreatment leads to a decrease in the molecular size of the lignin dissolved during oxygen bleaching. Dr. Ohi's report is attached.

#### Pulping

A Ph.D. thesis on alkaline sulfite anthraquinone pulping kinetics has been completed by Karyn Biasca. She used a fixed bed flow reactor to

develop a rate law by monitoring effluent lignin concentration with UV fluorescence. Effects on the delignification rate of temperature, alkalinity, sulfite concentration, anthraquinone concentration and alkalinity were quantitatively defined and incorporated into the rate law.

PLANS:

Collaboration with NCASI/API

Efforts to detect DBD and DBF in wood and to determine whether they are formed or destroyed during pulping have met with analytical difficulties. Attempts to resolve these problems are in progress at NCASI.

A study of the effects of chlorination variables on dioxins formation is in progress, but no results are yet available. The variables under study are timing of chlorine dioxide addition, temperature, oxygen delignification, spent liquor carryover to the chlorination stage, recycle of chlorination effluent, mixing and consistency.

Other Work Related to Bleaching

Modifications to the pulping and bleaching sequence that are prompted by environmental concerns often have the potential to reduce pulp quality. A better understanding of the nature and source of these quality differences would be of use in controlling them. Accordingly, conventional and low-chlorine sequences have been used to prepare bleached pulps in the laboratory and samples withdrawn at various points in both sequences. Analysis of the data from these experiments is in progress.

## MECHANISM OF NITROGEN DIOXIDE PRETREATMENT FOR OXYGEN BLEACHING

### INTRODUCTION

Pretreatment of kraft pulp with nitrogen dioxide has been shown to be an effective method for both improvement of delignification and protection of carbohydrate degradation in oxygen bleaching. However, the mechanism of its action is not clear. The objective of this research is to learn more about the mechanism.

Abrahamsson et al. <sup>1)</sup> have determined methanol in spent liquor obtained after the pretreatment of kraft pulp with  $\text{NO}_2$  and  $\text{O}_2$ , and supposed that the demethylation of lignin leads to formation of hydrophilic groups and that this will contribute to the enhanced delignification. Lindeberg and Walding <sup>2)</sup> have proposed a mechanism of action of  $\text{NO}_2$  whereby nitro groups introduced into the aromatic rings of non phenolic lignin units promote ether cleavage in alkali, which in turn creates new phenolic hydroxyl groups to serve as oxygen delignification initiation sites. However, they do not show any experimental results supporting the introduction of nitro groups into the non phenolic lignin units.

Oxygen delignification is known to be initiated at free phenolic hydroxyl groups. If methoxyl groups of non phenolic lignin units could be demethylated, oxygen delignification would be enhanced. Therefore, it is important to clarify the reaction of non phenolic lignin units in the pretreatment with  $\text{NO}_2$  as well as that of free phenolic lignin units. Furthermore, there is no clear evidence of nitro groups or nitroso groups introduced into lignin although nitrogen-containing groups are found to be introduced into lignin in the pretreatment <sup>1,3)</sup>.

Abrahamsson et al. <sup>1)</sup> have pointed out that the pretreatment leads to a modification of lignin and the formation of species which attack carbohydrates is suppressed. Byrd and Gratzl <sup>4)</sup> have speculated that the formation of catechol groups results in improved protection of carbohydrates. Lindeberg and Walding <sup>2)</sup> have reported that the presence of nitrated lignin in oxygen bleaching of kraft pulp leads to a decrease in carbohydrate depolymerization and retards delignification.

### RESULTS AND DISCUSSION

The reactivity of free phenolic lignin units should be higher than that of non phenolic lignin units in the pretreatment with  $\text{NO}_2$ . To clarify this, experiments were carried out using vanillyl alcohol and veratryl alcohol as lignin model compounds on a linter cellulose substrate. As shown in Table 1, vanillyl alcohol was easily decomposed by the pretreatment, even when the molar ratio of  $\text{NO}_2$  to vanillyl alcohol was 1.3. On the other hand, veratryl alcohol was relatively stable. These results indicate that the demethylation and the oxidation of lignin should occur mainly at free phenolic lignin units.

If a small amount of veratryl alcohol and, by implication, non phenolic lignin units could be demethylated and oxidized in the pretreatment, the reactivity of lignin in oxygen bleaching would be improved. Therefore, additional experiments for elucidating the reaction of veratryl alcohol will be carried out.

Table 1 Reactivity of vanillyl alcohol and veratryl alcohol during NO<sub>2</sub> pretreatment.

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

Note: Dosage of each model compound is 150mg on 10g of linter cellulose.

As shown in Table 2 and Fig. 1, in the NO<sub>2</sub> pretreatment of vanillyl alcohol, 4-nitroguaiacol (2-methoxy-4-nitrophenol) was identified by GC-MS using the authentic compound, and 4,6-dinitroguaiacol (2-methoxy-4,6-dinitrophenol) was considered to be formed. The total yield of the nitrated products increased with increasing NO<sub>2</sub> charge. This implies that the nitration rates of vanillyl alcohol became faster with higher concentration of NO<sub>2</sub>, and that the decomposition of vanillyl alcohol was retarded in spite of increasing NO<sub>2</sub> charge. In the case of veratryl alcohol, the corresponding nitro compounds were not detected in these experiments.

These results indicate that nitro groups should be introduced into free phenolic lignin units, and that the extent of nitration of free phenolic lignin units should be larger than that of non phenolic lignin units. Further studies on nitration of non phenolic lignin units will be done to confirm these results.

Table 2 Yields of nitrated products in NO<sub>2</sub> pretreatment of vanillyl alcohol.

Molar ratio of NO <sub>2</sub> 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

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

(Insert Figure 1 - Nitration of vanillyl alcohol in NO<sub>2</sub> pretreatment.)

It is known that phenolic compounds are nitrated with nitric acid. Compared with the concentrations of nitric acid normally used in this reaction, however, those of nitric acid in the NO<sub>2</sub> pretreatment should be low, even if most of the NO<sub>2</sub> were to react with water to form HNO<sub>3</sub> and NO. As shown in Table 3, 4-nitroguaiacol and 4,6-dinitroguaiacol were not detected in treating vanillyl alcohol in HNO<sub>3</sub> aqueous solution without NO<sub>2</sub>.

Table 3 Reactivity of vanillyl alcohol in HNO<sub>3</sub> aqueous solution without NO<sub>2</sub>.

Molar ratio of HNO <sub>3</sub> to vanillyl alcohol	1.6	21
Vanillyl alcohol recovered, %	76	67
4-Nitroguaiacol and 4,6-dinitroguaiacol	0	0

Notes: Dosage of vanillyl alcohol is 150mg into 30ml of HNO<sub>3</sub> aqueous solution. Experiments were carried out in the modified rotary evaporator for 10min at room temperature.

Furthermore, the yields of nitro compounds in the reaction of nitrous acid and lignin model compounds are known to be very low<sup>5)</sup>. The total yield of nitro compounds in the NO<sub>2</sub> pretreatment of vanillyl alcohol was 9.2-26.1% (Table 2). These facts suggest that the mechanism of nitration by NO<sub>2</sub> should be different from those by nitric acid and nitrous acid.

The results in Table 2 also suggest that side chains of free phenolic lignin units should be substituted by nitro groups, and that the 5-position of condensed free phenolic lignin units might be substituted (Fig. 2). These reactions as well as the oxidation by NO<sub>2</sub> should contribute to degradation of the lignin macromolecule.

(Insert Figure 2 - Substitution of side chains of free phenolic lignin units.)

As mentioned before, lignin in pulp is demethylated in the pretreatment<sup>1)</sup>. However, previous studies at IPST have shown that phenolic hydroxyl group contents of pretreated kraft pulp are not increased, and that the ortho-quinone structures in the pulp was three times as high as that in untreated pulp. The assessment of carboxylic acid groups in the pulp is in progress, and studies using FTIR will be continued.

In the absence of molecular size data, it was considered possible that the increased hydrophilicity of lignin by demethylation and oxidation might lead to dissolution of larger fragments at an earlier stage of lignin depolymerization and consequently more complete lignin removal. On the other hand, the degradation of lignin by both nitration and oxidation could result in the dissolved lignin from the pretreated pulp consisting of smaller fragments. To resolve this, we determined the molecular weight distributions by gel filtration chromatography of lignins dissolved during oxygen bleaching. As shown in Figure 3 the dissolved lignin from kraft pulp NO<sub>2</sub>-pretreated and oxygen-bleached has smaller fragments compared with that from pulp oxygen-bleached without the pretreatment. Furthermore, a part of the lignin in NO<sub>2</sub>-pretreated kraft pulp was dissolved in alkali without oxygen bleaching. These results indicate that lignin in kraft pulp was degraded by the pretreatment with NO<sub>2</sub>.

(Insert Figure 3 - Molecular weight distributions by GFC of lignins dissolved during oxygen bleaching.)

The mechanism of NO<sub>2</sub> enhancement of oxygen delignification may involve only demethylation and nitration of lignin at free phenolic lignin units. However, as mentioned before, the reactivity of lignin in oxygen bleaching would be similarly improved if non phenolic lignin units reacted in the pretreatment. On the other hand, previous work at IPST has cast doubt on the mechanism proposed by Lindeberg and Walding. NO<sub>2</sub>-pretreated kraft pulp was methylated with diazomethane and then oxygen-bleached. Contrary to expectations based on the Lindeberg mechanism, its bleaching rate was severely retarded by the methylation. This result, as well as the relative inertness of veratryl alcohol referred to above, has indicated that the effect of nitro groups in non phenolic lignin units on delignification should be small. To further clarify this, kraft pulp will be methylated with diazomethane, NO<sub>2</sub>-pretreated and oxygen-bleached.

A small amount of 4-nitroguaiacol was detected in NO<sub>2</sub> pretreatment of kraft pulp (Table 4). It might be a protector against carbohydrate degradation. An experiment using 4-nitroguaiacol and kraft pulp is in progress to obtain evidence for a carbohydrate protection effect.

Table 4 Formation of 4-nitroguaiacol in NO<sub>2</sub> pretreatment of kraft pulp.

NO <sub>2</sub> dosage, % on pulp	1.4	8.0
4-nitroguaiacol formed, ppm on pulp weight	180	100

Note: Pretreated pulp was washed with water, and 4-nitroguaiacol in the water was determined.

#### CONCLUSIONS

In summary, this research has shown that lignin monomeric units containing free phenolic hydroxyl groups are probably nitrated in the pretreatment while fully etherified ones probably are not. This casts doubt on the validity of a mechanism proposed by Lindeberg. Nevertheless, our molecular size determinations have shown that lignin is oxidatively degraded (or rendered more susceptible to degradation) by oxygen and alkali.

#### EXPERIMENTAL

##### NO<sub>2</sub> pretreatment

Vanillyl alcohol or veratryl alcohol (150mg) was dissolved in 150mL of ether and added to 10.0g of linter cellulose in a 1L round flask, and the flask was shaken thoroughly. After the ether was removed in an evaporator, water was added to adjust the consistency of the linter cellulose to 25%. NO<sub>2</sub> pretreatment was carried out according to a procedure <sup>6)</sup> which may be generally described as follows: The flask was placed on a modified Calab type rotary evaporator and a vacuum of approximately 28 in. of Hg was applied. Then cold N<sub>2</sub>O<sub>4</sub> (NO<sub>2</sub>) was placed in a chilled special pipette and the pipette was connected to the modified rotary evaporator. By opening the two inside valves, the N<sub>2</sub>O<sub>4</sub> was sent into the rotating flask. Then by adding small amounts of O<sub>2</sub>, any NO which might be present was converted to NO<sub>2</sub>. After a ten minute reaction time at room temperature, the flask was taken off the evaporator and water was poured into the flask.

The linter cellulose was washed with 200mL of water four times. The filtrate was gathered and diluted to 1000mL quantitatively, and 25mL of the filtrate was extracted with 25mL of ether five times without acidification. The ether fraction was washed with 5mL of water and treated with anhydrous sodium sulfate. Syringaldehyde, as an internal standard was added to the ether fraction, which was concentrated to 4mL.

##### Gas chromatography and mass spectrometry

The concentrated sample was subjected to gas chromatography (GC) directly. Conditions of GC are as follows: Column, HP17 Cross linked 50% Ph Me Silicone, 10m X 0.53mm X 0.002mm film thickness; Det. (FID) temp., 280 C; Inj. temp., 250 C; Column temp., 150 C, 5 C/min, 280 C, 20min. The relative retention times of compounds used are as follows: Vanillyl alcohol, 0.55; 4-Nitroguaiacol (2-Methoxy-4-nitrophenol), 0.76; Veratryl alcohol, 0.64; Syringaldehyde, 1.00. The weight-to-area ratio of 4,6-dinitroguaiacol (2-methoxy-4,6-dinitrophenol) for an internal standard is assumed to be 1.00 in this experiment.

Conditions of gas chromatography-mass spectrometry (GC-MS) are as follows: Hewlett Packard HP5985B GC/MS System, 70eV; Column, OV17, 2m X 2mm; Column temp., 100 C, 10 C/min, 300 C. A mass spectrum of 4-nitroguaiacol (2-methoxy-4-nitrophenol) which was compared with an authentic spectrum is shown in Fig. 4, and that of the other compound, which is considered to be 4,6-dinitroguaiacol (2-methoxy-4,6-dinitrophenol), is shown in Fig. 5 (molecular ion peak, 214; the relative retention time for GC using HP17 Cross linked 50% Ph Me Silicone, 1.20).

(Insert Figure 4 and Figure 5)

#### Preparation of dissolved lignin

Oxygen bleaching was carried out under the following conditions 7): Pulp consistency, 27%; NaOH charge, 2%; Mg<sup>2+</sup> charge, 0.1%; Oil bath temp. set, 120 C; Reaction time, 20min (from 100 C to 115 C). Oxygen pressure; 70psig at room temp.. Loblolly pine kraft pulp with Kappa number 38.7 was used in these experiments.

After being oxygen-bleached or left for 1hour at room temperature, pulp was put into a 10mL plastic syringe, and pressed to sample about 1mL of black liquor without dilution. The pulp was washed with 300mL of water three times after sampling, and its Kappa number was checked.

#### Gel filtration chromatography

The black liquor sample was diluted with 1.0M NaOH and soaked for 4days, and 0.15mL of the sample was subjected to gel filtration chromatography (GFC). Conditions of GFC are as follows: Column, Sephadex G-50 medium, 50cm X 2.5cm; Effluent, 0.5M NaOH; Detection, absorbance at 280nm. Chromatograms were calibrated by using the delignification degrees of corresponding bleached pulps.

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- 5) Bolker, H. I., Kung, F. L. and Kee, M. L., Tappi, 50(4): 199 (1967)
- 6) IPST Pulping and Bleaching Group Procedure No. 307
- 7) IPST Pulping and Bleaching Group Procedure No. 305

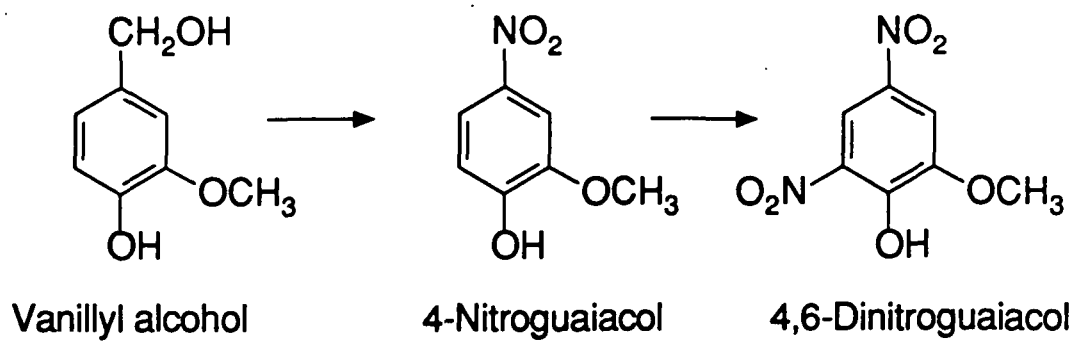


Fig.1 Nitration of vanillyl alcohol in NO<sub>2</sub> pretreatment.

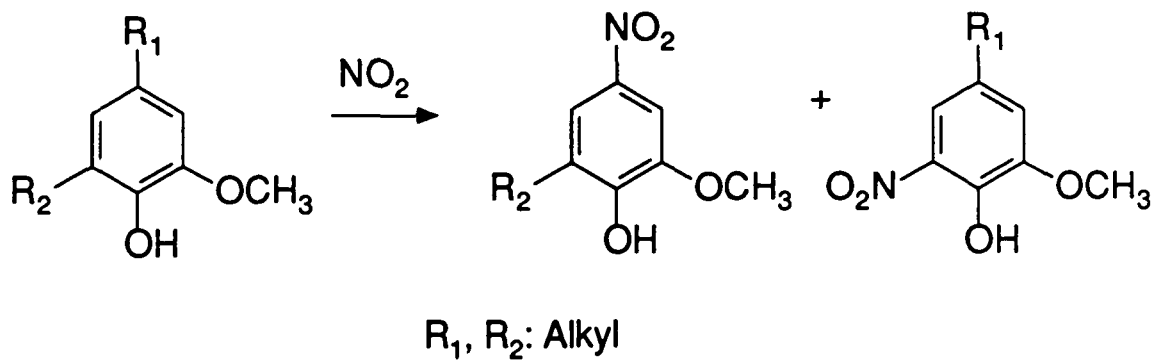


Fig. 2 Substitution of side chains of free phenolic lignin units.

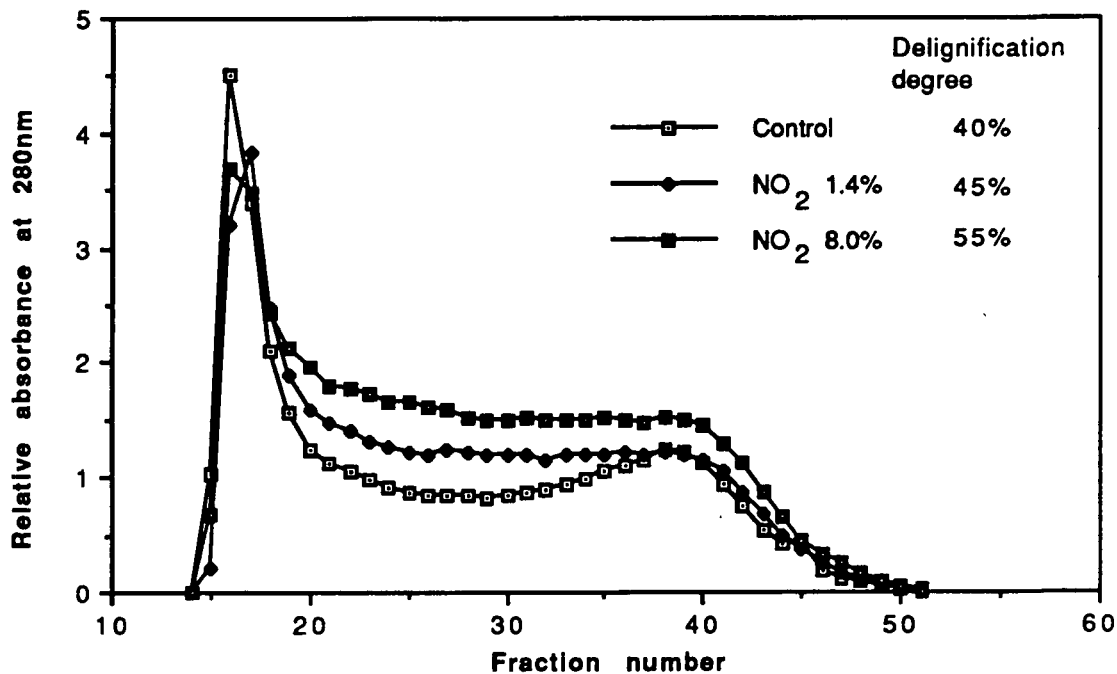


Fig. 3 Molecular weight distributions by GFC of lignins dissolved during oxygen bleaching.

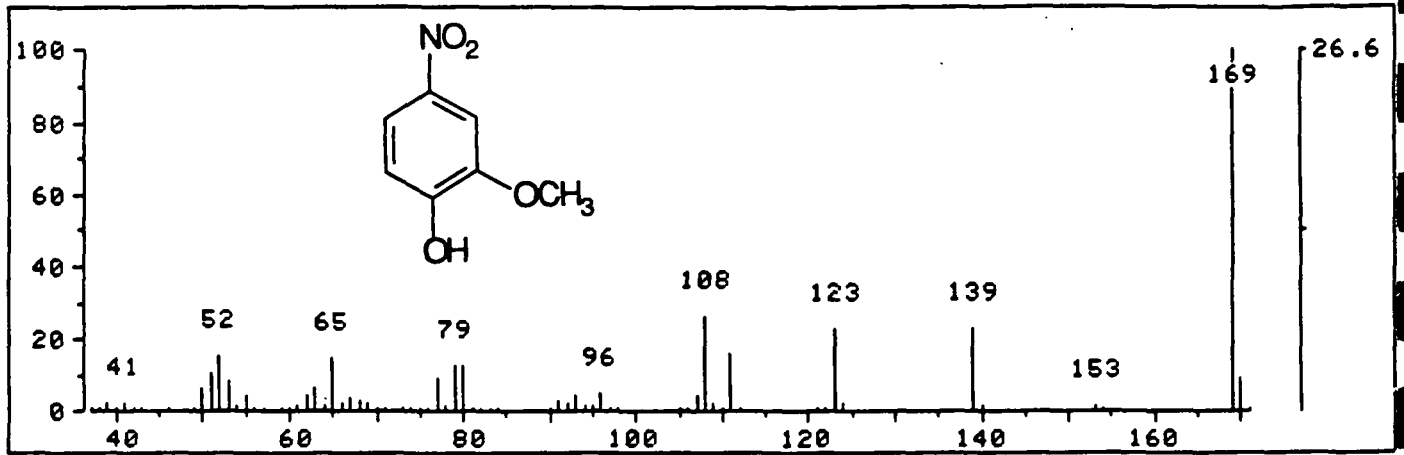


Fig. 4

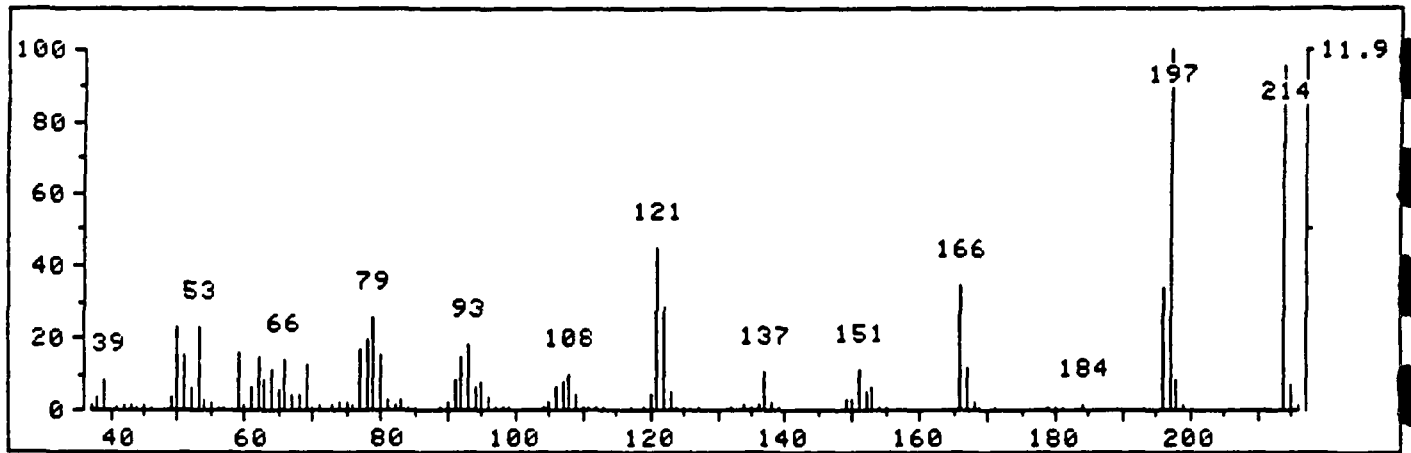


Fig. 5

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3475: FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

PROJECT LEADER: D. R. Dimmel

IPC GOAL:

Improved process for bleached chemical pulps

OBJECTIVE:

Provide a fundamental understanding of the chemical and physical reactions that control both:

- (1) the rate of lignin removal, hemicellulose dissolution, and cellulose degradation, and
- (2) the structures of the lignin, hemicelluloses and cellulose that remain in the pulp after pulping and bleaching.

CURRENT FISCAL YEAR BUDGET: \$90,000

PRIOR RESULTS:

The detailed mechanistic studies of pulping delignification chemistry conducted in this project have led to a greater understanding of the factors which control lignin fragmentation and condensation reactions. A significant portion of the research was directed towards understanding the reactions of anthrahydroquinone (AHQ) with lignin substrates. Our interest here relates to the fact that anthraquinone (AQ) pulping systems show improved selectivities. The research, including related student work has led to over 30 publications in the last 10 years, with several additional articles submitted and in preparation.

The project has also been concerned with understanding the chemistries associated with carbohydrate chain cleavage reactions that occur during alkaline pulping and bleaching. Such reactions cause a lowering of the degree of polymerization (DP) and thus a loss in paper strength properties. Changes in DP are seen by changes in pulp viscosities and molecular weight distributions. Earlier work in this project involved developing the GPC method.

Research activity in the past few years has concerned comparing the reactivity difference of amorphous crystalline and cellulose samples; any observed difference should reflect the importance of "physical effects" in carbohydrate chain cleavage reactions. A relatively high viscosity amorphous cellulose sample has been prepared from a cotton linters cellulose. The amorphous sample was reduced with sodium borohydride ( $\text{NaBH}_4$ ) to prevent "peeling" losses in monomer units when heated in alkali. The viscosity losses as a function of time of heating at  $150^\circ\text{C}$  in alkali ("pulping") were much greater for the stabilized amorphous cellulose sample than for a corresponding stabilized crystalline cellulose sample. The rate of DP loss was further increased slightly when either amorphous or crystalline cellulose was heated in alkali in the presence of AQ.

The reactivity trends observed for amorphous and crystalline cellulose in the "pulping" experiments were similar in an oxygen-alkali "bleaching" reaction at 100°C. The more reactive sample was the amorphous cellulose. The viscosity losses for amorphous cellulose in oxygen-alkali were inhibited by the presence of magnesium. The addition of cobalt, above a level of 0.162 mole CoSO<sub>4</sub>/100 g of cellulose greatly accelerated the amorphous cellulose viscosity losses. The combination of Mg and Co was even more harmful to the sample's viscosity. Treatment of cotton linters and amorphous cellulose with SO<sub>2</sub> to remove metals caused no loss of viscosities at pH 2.3; however, at pH values below 2.3, large viscosity losses were observed.

A sample of cotton linters (12% consistency) was treated with 0.2% hydrogen peroxide at 50° C and pH 11 and the viscosity determined as a function of time. In comparison to an amorphous cellulose, the linters displayed a much slower loss of viscosity with time. A combination of added magnesium sulfate and sodium silicate prevented viscosity losses during peroxide reaction with the amorphous cellulose.

Cotton linters were treated with dilute acid for a day to hydrolyze and remove any amorphous cellulose component. A portion of the product was reduced with NaBH<sub>4</sub>. Samples were then exposed to O<sub>2</sub>/NaOH and low levels of cobalt at 100°C for various time periods. The acid-treated linters showed severe viscosity drops with reaction time. The corresponding NaBH<sub>4</sub> reduced, acid-treated linters showed only small viscosity losses with time. A kraft pulp showed similar small losses. It is apparent that highly crystalline cellulose samples degrade much more slowly than amorphous cellulose under pulping and bleaching conditions.

#### SUMMARY OF RESULTS SINCE LAST REPORT:

A detailed oxygen-alkali/cobalt study of viscosity changes with crystalline, amorphous, and kraft celluloses was performed to confirm earlier results. The large backlog of results which exists from past carbohydrate research was organized in preparation for internal and external publications.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Publication of past research results and performing supporting experiments for the publications will be the focus of the fiscal year 1990 activities.

#### POTENTIAL FUTURE ACTIVITY:

The amorphous cellulose bleaching chemistry studies could be expanded to examine (1) additional chemicals (ozone, chlorine dioxide, etc.), (2) process variables, (3) the influence of selected metals and "dead load" salt effects, and (4) more detailed molecular weight distributions. The aim will be to develop a fundamental understanding of bleaching chemistry which may lead to better nonchlorine bleaching systems. Additional activities on delignification reactions will require additional personnel.

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3566: STRONG, INTACT HIGH YIELD FIBERS

PROJECT LEADER: A. W. Rudie, T. J. McDonough

IPST GOAL:

A significant increase in the yield of useful fibers

OBJECTIVE:

Develop wood fiber separation and treatment methods that will allow good control of the strength, physical form and bonding characteristics of the resulting fibers.

CURRENT FISCAL YEAR BUDGET: \$50,000

PRIOR RESULTS:

Results obtained since the inception of this project are summarized in the September 19, 1988 Status Report.

RECENT RESULTS:

Recent activity has consisted of support for the development of a consortium to do research on chemithermomechanical pulping and thermomechanical pulping. The consortium, combining the research efforts of Georgia Tech., IPST, and Herty Foundation, is to be led by Georgia Tech.

The consortium will make use of a two-stage continuous pilot refining system employing a Sunda Defibrator CD-300 pressurized first stage refiner and a Defibrator ROP-20 atmospheric second stage refiner. It is also equipped with a KMW chip classifier, atmospheric presteaming, atmospheric pre-impregnation, a pressurized, second stage of impregnation, pressurized steaming and interstage washing. The system was donated to Georgia Tech by Mead Corporation and has been installed at Georgia Power's Technical Applications Center, near IPST.

Proposals have been developed for three initial projects to be undertaken by the consortium. They deal with chip size effects, manufacture of CTMP from dense hardwoods, and pulping of juvenile wood of southern pines.

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3661: SULFUR-FREE SELECTIVE PULPING PROCESS  
(DOE FUNDED PROJECT)

PROJECT LEADER: D. R. Dimmel

IPC GOAL:

Improved process for bleached chemical pulps

OBJECTIVE:

To develop a sulfur-free pulping process based on conversion of lignin to pulping additives which will increase delignification rates and decrease the degradation of carbohydrate fibers.

CURRENT ANNUAL BUDGET: \$128,000

PRIOR RESULTS:

The research work of John Wozniak (Ph.D. 1988, IPC) has demonstrated that pulping catalysts can be prepared from lignin and lignin-derived chemicals. The aromatic rings of lignin were oxidized to benzoquinones, which in turn were modified by Diels-Alder reactions into anthraquinone type pulping catalysts. The synthetic yields achieved by Wozniak were respectable; the Diels-Alder products had moderate to excellent pulping activity. The process (lignin ---> catalysts) has potential for providing an inexpensive, selective, sulfur-free pulping process.

The oxidative procedures developed by Wozniak were reexamined by the Institute staff members in an attempt to develop accurate yield measurements when employing small sample sizes. Both peracetic acid and peroxide oxidation procedures when applied to small samples, gave inconsistent results. Many variables were examined to account for the results, including: stabilities of products and internal standard (I.S.) to reaction and work-up conditions, changes in extraction solvents, work-up conditions, points of addition of the I.S., levels of reagents, etc. Straight gas chromatography (GC) analysis and analysis after derivatization (reduction acetylation and methylation) have not given consistent results. High water solubility and volatility make the product analysis difficult.

The Fremi salt oxidation of lignin models has also been extensively studied. The analysis of products here was also complicated, primarily because of the suspected instability of the benzoquinones and hydroquinones on the GC columns. Analysis by UV and by reductive acetylation were partially successful. After much experimentation, we were able to get reproducible results on small samples.

Several Solar Energy Research Institute (SERI) samples have now been analyzed. The results are promising; reasonably good yields of benzoquinones have been obtained from the lignin isolated by EtOAc extractions of organosolv aspen pulping liquors.

#### SUMMARY OF RESULTS SINCE LAST REPORT:

Additional SERI samples have been oxidized with Fremi salt and yields determined. Supercritical fluid extracted aspen kraft black liquors and steam exploded lignin gave poorer benzoquinone yields than did EtOAc extracted liquors. However, the yields are still better than that observed with straight lignin.

According to Mr. Arthur Power's preliminary economic evaluation (Executive Summary attached), our ability to produce low cost anthraquinone pulping catalysts from lignin is highly dependent on the chemical yields of the synthetic steps. The IPST team (Dimmel and Molinarolo) has been examining better methods of converting benzoquinones (single-ring compounds) to anthraquinones (3-ring compounds). The first of two ring-forming reactions can be accomplished in high yield. If the structure of the product from the first step is not modified, the second ring-forming reaction generally does not occur. We have found that adding aluminum oxide to the benzoquinone/diene reaction promotes modification of the intermediate product and the yields of anthraquinones in the single step reaction go up. Other ring forming catalysts were also examined, but generally were less effective than aluminum oxide. The anthraquinone yields are still only modest (20%) by these procedures. Additional research may improve the situation.

Quite high yields (70%) have been demonstrated in the case where a specialized diene (ring forming reagent) is used. The practicality of using 1-acetoxy-3-methyl-1,3-butadiene in a low cost commercial process is questionable; however, we have at least demonstrated that high yield synthetic yields are possible.

Mr. Patrick VanVreede, a B.S. technician at IPST, was loaned to SERI for about 3 months to aid the continued progress in this project. Dr. Don Dimmel visited SERI twice in order to review accomplishments and help establish research goals. VanVreede's research efforts were mainly centered on attempting to optimize benzoquinones yield from hydrogen peroxide oxidation of lignin model compounds and learning to obtain product yields via liquid chromatography analysis.

Dr. Joseph Bozell at SERI has been examining more efficient ways to prepare benzoquinones by way of cobalt promoted oxidations, establishing procedures for performing high yield Diels-Alder products, and characterizing Diels-Alder products.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1990:

We will continue to assess the suitability of different substrates as starting materials for the synthesis of pulping catalysts from lignin. A number of different oxidizing agents and conditions will be tested with lignin and lignin model compounds in an attempt to achieve high yields of benzoquinones. For economic reasons, hydrogen peroxide will be thoroughly examined. More efficient, economical

methods of producing anthraquinones will be sought. The possibility of performing Diels-Alder reactions in supercritical solvents will be examined.

POTENTIAL FUTURE ACTIVITY:

The following areas would appear to be suitable research goals:

- ° Evaluate electrochemical procedures for generating Fremi salts and benzoquinones
- ° Optimize oxidation and Diel-Alder reaction yields
- ° Decide which oxidation agent, starting lignin, diene, and quinone catalysts to pursue for commercial development

ECONOMIC EVALUATION

Arthur Power

I. INTRODUCTION

I.A EXECUTIVE SUMMARY

The kraft process is the most widely used method for producing pulp today. However, it requires the use of a sulfur promoter, resulting in malodorous emissions to the environment. Kraft pulp is also highly colored, requiring extensive bleaching to obtain bright, light-stable pulp. This bleaching step is expensive and when chlorine is used produces undesirable effluents. The environmental concerns associated with the kraft process makes study and development of new pulping processes desirable.

It is now recognized that the production of pulp is catalyzed by the addition of anthraquinone or certain substituted anthraquinones at levels as low as 0.1% of the weight of the wood used. The result is a higher yield of pulp in a shorter time under less vigorous conditions. Importantly, the sulfur promoter used in the kraft process can be completely replaced by anthraquinone using a method known as soda/anthraquinone pulping. There are important advantages to the anthraquinone catalyzed process. First, a significant energy savings is realized. An estimated 0.07 quads/year could be saved with a 4% improvement in the pulping phase of the process alone. Second, the process offers economic advantages. An estimated savings to the U.S. paper industry of \$236 million/year is possible. However, anthraquinone catalyzed pulping has not been widely accepted by the industry because of the cost of the anthraquinone (currently about \$3.00/lb). A sufficiently inexpensive anthraquinone process would allow use of even higher catalyst levels during pulping resulting in even greater energy savings and economic gain.

Scientists at the Institute of Paper Science and Technology (IPST) and the Solar Energy Research Institute (SERI) are collaborating to develop a low cost synthesis of anthraquinone using inexpensive lignin as a starting material. Large quantities of lignin are readily available from pulping black liquor streams or other sources.

The process we envision begins with a selective fractionation of the lignin derived from black liquor using either a supercritical fluid or solvent extraction in order to obtain low-molecular-weight (LMW) lignin fragments. These fragments are most conducive to subsequent chemical transformation. After fractionation, the lignin fragments will first be oxidized with H<sub>2</sub>O<sub>2</sub> or oxygen to give an anthraquinone precursor. The conversion to an anthraquinone pulping catalyst will be accomplished by subsequent Diels-Alder reaction of the anthraquinone precursor with two equivalents of an inexpensive diene (butadiene or isoprene) and finally, dehydrogenation to give the anthraquinone.

SERI has retained Mr. Arthur Power, an independent engineering consultant, to prepare a rough appraisal of the economic feasibility of the manufacture of anthraquinone (AQ) prepared by our proposed process. The results of this study show that above a specific overall yield for the fractionation and chemical steps, anthraquinone can be produced using this process at a significant savings over current costs. Since our economic study was purposely carried out very early in the project, the projections were made using a series of reasonable approximations of yields, reaction times, conditions, etc., based on similar reactions reported in the literature. To further insure a reasonable projection, we have also looked at ranges of yields and times. A wide variety of parameter variations were thus developed and studied, however, they are all subcases of two larger categories: 1) anthraquinone synthesized by selective extraction and chemical treatment of 10% of a lignin containing black liquor waste stream; and 2) anthraquinone synthesized by selective fractionation and chemical treatment of 100% of a lignin containing black liquor waste stream. As the work progresses, detailed assessments of competitive conventional routes from fossil resources to anthraquinone will be performed to guide the present development.

The conclusions of the study are encouraging and reveal the following key points:

- a. The overall yield of the chemical steps is very important and has by far the greatest influence on the final cost of the anthraquinone. A range of overall yields from 5-100% for the chemical processing of the lignin was investigated and showed that at the lowest overall yield, the cost of anthraquinone would be \$27/lb. However, the cost drops exponentially with increasing overall yield to about one dollar per pound at 95% overall yield.
- b. The efficiency of the fractionation is important. The more usable material that is extracted, the lower the overall cost. A 30-50% recovery of the necessary low molecular weight lignin fraction gives the lowest projected cost.
- c. The actual method used for lignin fractionation is also important. Supercritical fluid extraction gives the most selective fractionation of the lignin, but must be performed at the lowest temperature and pressure possible to minimize the capital costs. A simple solvent extraction has lower capital and operating costs, but must be made more selective in order to keep the costs of the chemical conversion to anthraquinone catalyst reasonable.
- d. The lowest cost route results from chemical treatment of 100% of the black liquor stream. At an overall yield of 50%, the projected anthraquinone chemical processing cost drops to less than one dollar per pound.

- e. The feedstock will have a major impact on the process. Both softwoods and hardwoods have been considered. Solvent pulping processes were also examined, particularly of hardwoods.

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3667: MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION  
(API/NCASI FUNDED PROJECT)

PROJECT LEADERS: D. R. Dimmel, L. B. Sonnenberg

IPST GOAL:

Eliminate, or minimize, chlorinated dioxins and chlorinated furans in pulp production.

OBJECTIVE

The proposed research involves developing a fundamental understanding of the chemistries associated with polychlorinated dioxins and polychlorinated furans (PCDD/Fs) production and degradation during wood pulping and bleaching operations. The levels of PCDD/F appear to be related to the levels of dibenzo-p-dioxane (DBD) and dibenzofuran (DBF) in pulp and liquors. Therefore, understanding the reactivities of the DBD/F compounds appears critical. One goal is to find a method to chemically modify precursors in order to prevent their conversion to PCDD/Fs. The second set of goals is to determine which wood component is responsible for precursor formation, to further define what structural features are necessary for precursor formation and, from these data, to postulate mechanisms of precursor formation.

PRIOR RESULTS

The literature has been searched to provide information on the reactivities of DBD/F compounds, especially towards typical pulping and bleaching chemicals. The search also included examining the reported reactions of eight closely related compounds. The literature contains few reports of reactions of DBD/F, other than chlorination and nitration. The information provided the foundation for a research proposal to API/NCASI.

SUMMARY OF RESULTS SINCE LAST REPORT

Funds for Insitute research to develop a fundamental understanding of DBD/F and PCDD/F reactivities, especially related to reactions of the type encountered in pulping and bleaching, were approved by API/NCASI in June. Dr. Sonnenberg was hired in late August to head the project. To date, Dr. Sonnenberg has been learning the background literature, planning specific research goals and developing experimental strategies to attain these goals.

Plans for a companion study have been developed. The study will help define the importance of the DBD/F precursors and examine ways to minimize PCDD/Fs by inhibiting their formation from their precursors. Destructive reactions of PCDD/F will also be examined. These investigations focus on chlorination and involve analysis of PCDD/Fs. Agencies outside the Institute have been evaluated for their abilities to conduct a large part of the experimentation and analysis and the associated costs for the latter study.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1990:

Laboratory work will begin in a few weeks to evaluate the reactivities of DBD/F to nitrogen dioxide, nitric acid, sulfuric acid, ozone, oxygen and peroxides. Once the effective reagent(s) are determined, the procedure(s) will be applied to DBD/F-spiked pulp under varying conditions to determine the applicability of the procedure to DBD/F destruction under realistic industrial conditions. The sequence of experiments will determine the wood components that are potential competitors of the DBD/F reactions and evaluate their relative selectivities.

The chlorination investigations will begin once negotiations with outside agencies have been completed. Chlorination patterns and reaction rates will be determined for DBD/F in model systems and in bleached and unbleached pulp. Selectivities of chlorine and chlorine dioxide for DBD/F and lignin will be determined. Possible PCDD/F control measures will be evaluated, including the use of nitrogen dioxide and oxygen in conjunction with chlorine. The possible destruction of PCDD/Fs with ozone, peroxide and oxygen will also be examined.

#### POTENTIAL FUTURE ACTIVITY

Experiments will be conducted to determine the wood component responsible for DBD/F formation. The investigation will also consider precursors other than DBD/F (should they exist). Methods for inhibiting precursor formation could then be researched. The possibility of precursor formation during bleaching may also be evaluated.

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3671: A STUDY OF THE FEASIBILITY OF THERMAL DESTRUCTION OF CHLORINE-CONTAINING CONCENTRATED STREAMS FROM CLOSED CYCLE PROCESSES (NCASI FUNDED, as part of the 301(m) Research and Development program)

PROJECT LEADER: K. M. Nichols

IPST GOAL:

Part of overall IPST program goal to improve pulping and bleaching technology, with emphasis on environmental impact.

OBJECTIVE:

Evaluate potential technologies for thermal destruction of concentrated streams from closed cycle processes in a device other than a kraft recovery furnace.

CURRENT FISCAL YEAR BUDGET: \$75,000

PRIOR RESULTS: N/A (new project)

SUMMARY OF RESULTS SINCE LAST REPORT:

Work began in August 1989 to characterize the closed cycle streams. The first task was to identify whether or not there are closed cycle technologies (such as the Rapson-Reeve technology practiced until recently at Thunder Bay) being used in existing mills. After searching the literature and making contact with key industry personnel, the conclusion was had that no bleached kraft mills in North America are currently practicing the closed cycle concept.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1990:

The first year of this project will proceed as outlined below.

1. Characterization of the Closed Cycle Streams

Representative samples of a closed cycle stream will be obtained. Since there are no kraft bleached mills practicing closure at the bleach plant, the streams will need to be simulated. This will be accomplished by constructing a small scale version of one of the closed cycle technologies (e.g., a small activated carbon column) and treating bleach plant effluent at a nearby mill in order to obtain sufficient quantity of concentrate.

Once samples of the closed cycle streams are obtained, quantification

of the chemical nature and physical properties will take place. Properties to be measured will include elemental composition, heating value of the solids, viscosity, density, heat capacity and boiling point elevation.

## 2. Combustion Behavior of the Streams

In order to evaluate the effectiveness of any thermal destruction device, it is necessary to know some of the general combustion characteristics of the fuel, which in this case is the closed cycle concentrate. Guidelines for the specific combustion measurements to be made are as follows.

- \* A determination of the fate of the chlorine during combustion. This will be accomplished by measuring the HCl/NaCl ratio under various conditions.
- \* A determination of the extent of destruction of chlorinated organics under various combustion times, temperatures and stoichiometries. The amounts of chlorinated organics will probably be determined by AOX measurements.
- \* A determination of the volatiles content of the dried solids.
- \* A determination of the ash characteristics, such as the chemical composition and the melting temperatures.

## 3. Review of Incineration Technology

This review will be made from a literature survey, and by contact with personnel in industry and government associated with hazardous waste incineration. An evaluation will be made of the feasibility of applying these technologies to closed cycle concentrates. This evaluation will take into account the characteristics and burning behavior of the concentrate.

## 4. Definition of Process Concepts

From the review above, and based on the physical properties, two or three of the thermal destruction techniques will be selected as most promising for destroying closed cycle streams. Process diagrams and preliminary material and energy balances will be constructed, as well as advantages and disadvantages enumerated for each technique. The goal of this is to provide a basis for selecting the most promising approach for further development.

PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3657-2: KRAFT BLACK LIQUOR DELIVERY SYSTEMS

PROJECT LEADER: T. N. Adams, H. L. Empie

IPST GOAL:

Increase recovery boiler throughput and operating efficiency through improved liquor spraying technology at modest capital cost.

OBJECTIVE:

Develop new and improved black liquor spraying nozzles by understanding the characteristics of spray behavior and reducing the fraction of undersize droplets to avoid carryover and pluggage and to accommodate firing higher solids liquors.

CURRENT FISCAL YEAR BUDGET:

PRIOR RESULTS:

The project started in October, 1988 with the design and installation of an enclosed spray chamber, into which black liquor was sprayed and the results recorded by flash x-ray imaging techniques.

SUMMARY OF RESULTS:

Spray trials were carried out at the IPST (IPC) spray facility in Appleton using black liquor from a local paper mill. These were primarily directed at increasing the data base on black liquor nozzle flow and pressure drop characteristics as well as sheet thickness and velocity. Limited droplet size distribution data were taken using a flash x-ray imaging technique. Since this method is limited in the number of pictures that can be taken per run, and hence can't record the history of a given droplet, a high-speed video camera was identified as being a superior alternative. Initial runs with this equipment gave encouraging results, but repairs by the manufacturer were required.

Data were taken on two nozzles (a B&W splash plate and a CE V-type) for a black liquor solids range of 55% to 66%, liquor temperature of 200° to 225° F, and liquor flows of 7.5 to 25 gpm. Data were also taken using corn syrup as the working fluid. The flow and pressure drop characteristics for these nozzles are consistent with the specific geometry of each, allowing reasonable speculation about the flow characteristics of other nozzle designs. Neither the splashplate nor the U-type nozzle is very sensitive to normal fluctuations in liquor property variations. When firing high solids liquors, minimum nozzle operating pressure will have to be increased significantly to suppress flashing ahead of the nozzle.

Fluid sheet thickness was measured using the splashplate nozzle. Limited data indicate that sheet thickness (and likely droplet size) will increase by less

than a factor of two for a ten-fold increase in viscosity.

Black liquor spray trials were carried out at the Camas Mill of James River Corp. to compare the performance of three types of black liquor nozzles under a range of liquor temperature and pressure conditions. The CE recovery boiler at Camas was operated at normal load conditions with one gun location using three alternative nozzle designs - a CE V-type, a CE swirl cone, and a B&W splashplate. High speed video recordings of the spray pattern were made for each condition. Due to spray geometry the video pictures for the V-type nozzle were not clear, but the recordings of the other two nozzles were good. Patterns of spray breakup could be seen for each that are very similar to the breakup observed in the spray booth facility at the Institute. Data reduction is in progress.

The spray facility at Appleton has been dismantled and moved to Atlanta, during which time design changes have been instituted for odor control. The redesigned facility will use a combined spray chamber and holding tank to reduce both odor release and black liquor inventory. The new facility will also give improved image quality with high speed video recording of spray behavior.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1990:

The first priority will be to complete reinstallation of the spraying equipment, consistent with the environmental regulations imposed by the city of Atlanta. Data on droplet formation characteristics for various liquors and commercial nozzles will be gathered, including dependence of drop size distribution and sheet thickness on nozzle type and liquor solids content, viscosity, and velocity.

#### FUTURE WORK:

Succeeding phases of this project will involve optimization of present nozzle designs, followed by development and evaluation of new nozzle concepts. Finally, the potential for using innovative techniques to introduce liquor to the furnace apart from generating droplets will be explored.

STUDENT RESEARCH: Spielbauer, MS 1988, PhD 1991.

BLACK LIQUOR DELIVERY SYSTEMS: (Adams, Obuskovic, Spielbauer)

SUMMARY

The performance of spray nozzles for kraft black liquor has recently been the subject of several investigations. Though research is incomplete, some information is available about the performance of the three basic types of black liquor spray nozzles: the splashplate, the swirl cone, and the U- or V-type. Data are presented on the flow and pressure drop characteristics of two of these nozzles which allows judgment of the sensitivity of the flow to normal mill variations in liquor properties. Data are also presented on several aspects of spray formation and droplet size distribution. Nozzle stability is discussed with respect to flashing ahead of the nozzle. It is found that the minimum nozzle operating pressure will have to be significantly increased to suppress flashing ahead of the nozzle with high solids firing of viscous liquors.

DISCUSSION

Present demands on recovery boiler capacity require nozzle optimization. Both improved control of droplet size to avoid carryover and pluggage, and accommodation of the trend toward higher liquor dry solids content is needed. For these reasons the U. S. Department of Energy (DOE) has funded this study of black liquor droplet formation [1,2].

Black liquor viscosity, surface tension, and density are known to affect droplet size from spray nozzles [3-5]. Viscosity has been the most difficult to characterize, but is now reasonably understood through the DOE project led by Fricke [6], and subsequent DOE-funded work on viscometer development [7,8]. Thorough work on Scandinavian liquors by Soderhjelm [9-11] and Wennberg [12,13] have added to our understanding of black liquor viscosity. Current data support the use of the simple low-shear Newtonian viscosity in characterizing black liquor for spray and droplet formation [5,8,14]. Work at The Institute of Paper Chemistry on black liquor nozzles [2] has resulted in flow coefficient correlations for two types of black liquor nozzles: the B&W splashplate and the CE U-type, and to estimates for the CE swirl cone and V-type [14]. These are based on data taken with both hot and cold black liquor, and corn syrup.

Pressure drop across any flow element can be expressed in the form:

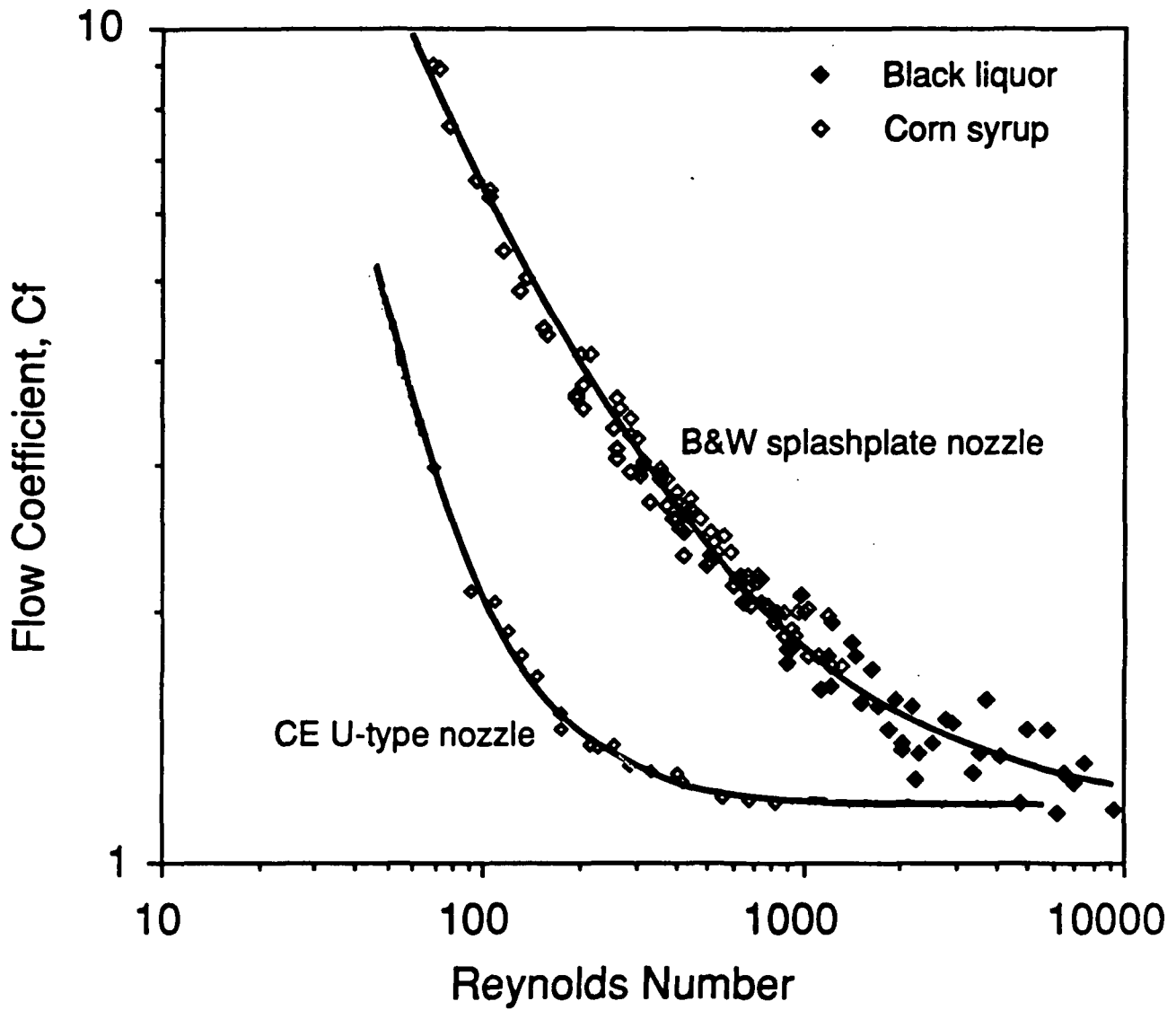
$$\Delta P = C_f \frac{1}{2} \rho V_n^2$$

where:

$\Delta P$ =pressure drop across the nozzle  
 $C_f$ =flow coefficient  
 $\rho$ =fluid density  
 $V_n$ =nozzle exit velocity

The flow coefficient is often taken as a constant for many flow elements such as elbows, expansions, and contractions. However, the flow regime covered by black

\*Taken in part from a paper written by T. N. Adams for the 1990 Kraft Recovery Operations Seminar to be held in Orlando, FL in January, 1990.



*Figure 1 – Flow coefficient data and correlation for two black liquor nozzles using two fluids, black liquor and corn syrup.*

liquor nozzles stretches from laminar flow through transition flow, to almost fully turbulent flow. Data taken of the flow coefficient for two black liquor nozzles are shown in Figure 1 along with correlation curves for each. Comparing these curves to practical mill flow conditions, both the B&W splashplate and the CE U-type nozzles operate in the region of constant flow coefficient, except at the extreme lower end of operation. The equations for the flow coefficients are:

$$\text{B\&W splashplate: } C_f = 1.17 + \frac{373}{\text{Re}^{0.92}} \quad (2)$$

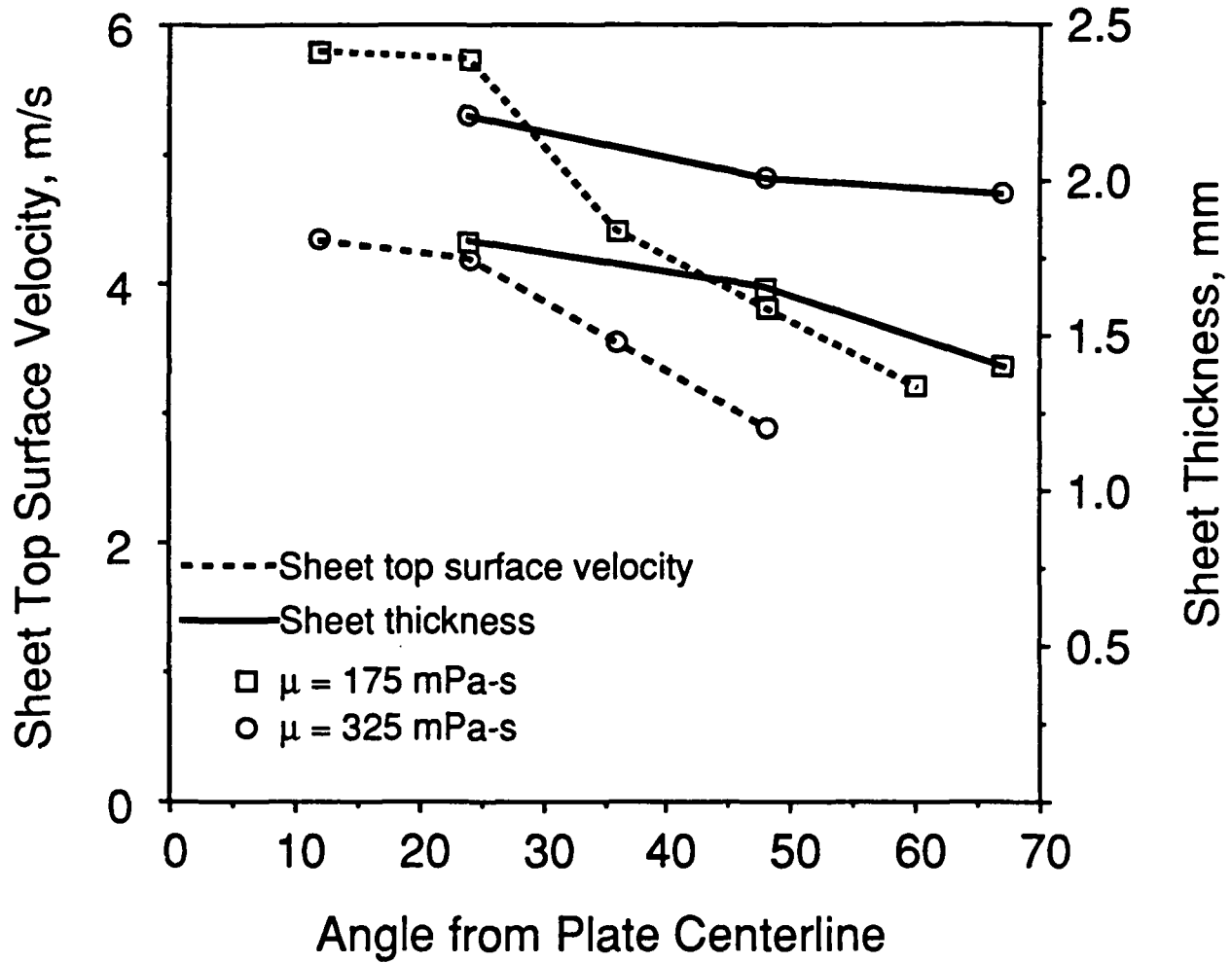
$$\text{CE U-type: } C_f = 1.19 + \frac{3437}{\text{Re}^{1.7}} \quad (3)$$

where Re = Reynolds number,  $\rho DV/\mu$ .

The general physical similarity of the CE U-type and V-type nozzles means the data for the flow coefficient of the U-type can probably be applied with confidence to the V-type nozzle. The CE swirl cone nozzle, despite its obvious geometrical difference, probably has a flow coefficient correlation similar to the B&W splashplate [14]. The CE swirl cone nozzle will have a flow coefficient which varies considerably over its normal range of operation. The B&W splashplate and CE U-type nozzle will have nearly a constant flow coefficient in the normal range of operation and therefore will be very insensitive to normal fluctuations in black liquor viscosity, temperature, and percent dry solids. The CE swirl cone nozzle, however, will be quite sensitive to these normal mill fluctuations. This will make the swirl cone nozzle harder to use and harder to adapt to new operating conditions such as high solids firing.

#### FLUID SHEET THICKNESS

The formation of droplets from a black liquor stream requires first the formation of a fluid sheet for all types of liquor nozzles. The ultimate droplet size can be directly related to the initial sheet thickness and velocity [15]. For most commercial spray nozzles it has been impossible to measure sheet thickness and velocity directly. Due to their large physical size, black liquor nozzles provide a unique opportunity to measure these parameters. Determining the sheet thickness and velocity of black liquor nozzles has also been a part of the IPC project [2] and has been reported in detail [5]. Shown in Figure 2 is sheet thickness and surface velocity data for one B&W splashplate nozzle. Data on sheet thickness and velocity were taken with both black liquor and corn syrup over a range of conditions which spans the normal range of mill operating viscosity, temperature, and percent dry solids.



*Figure 2 – Sheet top surface velocity and sheet thickness data for a B&W 1552 nozzle using corn syrup as a working fluid at a nozzle flow of 0.79 l/s (12.5 gpm). The nozzle diameter is 11.9 mm and the nozzle velocity is 7.1 m/s.*

By themselves the data are very limited in their application. However, by using a simplified geometry, the equations of continuity and momentum can be solved to yield useful correlating equations of the form:

$$\frac{V_n}{V} = C_1 \frac{\mu}{\rho D V_n} + C_2 \tag{4}$$

$$\frac{Y}{D} = C_3 \frac{\mu}{\rho D V_n} + C_4 \tag{5}$$

where:

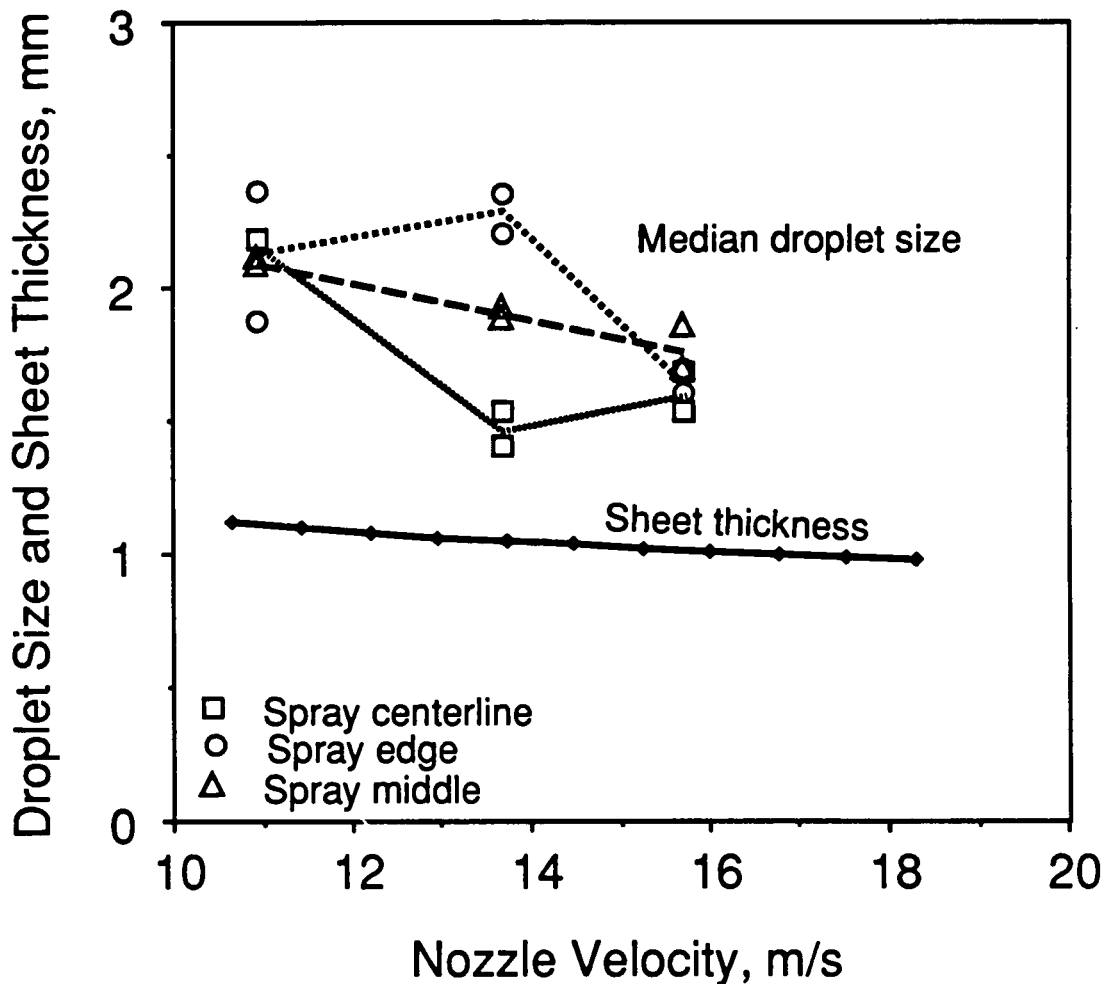
- D = nozzle exit diameter
- V = sheet top surface velocity
- V<sub>n</sub> = nozzle exit velocity
- Y = sheet thickness
- ρ = density of the fluid
- C<sub>1</sub>...C<sub>4</sub> = constants for each nozzle

These equations allow comparison of the sheet thickness data to data which show the impact of flow velocity on black liquor drop sizes [4]. Shown in Figure 3 is comparison of droplet size data and fluid sheet thickness based on the correlation of Equation (5) for a B&W 12-49 nozzle. (The B&W splashplate exit orifice is circular and designated by the nozzle number measured in thirty-seconds of an inch. A B&W 24-49 nozzle has an exit orifice diameter of 24/32 inches (3/4 inches or 1.9 cm). The second number indicates the angle of the splashplate relative to the nozzle exit flow.) The trend of the correlation is quite good and it is offset downward from the drop size data, consistent with the theory of droplet formation [15].

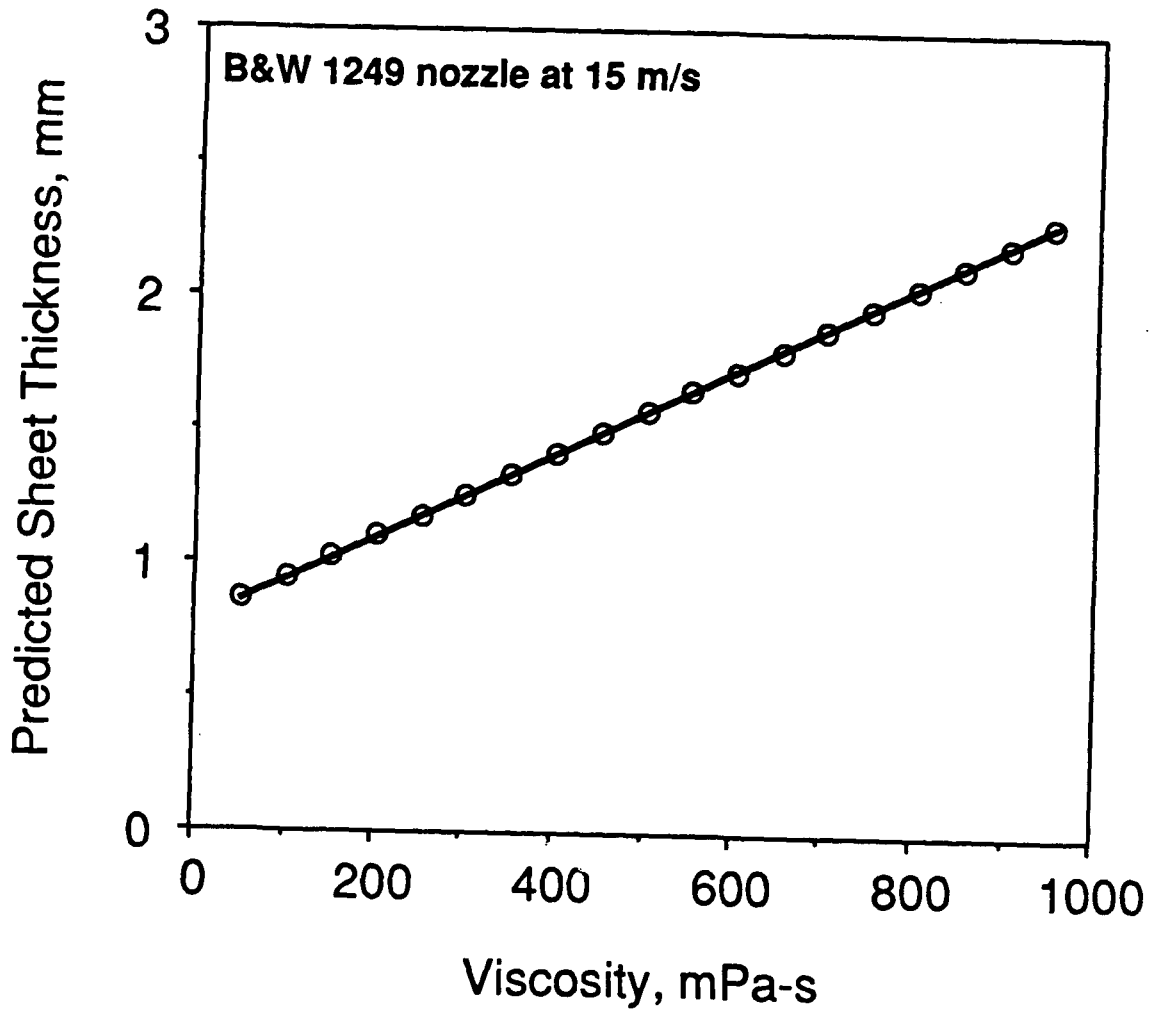
Of more interest are the anticipated effects of high solids firing on droplet size from black liquor sprays. One impact of higher solids is increased viscosity. Typically black liquor viscosity at firing conditions ranges from about 30 to 300 cP (30 to 300 mPa-s). Liquor temperature can be used to control viscosity under most circumstances, but for firing solids near 80% the viscosity is likely to be between 250 to 300 cP (250 to 300 mPa-s) [16,17]. Shown in Figure 4 is a plot of fluid sheet thickness as a function of viscosity based on Equation (5). Fluid sheet thickness, and therefore ultimate liquor droplet size, does increase with viscosity. However, this increase is less than a factor of two for an increase in viscosity of a factor of ten. This change in nozzle performance at high solids for the B&W splashplate nozzle would be mild enough to allow routine mill optimization of existing nozzles without resorting to entirely new liquor nozzles when changing to high solids firing.

#### BLACK LIQUOR DROPLET SIZE DISTRIBUTION

Some data are available on the droplet size and size distribution from black liquor nozzles [3,4], but considerably more data are needed to provide practical guidance in control and optimization of nozzles in normal pulp and paper mill operation [2].



*Figure 3 – Comparison of droplet median size data and calculated sheet thickness as a function of nozzle velocity for a B&W 1249 nozzle firing liquor at a viscosity of 150 mPa-s.*



*Figure 4 – Calculated sheet thickness as a function of fluid viscosity for a B&W 1249 nozzle operating at 15 m/s (17 gpm).*

Black liquor nozzles, like all nozzles which depend on chaotic breakup, produce not a single size but a range of droplet sizes. Data on the droplet size distribution from a B&W splashplate nozzle and a CE swirl cone nozzle are presented in Figures 5 and 6 [4]. The data for the CE nozzle is slightly truncated because the measurement technique used had a lower cutoff limit of 0.5 mm. The CE data were taken for hot black liquor at normal mill firing conditions. The B&W splashplate data were taken with slightly diluted black liquor (approximately 53% solids) at room temperature.

A few general conclusions can be drawn from the available data. First, the mean droplet size does vary with operating conditions. The data in Figure 3 show the effect of nozzle velocity on mass median droplet size. Droplet size is only a fairly weak function of liquor velocity or flow rate. Available data indicate that droplet size is a fairly weak function of all fluid and operating parameters, and this is consistent with droplet formation theory [15]. This is initially inconsistent with field operations where small changes in liquor temperature, for example, have a pronounced effect on recovery boiler performance. However, this apparent inconsistency probably only indicates that there are features of nozzle performance other than droplet size which impact boiler performance, such as droplet trajectory and subsequent droplet combustion.

The second important conclusion from the available black liquor spray data is that the size distribution is almost the same for all nozzles. Just as indicated in Figure 5, conditions which produce larger mean droplets also produce broader size distributions. This is most neatly demonstrated with data from the work of Bennington [3] on black liquor sprays. Shown in Figure 7 is a plot of droplet size distribution for one very small swirl cone nozzle for three fluids: water, glycerol, and black liquor. The three are clearly different with black liquor being, by far, the largest and broadest. However, when these data are normalized by dividing the actual droplet size by the mass median droplet size, the three curves collapse into one as shown in Figure 8.

The curve shown in Figure 8 proves to be nearly universal for pressure atomized spray nozzles including black liquor nozzles. There appears to be very little impact of nozzle geometry, fluid properties, or operating conditions. This is still under intense investigation because of the dramatic impact on carryover of the tail of this curve [2].

Practical interpretation of this information suggests that any two nozzles and operating conditions which produce the same mean size also produce the same size distribution. Major emphasis should first be on understanding the impact of nozzle geometry, fluid properties, and operating conditions on the mean size of droplets formed in a spray. After this is available in a practical form, then control of droplet size distribution by advanced techniques such as vibratory assist [1] should be pursued.

#### NOZZLE STABILITY AND THE IMPACT OF HIGH SOLIDS

The term nozzle stability refers to the ability of a nozzle to produce a steady spray pattern over a range of operating conditions. Every recovery boiler operator has had to deal with black liquor roping when the liquor was either too

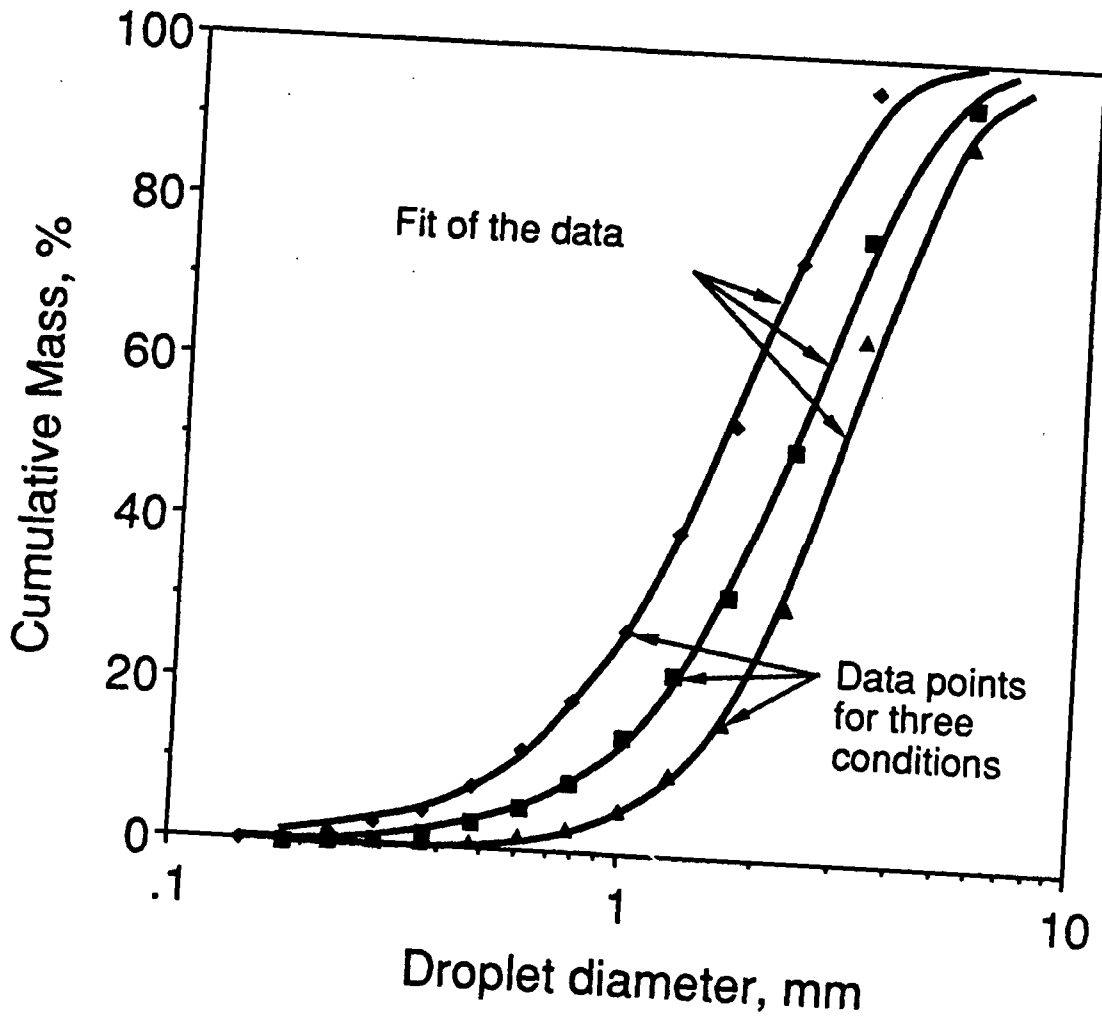
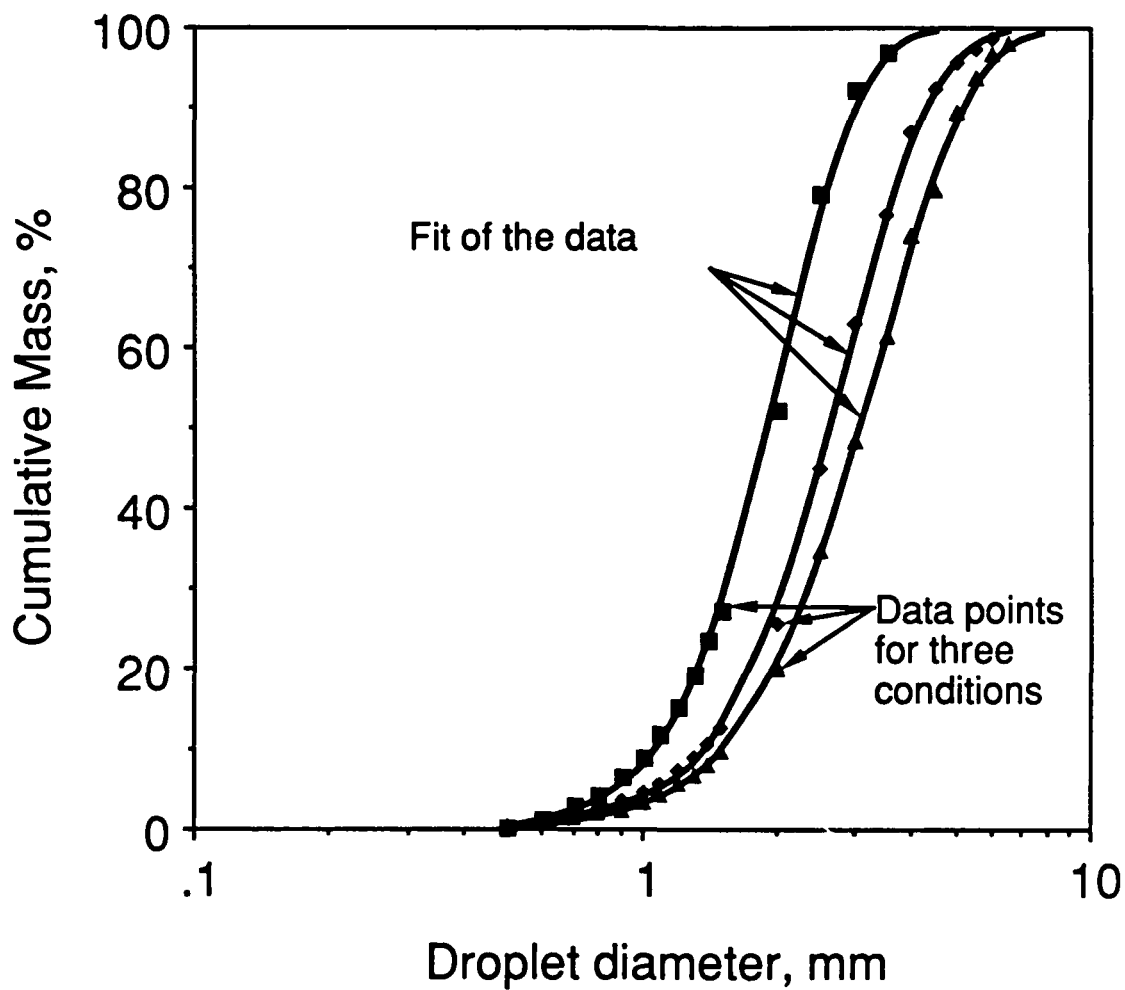


Figure 5 – Comparison of droplet size distribution data for three conditions for a B&W 12-49 splashplate nozzle.



*Figure 6 - Comparison of droplet size distribution data for three conditions for a CE swirl cone nozzle.*

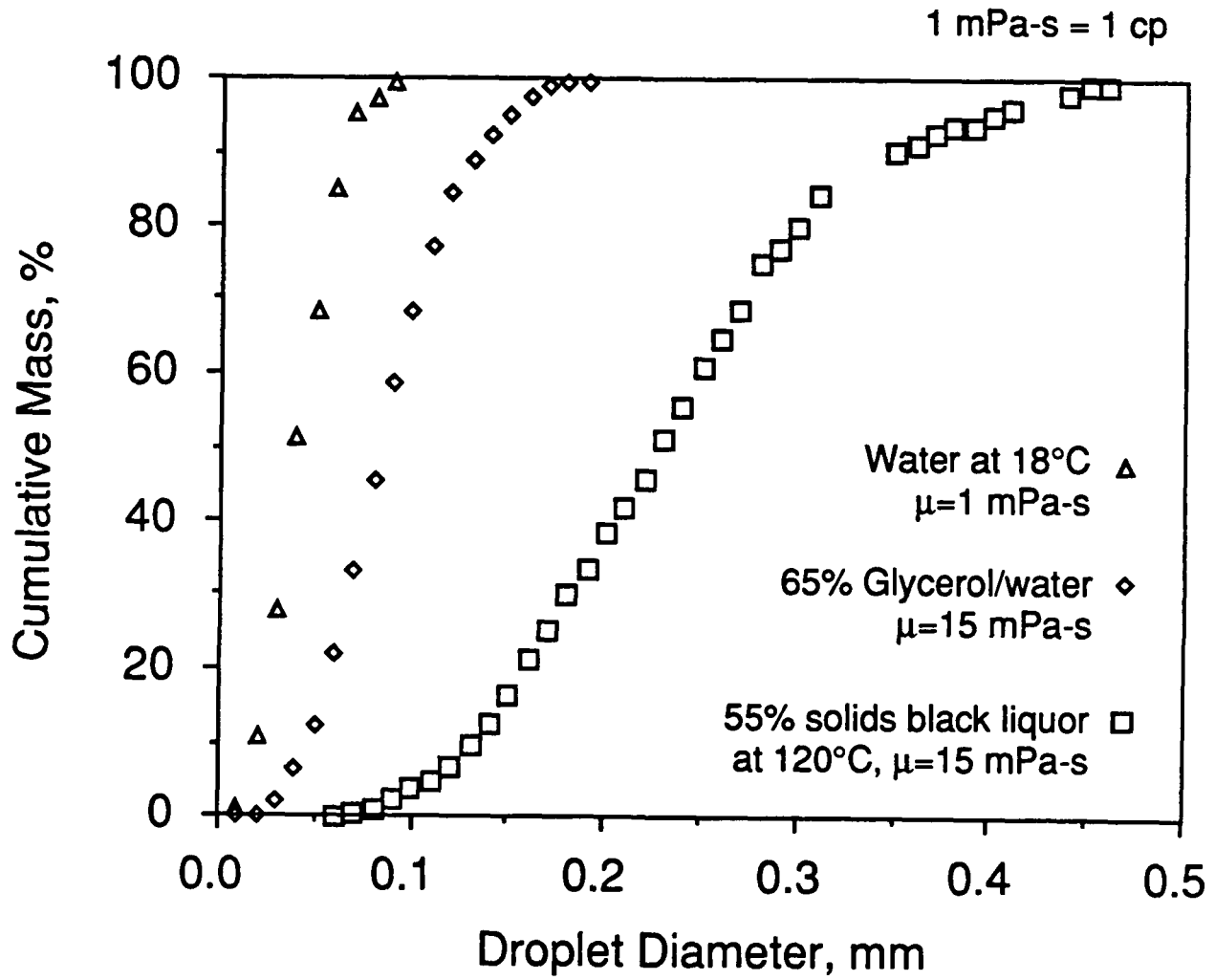
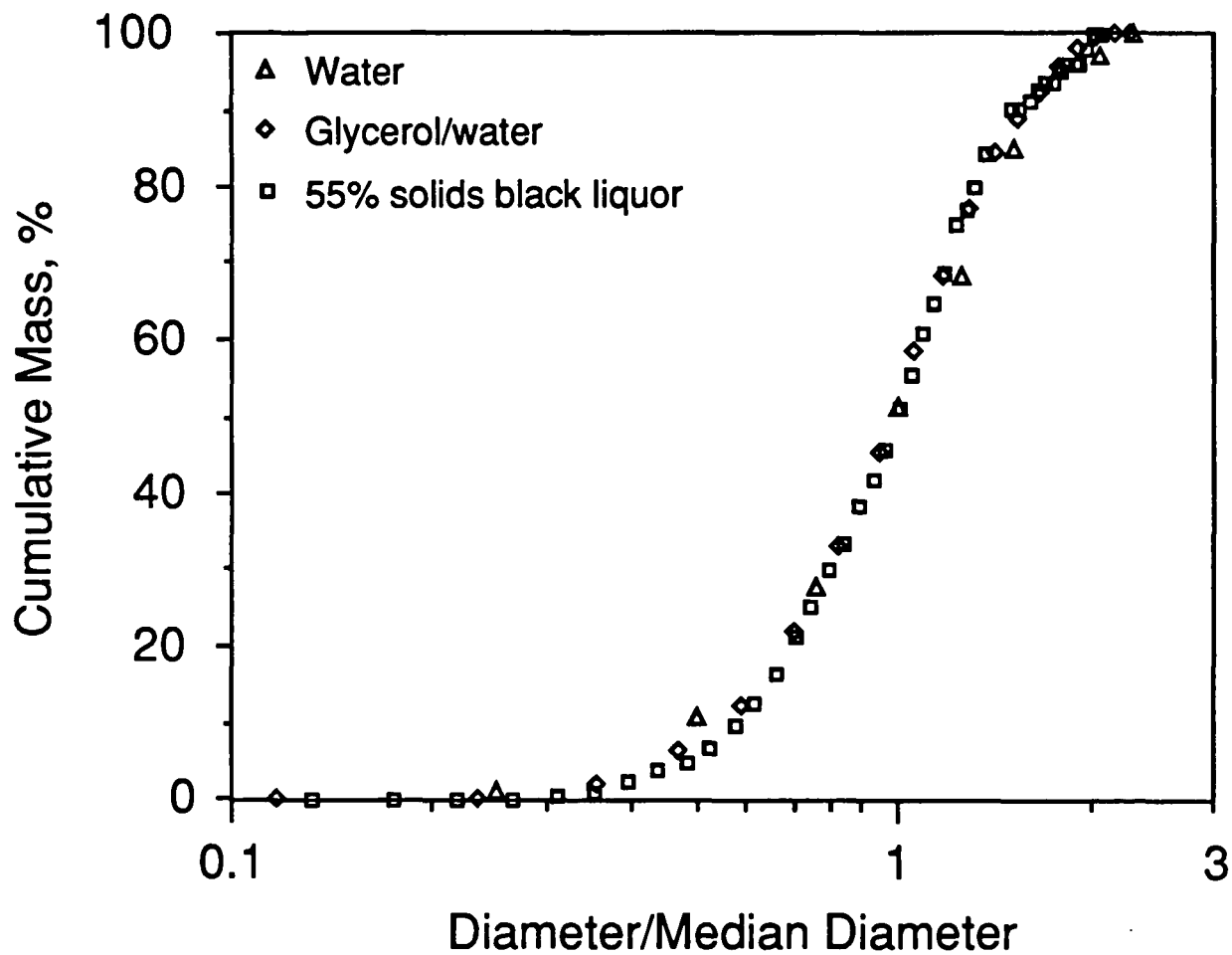


Figure 7 – Droplet size distribution data for a small grooved-core nozzle [3].



*Figure 8 – Droplet size distribution data normalized by dividing the actual diameter by the mass median diameter [15].*

cold or being fired at too low a pressure. Likewise, liquor that is too hot will flash ahead of the nozzle and produce intermittent spurts of flow. Neither of these conditions is safe and efficient. Experience with these two instabilities leads to operation in a fairly narrow range of liquor temperature and operating pressure.

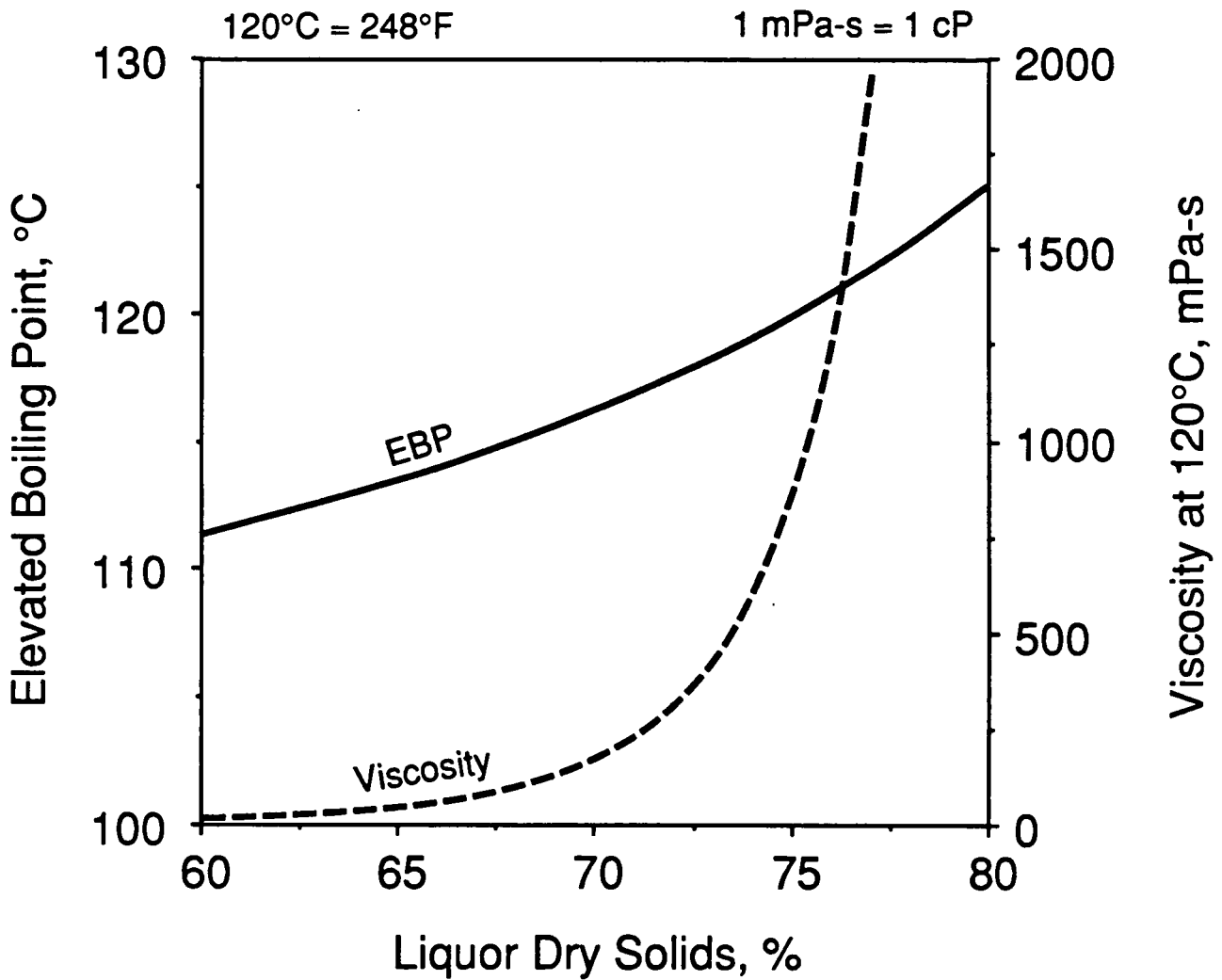
Observations of nozzle operation at The Institute of Paper Chemistry [2] under liquor conditions very similar to normal mill operation have identified nozzle stability as a key element of practical nozzle design. Little data are available for any nozzle on stability, but the physical situation of flashing is relatively easy to quantify.

Flashing of the liquor will occur whenever the black liquor is operated at a temperature above its elevated boiling point (EBP). What is important is the degree of flashing and its location. With mild superheat, the nozzle operating pressure suppresses flashing until the liquor exits from the minimum flow area. For the B&W splashplate and CE V- or U-type nozzle, this is at the nozzle exit. For the CE swirl cone the minimum flow area is inside the nozzle cap, so flashing will always occur within the nozzle. When liquor operating temperature is higher than the boiling temperature at operating pressure, then flashing will occur inside all black liquor nozzles and unstable flow will occur.

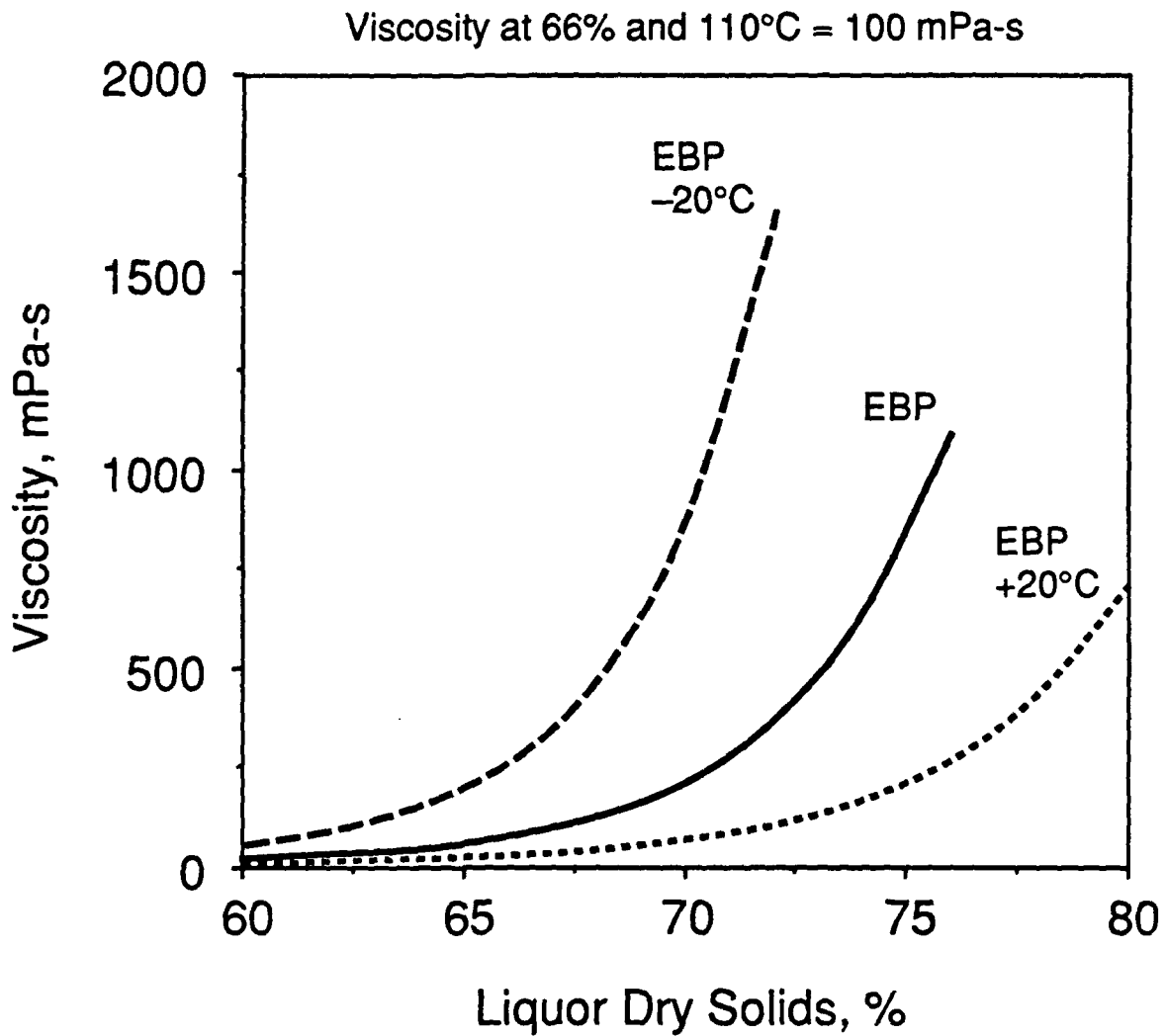
To entirely avoid flashing ahead of the nozzle, it is only necessary to use operating temperatures below the elevated boiling point of the liquor. With lower as-fired dry solids levels this was possible because temperatures below the elevated boiling point yielded acceptable liquor viscosities. With dry solids above 75% this will be more difficult because viscosity increases more quickly than boiling point when dry solids are increased. This is shown in Figure 9 for a typical black liquor. The viscosity curve is dramatically more sensitive to dry solids content than the elevated boiling point.

These same data can be cast in a slightly different form which clarifies the impact of high solids firing on flashing. In Figure 10 the liquor viscosity at the elevated boiling point and at temperatures above and below the elevated boiling point by fixed amounts is plotted as a function of solids. Remember that EBP is not a constant, so the curve of viscosity at the EBP corresponds to an increasing temperature with liquor solids.

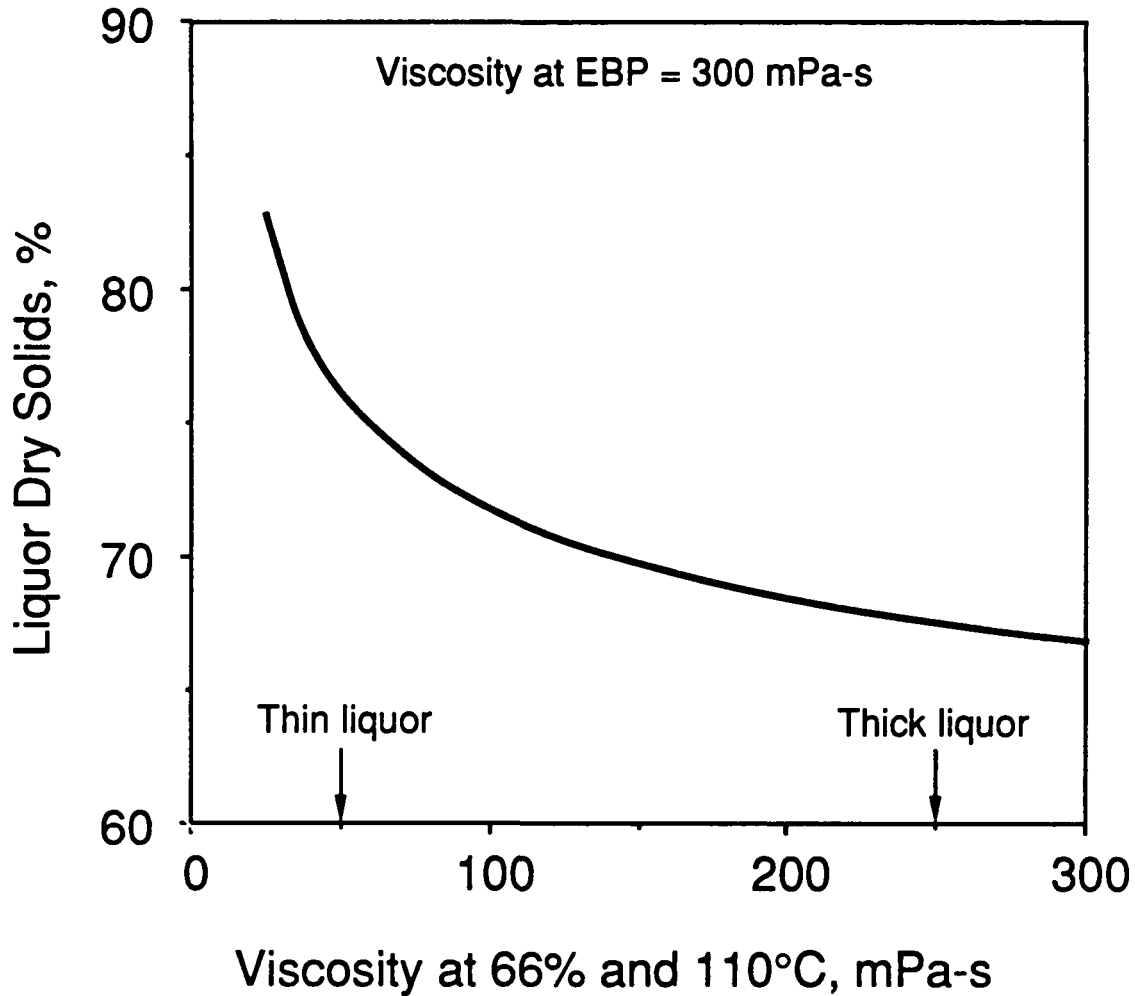
The range of viscosities known to produce acceptable black liquor sprays is from about 30 to 300 cP (30 to 300 mPa-s). This range may be extended as greater understanding of black liquor sprays is developed [1,2]. However, the problem of high solids firing with current limits on viscosity is clear. Black liquor with properties similar to those shown in Figure 9 could not be fired at temperatures below the EBP for dry solids greater than 72%. At 80% solids more than 36°F (20°C) of superheat would be required to keep the liquor viscosity below 300 cP (300 mPa-s). This specific conclusion is only true for one black liquor, the one used in the example. Other liquors will show the same general trend, but with curves shifted along the solids axis.



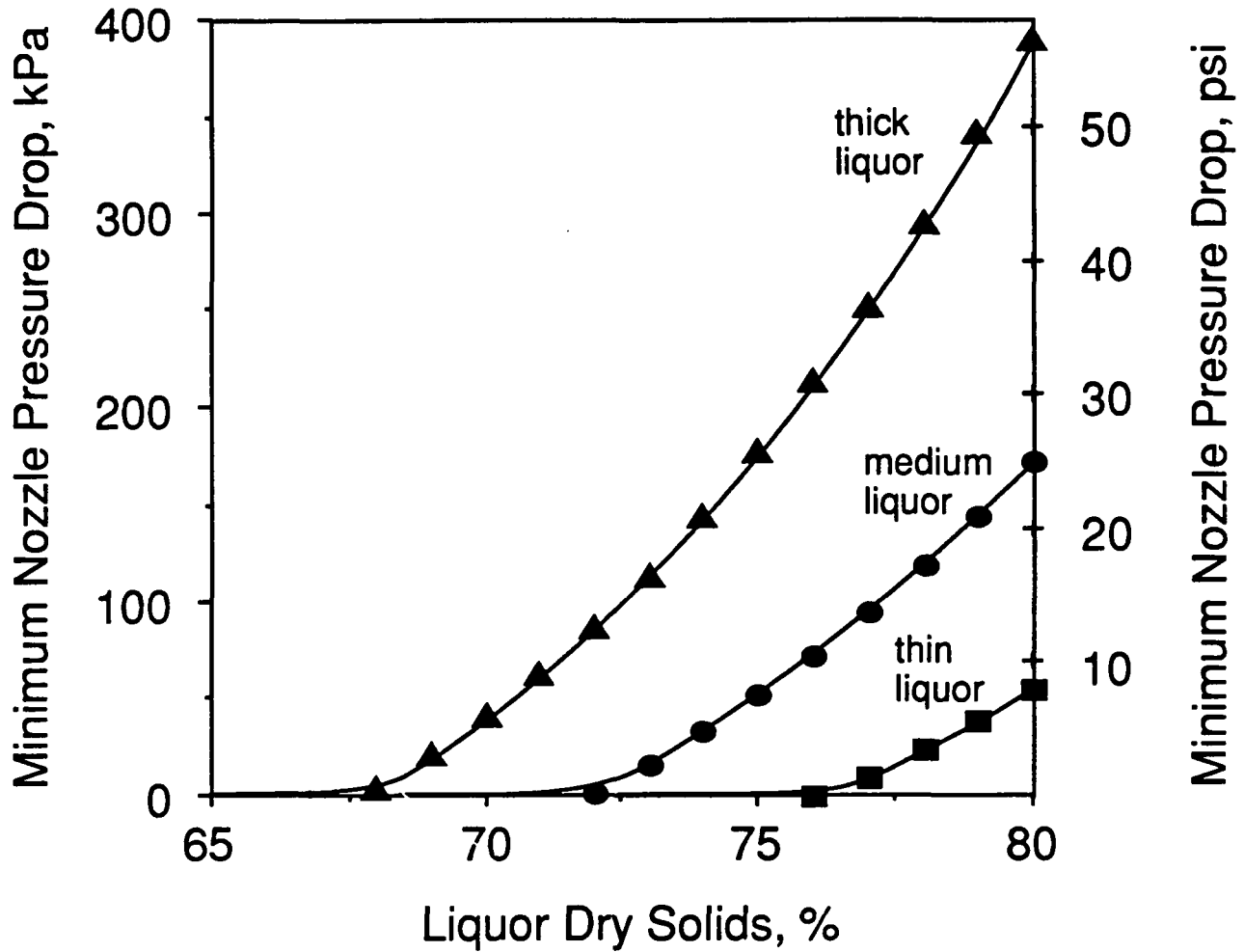
*Figure 9 – Viscosity and elevated boiling point (EBP) as a function of liquor dry solids content for one liquor which has a viscosity at 66% and 110° C of 100 mPa-s.*



*Figure 10 – Viscosity at the elevated boiling point and at temperatures above and below the EBP by 20° C as a function of liquor dry solids for one liquor which has a viscosity at 66% and 110° C of 100 mPa-s.*



*Figure 11 – Maximum liquor dry solids content which has a viscosity less than 300 mPa-s at the elevated boiling point (EBP) as a function of the viscosity at 66% solids and 110°C.*



*Figure 12 – Minimum nozzle pressure drop required to suppress flashing ahead of the nozzle for three liquors.*

*Viscosities at 66% solids and 110° C are: thick liquor = 250 mPa-s, medium liquor = 100 mPa-s, thin liquor = 50 mPa-s.*

A convenient way of characterizing liquor properties is to use a viscosity and elevated boiling point specified at some "standard" condition. The "standard" condition arbitrarily chosen here is 66% solids and 230°F (110°C). These conditions are fairly near actual firing conditions in many mills, but are low enough so it is still relatively easy to measure the two important properties. The liquor used above has an EBP at 66% solids of 237°F (114°C), and a viscosity at the "standard" conditions, 66% solids and 230°F, of 100 cP (100 mPa-s.) This is a fairly normal liquor. A thin liquor would have a viscosity of 50 cP (50 mPa-s) at these conditions, while a thick liquor would have a viscosity of 250 cP (250 mPa-s.)

The range of EBP at 66% dry solids is fairly narrow for kraft black liquor, from about 232°F to 243°F (111 to 117°C). However, viscosity at 66% solids and 230°F can vary more widely from liquor-to-liquor, mill-to-mill, and hour-to-hour. The range is at least from 10 to 250 cP (10 to 250 mPa-s).

Shown in Figure 11 is the dry solids content which yields a viscosity of 300 cP at the EBP plotted as a function of the viscosity as measured at "standard" conditions. For the thickest liquors (viscosity of 250 cP at 66% and 230°F) the viscosity at the EBP is greater than 300 cP even at current firing solids between 67% and 72%. Even for the fairly light liquors (viscosity of 50 cP at 66% and 230°F) operation above the EBP will be required at 80% solids to keep the viscosity below 300 cP.

Flashing ahead of the nozzle can be suppressed by the operating pressure of black liquor nozzles. Close attention to this fact, and knowledge of the flow/ $\Delta P$  characteristics of black liquor nozzles, will allow practical selection of nozzles for a particular boiler and liquor at all solids levels. It is the lower pressures which must be avoided in order to avoid flashing ahead of the nozzles. Shown in Figure 12 is a plot of the minimum nozzle pressure to suppress flashing ahead of the nozzle as a function of as-fired liquor dry solids for three liquors. Flashing is clearly not a problem for the light liquor (viscosity = 50 cP at 66% solids and 230°F). For the typical liquor with 100 cP at the same "standard" conditions, flashing is also not a problem below 72%, but minimum pressures of at least 25 psi (172 kPa) would be required to suppress flashing at 80% solids. This would require drastic changes in the usual operating pressures of CE swirl cone, V-type and U-type nozzles, but would be accommodated fairly easily by a B&W splashplate nozzle.

With the thickest liquor, flashing is always a problem. Pressures well beyond the normal range for black liquor service would be required to suppress flashing ahead of the nozzle.

Complications with flashing at high solids will manifest themselves in different ways. First, the nozzle stability will be reduced at the low pressure end of their operating range. This will complicate trials of high solids firing and subsequent optimization of recovery boiler operation. Second, increasing operating pressure means higher velocities. From Figure 3 above this means smaller droplet size, all other factors being equal. Current understanding of recovery boiler operation would indicate that this is the wrong direction to minimize carryover. Third, higher velocities, particularly much higher veloci-

ties for heavy liquors, mean significant changes in liquor droplet trajectory. This element by itself could easily confuse the apparent benefit of high solids firing. Very careful nozzle selection will be required for valid mill trials of high solids firing or other liquor system modification.

#### CONCLUSIONS

1. The flow and pressure drop characteristics for two nozzles, the splashplate and the U-type, have been measured. The flow coefficient correlations for these nozzles are consistent with the specific geometry of each. This allows reasonable speculation about the flow characteristics of the other two nozzles.
2. Within their typical range of operation, neither the splashplate nor the U-type (and V-type) nozzle is very sensitive to normal fluctuations in liquor property variations. This is apparently not the case for the swirl cone nozzle, and additional investigation of this type nozzle is needed.
3. Fluid sheet thickness is a key element in determining the ultimate droplet size of a spray. Sheet thickness has been measured for one black liquor nozzle, the splashplate. Correlations of sheet thickness are consistent with other data for this nozzle and allow assessment of the sensitivity of droplet size to changes in fluid properties and operating conditions. Increased liquor viscosity will be one impact of firing at higher liquor dry solids. Available data indicate that sheet thickness (and likely droplet size) will increase by less than a factor of two for a ten-fold increase in viscosity.
4. Nozzle stability is an important aspect of nozzle performance. Both roping and flashing are instabilities well known with black liquor nozzles. The impact of high liquor solids on one of these, flashing, has been estimated. Higher solids require higher operating pressure to suppress flashing ahead of the nozzle. This will be a significant problem for heavy liquors at higher dry solids firing conditions.

#### ACKNOWLEDGEMENT

The research on black liquor spray nozzles at the Institute of Paper Science and Technology is supported by a grant from the U. S. Department of Energy.

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PROJECT SUMMARY FORM

DATE: October 17, 1989

PROJECT NO. 3473-1: FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES

PROJECT LEADERS: H. L. Empie, K. M. Nichols, T. M. Grace

IPST GOAL:

Increase capacity of existing systems

OBJECTIVE:

A quantitative description of all key processes in the burning of alkaline process black liquor, encompassing reaction paths and rate equations for drying, pyrolysis, gaseous combustion, char oxidation, sulfide formation and fume formation. The overall goal is a comprehensive understanding of black liquor combustion and application of that knowledge to improve recovery boiler performance.

CURRENT FISCAL YEAR BUDGET: \$250,000

PRIOR RESULTS:

Data on the release of sulfur gases as a function of temperature, rate of heating, and the nature of the sulfur compounds present in the liquor. Sulfate and sulfite sulfur were found to be stable to volatilization during black liquor pyrolysis, while sulfide and thiosulfate sulfur were not.

The mechanism of deposition of fume particles on cooled surfaces was shown to be governed by thermophoresis, where rates are directly proportional to thermal gradients near the cool surface.

Data acquisition for single particle burning of black liquor was completed and development of a quantitative model characterizing the process continued. Comprehensive data analysis was pursued at both IPST and Abo Akademi in Finland under Dr. W. J. Frederick. The development of a non-intrusive method for measuring CO, CO<sub>2</sub>, and temperature during laboratory-scale black liquor char combustion was initiated. The method selected was FT-IR spectroscopy. Initial spectra were obtained.

A study of the production of fume during single-particle burning was initiated whereby fume particles will be caught on a moving filter tape to provide a time record of fume production during a particle burn.

An apparatus for studying the corrosion of mild steel in molten smelt under conditions where a frozen layer of smelt adheres to the metal surface was developed. Data acquisition was underway, with early emphasis being given to reproducibility issues.

An advanced version of the sulfate-sulfide cycle model for char burning was developed which incorporates a path for direct oxidation of carbon, helping to avoid the need to postulate extremely high burning temperatures when trying to predict char burning times.

SUMMARY OF RESULTS SINCE LAST REPORT:

Sulfur Release

Frank Harper's Ph.D. work on sulfur release during pyrolysis and burning of black liquor has been completed. A model has been developed that predicts the amount of sulfur volatilized from a black liquor drop during pyrolysis. This model accounts for the effects that important compositional and physical variables have on the release of sulfur during pyrolysis. Very little (<2%) sulfur was released during pyrolysis of liquors containing sodium sulfate or sodium sulfite. About forty per cent of the sulfur could be released from liquors containing sodium thiosulfate or sodium sulfide. Sulfur release was found to decrease with increasing temperature for pyrolysis temperatures above 490° C. Equations were developed to predict the amount of sulfur released from thiosulfate and sulfide as a function of pyrolysis time and temperature. The equations describe sulfur release using a modified first order decomposition model. The results of the study show that, although the amount of sulfur that can be released from either sodium thiosulfate or sodium sulfide is similar, the thiosulfate release rate is much lower.

The effects that changing a drop's physical parameters had on the transfer of heat to and through a pyrolyzing black liquor drop were determined. Drops of varying size, solids contents, and swelling characteristics were pyrolyzed and their external and internal temperatures were measured. These temperature measurements were used to develop a model predicting a black liquor drop's temperature. The model assumes that external heat transfer controls the rate of temperature increase and that the drop swells linearly with temperature between 250 and 500 degrees C.

The kinetic and heat transfer models were combined to produce a model that predicts the amount of sulfur that will be released from a pyrolyzing black liquor drop as a function of the drop's physical characteristics, its sulfur composition, and the heating environment to which it is exposed. Predictions from the model were compared with sulfur releases obtained from pyrolysis tests of actual black liquor drops. The model was also used to predict changes in sulfur release that would result from oxidizing the liquor, which converts the liquor's sulfide to thiosulfate. Because of thiosulfate's lower sulfur release rate, lower sulfur releases can be obtained by oxidation of kraft black liquor.

Fume Deposition

K. Georg's Ph.D. work on chemical fume is partly responsible for fire-side deposits formed on heat transfer surfaces in the recovery boiler. These deposits reduce the heat transfer coefficients, contribute to the plugging of gas passages, and require sootblowing for their removal.

Mechanisms responsible for fume deposition on kraft recovery furnaces have been studied. The main reason for determining the mechanisms is to understand the controlling parameters, thereby obtaining the ability to affect the deposition rate by changing these parameters. The following mechanisms were reviewed and examined as possible fume deposition mechanisms: molecular diffusion, Brownian motion, turbulent diffusion, particle impaction, thermophoresis, and vapor diffusion/crystallization.

Thermophoresis was found to be the main deposition mechanism for fume particles under the following experimental conditions:

1. Fume particle sizes from 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$  in diameter.
2. Flue gas temperatures from 250° C to 580° C.
3. Reynolds numbers less than 3 (based on cooled tube diameter).

A rate equation was derived for  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , and simultaneous  $\text{Na}_2\text{SO}_4/\text{NaCl}$  fume deposition. The results are directly applicable to fume deposition in the generating bank and the economizer section in recovery boilers, where flue gas temperatures range from 200° C to 700° C. The Reynolds number in a boiler bank is between 3000 and 5000; however, once the difference in flow rate between the experimental system and the recovery boiler is taken into account, the experimental results show close agreement with actual recovery boiler data. Water vapor in the system was found to affect the fume composition; fume composition was less  $\text{Na}_2\text{CO}_3$  and more  $\text{Na}_2\text{SO}_4$  when water vapor was present.

#### Single-Particle Burning

Kathy Kulas' Ph.D. work on single-particle burning behavior of black liquor has been completed. Models for each of the first three burning stages of a black liquor droplet have been developed. Sequentially, the output from the drying model is input to the volatiles burning model, and the output from the volatiles burning model is input to the char burning model. Each model was verified with data obtained from the convective single particle reactor (SPR).

Drying was modeled as an external heat transfer limited process. The drop temperature and mass were predicted by simultaneous mass and energy balances around the drop. The model was verified by comparing predicted and measured drop temperatures as a function of time. Low gas temperatures (550° C and 650° C) were used to exaggerate the drying time. The predicted drop temperature was within 10% of the measured drop temperature. Model predictions were approximately the same when either an assumed average surface area or the measured dynamic surface area were used in the heat transfer calculations.

Volatiles burning was also modeled as an external heat transfer limited process. A volatiles combustion flame was not observed surrounding single particles burning at typical furnace conditions (<10% O<sub>2</sub>) in the SPR. Combustion of volatiles near or in the surface pores was included in the model. Volatiles burning ends when the particle has swollen to its maximum size, and this diameter can be empirically predicted from the initial dry mass. As the break point between drying and volatiles burning is impossible to measure experimentally, the two models (drying and volatiles burning) were combined to predict the time to maximum volume. The rate of volatilization was accurately predicted by the model, fitting the data over the entire oxygen range tested (0% - 21%).

Char burning was modeled as limited by oxygen mass transfer to the char surface. The carbon consumption reactions considered were the carbon/sulfate, carbon/oxygen, and carbon/carbon dioxide reactions. The presence of the sulfate/sulfide cycle in char burning was established through tests with pure soda liquor and soda liquor loaded with sodium sulfate. The char burning model accurately predicted the time for char burn (from maximum volume to smelt coalescence) for both kraft and soda liquors.

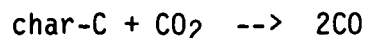
#### Char Gasification

Char is the residual solid product from black liquor pyrolysis. It is a black, porous, friable material which contains nearly all of the sodium and about one-half of the carbon from the as-fired black liquor. Char burning is concerned with the rates of carbon burnup, or in other words, the rate at which the carbon is removed (oxidized to CO and or CO<sub>2</sub>) from the char.

The primary species which serve as oxidizers for carbon removal are oxygen, carbon dioxide, and water in the gas phase, and sulfates such as sodium sulfate in the solid phase. The reactions of char-carbon with carbon dioxide and with water vapor are referred to as gasification reactions.

Very little data are available on the rates of these gasification reactions. Recent 3-D recovery furnace modeling at IPST has suggested that gasification reactions represent a significant portion of the overall carbon removal rate. There is a need for laboratory experiments to quantify the rates of these gasification reactions.

Stacy Lee (M.S. student) has constructed an experimental apparatus for determination of the rate of reaction of char carbon with CO<sub>2</sub>. Quantities of char were obtained by pyrolyzing black liquor using the larger DOE flow-reactor. In the gasification experiments, a known quantity of char is exposed to varying concentrations of CO<sub>2</sub> in N<sub>2</sub> (in the absence of other oxidizers such as O<sub>2</sub>, and H<sub>2</sub>O). The rate of the gasification reaction



can be determined from a knowledge of the temperatures involved, and the concentration of CO produced.

Initial demonstration tests were performed with the experimental apparatus. These tests showed that temperature could be controlled, and that time resolved CO and CO<sub>2</sub> concentration data could be obtained during the burning of a sample char.

The spectroscopic measurements of Pat Medvecz (Ph.D. student) are continuing. The goal of these measurements is to utilize FT-IR (Fourier Transform Infrared) spectroscopy to non-intrusively measure species concentrations and temperature in a lab-scale char burning environment. Very limited data exist on the gas composition just above the char-bed in a recovery furnace, or in a laboratory-scale black liquor combustion device. Obtaining such measurements is challenging because of secondary reactions. Any gas sample collected for CO/CO<sub>2</sub> analysis is subject to continued reactions which can change the levels significantly during the time between sample collection and sample analyses. This has prompted the development of the in-situ FR-IR measurement system.

Recent efforts have been directed towards both the obtaining of spectra from laboratory prepared gas mixtures at temperatures up to 1000° C, and towards the theoretical and numerical analysis of the absorption spectra of CO to determine temperatures. The procedures for temperature analysis from CO spectra which were reported by previous workers doing coal combustion experiments provided unsatisfactory results because of instrument distortion effects. Efforts have been made to understand the nature of the instrument distortion and to improve upon the temperature analysis of previous workers.

#### Fume Formation

The first step in obtaining a better understanding of fume formation during black liquor droplet combustion will be the determination of the time period during combustion when the fume is formed. A method is being developed by Chris Verrill (Ph.D. student) which coordinates timed observation of combustion with the resulting generated particulate. The morphological and chemical information obtained during this experimentation may suggest potential fume formation mechanisms.

A performance evaluation of the gas heater and droplet reactor (which were designed and constructed previously) was completed. Several trials of black liquor droplet combustion were conducted over the projected range of operating conditions (600-900° C, 2-6 ft/s). These preliminary experiments indicate that the video equipment is a satisfactory combustion monitor and that, with a sufficient vacuum source, glass fiber filters are effective at capturing fume.

The final items of experimental equipment (replacement quartz reactor tubes, filter media, flow meter, and miscellaneous hardware) have been

### Fume Formation and Deposition

Chris Verrill will continue his work on the quantification of fume formation during single-particle burning. Development of an in-situ method of monitoring fume concentration and size distribution will continue once a post-doctoral fellow is hired. An experimental method for measuring fume deposition rates at gas velocities representative of recovery boiler operation needs to be established.

#### Single-Particle Burning

Once the single-particle burning apparatus is reinstalled, rate data will be obtained for natural convection conditions where gas flow rates past the particle will be varied. Jim Frederick will complete the analysis of single droplet combustion data.

#### Char Burning

Once the char bed reactor is reinstalled, data on continuous char burning will be sought. Pat Medvecz will continue to develop a spectroscopic analysis technique for measuring concentrations of selected gases above the char bed in the DOE reactor. Stacy Lee will continue his measurements of char gasification rates.

#### Recovery Furnace Model

Computation time for the model must be significantly reduced if the model is to be used as an effective tool in the improvement of recovery boiler operation. Options to be explored include speed-up of the FLUENT/RFM code, model simplification, and adaptation of the model to a faster state-of-the-art computer. The model must also be validated if it is to be used by industry. To accomplish this, a velocity probe will be developed to measure flue gas velocities in the furnace cavity of an operating recovery boiler. Results will be compared with model predictions, and if significant discrepancies exist, revisions to the model will be considered. We anticipate hiring a new faculty member in the area

#### Student Research:

P. Miller, Ph.D.-1986; K. Goerg, M.S.-1986, Ph.D.-1989; K. Kulas, M.S.-1986, Ph.D.-1989; D. Sumnicht, M.S.-1986, Ph.D.-1989; G. Aiken, Ph.D.-1987; C. Verrill, M.S.-1987, Ph.D.-1990; M. Robinson, Ph.D.-1987; F. Harper, Ph.D.-1989; G. Kulas, Ph.D.-1989; G. Maule, M.S.-1988; P. Medvecz, Ph.D.-1990; T. Spielbauer, M.S.-1988, Ph.D.-1990; S. Lee, M.S.-1990; T. Kindler, M.S.-1990.

Executive summaries from recently completed Ph.D. theses are attached. Complete theses are available on loan from the IPST library.

ordered. The fume filter tape drive mechanism will be constructed once the gas heater and droplet reactor are reassembled and on-line at the new facility in Atlanta.

#### Corrosion

Greg Kulas completed his study of the corrosion of mild steel in molten smelt under conditions where a frozen smelt layer adheres to the metal surface. The corrosion rate was found to be a logarithmic function of time with the long term rate being less than 1 mil per year. When a small amount of polysulfide existed in the frozen smelt, the corrosion rate of carbon steel was accelerated over that for sulfide/sulfate/carbonate smelt, and the corrosion products changed from iron oxides to iron sulfide.

#### Recovery Furnace Model

Dan Sumnicht completed a computer model of a kraft char bed as part of a three-dimensional model of the recovery furnace. The char bed model calculates mass and energy exchange between the char bed surface and the gases in the furnace. The three-dimensional distribution of temperatures, gas velocities, and gas concentrations is used to calculate both local and global bed burning rates. The sulfate/sulfide cycle theory of char burning is used as a basis for calculating reduction efficiency.

The results of model calculations suggest that the bed influences gas flow patterns as well as playing an important role in overall char combustion. Most of the char combustion can occur on the bed surface, and C/CO<sub>2</sub> and C/H<sub>2</sub>O reactions make a significant contribution to bed burning. The reduction efficiency is not threatened by a large oxygen supply except around the periphery of the bed where cool, oxygen-rich air lowers the reduction efficiency. Three bed shapes - a high bed, a crater-shaped bed, and a low bed - resulted in different flow patterns in the lower furnace for each case. The high bed forced the secondary jets upward while the crater bed and low bed resulted in the development of gas recirculation patterns above the bed. The low bed case appeared to have the lowest carryover although solution convergence issues make this conclusion tentative.

#### Planned Activity Through Fiscal Year 1990:

With the move to Atlanta this past summer, significant time will be devoted to reinstalling equipment and making it operational. Many of the on-going studies of the past few years have been completed and PhD theses written. Nonetheless, many loose ends need to be tied up so that the ultimate goal of gaining a comprehensive understanding of black liquor combustion and applying that to improvement of recovery boiler performance can be realized.

1. Sulfur Release During the Pyrolysis of Kraft Black Liquor

(F. D. Harper)

Sulfur release during kraft black liquor combustion results in several significant recovery boiler problems. Much of this release occurs during the pyrolysis stage of burning, with the sulfur being released in the form of reduced sulfur compounds. Despite the importance of this phenomenon, much of the information available on sulfur release during black liquor pyrolysis is incomplete or contradictory.

A model has been developed to describe sulfur release from a black liquor drop undergoing pyrolysis. This model predicts the amount of sulfur volatilized as a function of the concentration of the various sulfur species contained in the black liquor, the drop's size, solids content, and swelling characteristics, and the heating environment to which the drop is exposed.

The model employs a modified first order decomposition rate to predict the amount of sulfur released by sodium thiosulfate and sodium sulfide. The maximum amount of sulfur that can be released at any temperature is controlled by an empirically derived factor that decreases with increasing temperature. About forty per cent of the sulfur contained in sodium thiosulfate can be volatilized during black liquor pyrolysis. The amount of sulfur that can be released from thiosulfate is a maximum at temperatures around four-hundred eighty degrees C. The sodium sulfide contained in the black liquor can also release up to forty per cent of its sulfur during pyrolysis. Sulfur release from sulfide begins to decline above temperatures of about four-hundred ninety degrees. Sodium sulfate and sodium sulfite are modeled as being non-volatile, as the amount of sulfur released from these compounds is small.

The results obtained in this study for the maximum amounts of sulfur that can be released from thiosulfate or sulfite are similar to the values reported by Douglas and Price<sup>1</sup> during pyrolysis of inorganic sulfur species with soda lignin. Douglas and Price found that thirty-seven to thirty-eight per cent of the sulfur contained in either sulfur compound volatilized during pyrolysis with soda lignin.

The model also calculates the temperature of a black liquor drop undergoing pyrolysis as a function of the liquor particle's physical characteristics and the heating environment to which the drop is exposed. This temperature is then used to predict the total amount of sulfur released from the drop. Any changes in black liquor characteristics that slow the heating rate, such as increasing drop size or solids content, or decreasing the amount of swelling that the drop undergoes during pyrolysis, result in increasing the amount of sulfur volatilized.

The following conclusions have been reached:

1. The amounts of sulfur that are volatilized from various sulfur species contained in kraft black liquor have been determined as functions

of time and temperature. Sodium sulfide can release up to forty per cent of its sulfur during pyrolysis. This maximum release can be obtained at temperatures of up to 490° C. At higher pyrolysis temperatures, the maximum sulfur release decreases with increasing temperature. Sodium thiosulfate also releases up to forty per cent of its sulfur during pyrolysis. This maximum release is possible at or below temperatures of 480° C; at higher temperatures the amount that can be released declines. The rate of release from thiosulfate is lower than the sulfide release rate. Sodium sulfate releases only small amounts (1% or less) of sulfur during pyrolysis. Sodium sulfite also releases only minor amounts (2%) of sulfur when undergoing pyrolysis. Organic sulfur is volatile under pyrolysis conditions. However, because of the small amounts of organic sulfur contained in the test sample and the wide variation in the test results, no conclusions about the amount of sulfur that can be released from organic sulfur can be drawn.

2. Increasing drop size increases the amount of sulfur that is volatilized from a pyrolyzing black liquor drop. Increasing the liquor's solids content results in an increase in the amount of sulfur released by the drop. Decreasing the liquor's swelling by addition of a swelling retardant increases the amount of sulfur released from a drop during pyrolysis. The amount of increase that is observed will depend on the liquor's sulfur composition and the environment in which it is pyrolyzed.

3. A model describing sulfur release from a pyrolyzing black liquor drop has been developed. This model uses external heat transfer to determine the drop temperature. The drop temperature is then used in kinetic models that calculate sulfur release from thiosulfate and sulfide.

4. The model developed indicates that the sulfur release rate is at a maximum when the liquor temperature is in the 350 - 550° C range. Therefore, any change in recovery boiler operation that minimizes the length of time liquor particles are at these temperatures will reduce the amount of sulfur volatilized. Changes that could result in lower sulfur release include increasing lower furnace temperature and adjusting spray distribution so that the liquor pyrolyzes in the hottest section of the furnace. Oxidation of the black liquor may also reduce the amount of sulfur volatilized during pyrolysis, if the liquor is rapidly heated to temperatures above those where sulfur release occurs.

#### Implications For Recovery Boiler Operation:

The results of the present work show that similar amounts of sulfur can be released from either sodium sulfide or sodium thiosulfate during pyrolysis of kraft black liquor. However, the rate of release from sulfide is much greater than that of thiosulfate. Therefore, a black liquor drop whose sulfur content is chiefly thiosulfate, as a result of black liquor oxidation, may release less sulfur during pyrolysis than will a similar drop whose sulfur content is mainly in the form of sulfide, especially if the drop is rapidly heated through the temperatures at which sulfur volatilization is at a maximum. Tests of the

overall drop model on black liquor drops having similar size, solids, and swelling characteristics, but whose sulfur content is composed entirely of single sulfur compound (thiosulfate or sulfide) have given significantly different results. About 20% less sulfur is released from a drop whose sulfur is present as thiosulfate than from a similar drop whose sulfur is present as sulfide. This reduced sulfur release could result in additional benefits for the boiler, as the amount of fuming required to react with the sulfur will decrease. A decrease in generated fume will reduce the particulate loading in the gas passages of the boiler's convective heat transfer section.

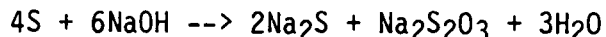
It should be emphasized, however, that the benefit of reduced sulfur release can only be realized if the oxidized liquor is heated rapidly so as to spend a minimum amount of time at temperatures where sulfur release is at a maximum.

Black liquor oxidation affects other liquor properties in addition to converting the sulfide to thiosulfate. Perhaps the most important of these changes in liquor properties is in an increase in liquor viscosity due to the lowering of the liquor's alkali level. Changing the liquor's viscosity may result in an altered drop-size distribution when the liquor is fired inside the boiler. Changing the distribution of drop sizes produced during spraying will affect the amount of sulfur that is released during pyrolysis or burning. The impact on drop-size distribution due to viscosity changes could, however, be offset by an appropriate change in the liquor's temperature.

Black liquor oxidation also lowers the liquor's fuel value and offers the possibility of increased liquor solids throughput at the same steaming rate. One such patent proposes this concept<sup>2</sup>. In this process, part of the black liquor generated by the pulping operation is oxidized to an extent that its heating value is substantially reduced. This oxidized liquor is then mixed with the remaining, unoxidized, liquor to form a black liquor with a lower fuel value, allowing an increase in boiler firing capacity.

Many mills use elemental sulfur as a makeup chemical to replace sulfur lost by the liquor during the pulping and recovery cycle. This sulfur, usually in the form of a high-solids emulsion, is added to the black liquor just prior to firing it into the recovery furnace. This method of adding sulfur to the liquor, rather than the traditional one of adding saltcake (sodium sulfate), results in several advantages, including easier handling and mixing of makeup chemical, an increased furnace efficiency (the elemental sulfur does not have to be reduced), lower lime usage, and lower sulfur release because of a hotter furnace temperature and an increased generation of fume. The lower sulfur release results in less plugging of the boiler's air passages, as the generation of sulfur-containing sticky deposits is lowered. It has also been claimed by Nelson<sup>3</sup> that adding elemental sulfur to the black liquor increases the amount of sulfur released during burning. This sulfur, in the form of SO<sub>2</sub>, is said to result in increased corrosion and fouling as the sulfur dioxide is absorbed by ash deposits on the convective heat transfer surfaces.

In addition to the possibility of being burned to SO<sub>2</sub> in the recovery furnace, elemental sulfur can react with the sodium hydroxide contained in black liquor<sup>4</sup> to form sodium sulfide and sodium thiosulfate according to the reaction:



Both of these products can release large amounts of sulfur during black liquor pyrolysis. Sodium sulfate, on the other hand, is essentially stable with respect to sulfur release during pyrolysis. Although the burning temperature of the liquor should increase with use of elemental sulfur as a makeup chemical, due to its fuel value and the fact that it does not need to undergo an endothermic reduction reaction, this increase in combustion temperature is likely to be small. Thus, it seems probable that the addition of elemental sulfur to kraft black liquor as a makeup chemical, instead of saltcake, will result in increased sulfur volatilizations during black liquor combustion.

#### Recommendations:

Additional research is recommended in two areas: determining the causes of the increase in sulfur release due to increasing size and solids content; and extension of the study of compositional variables to burning drops.

The present study has shown that heat transfer effects, by themselves, do not account completely for the increase in sulfur release observed when particle size or solids content is increased. It is suspected that this increase may be the result of reaction of sulfur species contained in the outer portions of the drop with pyrolysis products being released from the particle's inner regions. Quantifying the production of other pyrolysis products, especially CO<sub>2</sub> and H<sub>2</sub>O, which have been suggested as reactants in sulfur release reactions, would aid in determining the reasons for the enhanced sulfur release seen when particle size or solids content is increased.

Sulfur release during pyrolysis is greatly affected by the compounds in which the sulfur is present and the physical characteristics of the drop, such as size and solids content. However, pyrolysis is only one of the stages of burning that a black liquor drop goes through during combustion in a recovery boiler. Study of the effect of the compositional and physical variables during burning in oxygen containing atmospheres will provide additional insight into the release of sulfur in recovery boilers.

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2. A Study of Fume Particle Deposition (K. A. Goerg)

One of the products of kraft black liquor combustion is fume. Fume consists of 0.25 m to 1 m diameter particles mainly composed of Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaCl and potassium salts. Chemical fume formation is of interest because the fume is partly responsible for fireside deposits formed on heat transfer surfaces in the recovery boiler. These deposits reduce the heat transfer coefficients, contribute to the plugging of gas passages, and require sootblowing for their removal.

Mechanisms responsible for fume deposition on kraft recovery furnaces were studied. The main reason for determining the mechanisms is to understand the controlling parameters, thereby obtaining the ability to affect the deposition rate by changing these parameters. The following mechanisms were reviewed and examined as possible fume deposition mechanisms: molecular diffusion, Brownian motion, turbulent diffusion, particle impaction, thermophoresis, and vapor diffusion/crystallization. Thermophoresis is the result of gas molecules impinging on a surface from opposite sides with different mean velocities. The molecular bombardment of particles on a surface is more energetic on the hot side than on the cold side, which causes the particles to migrate toward the cooled regions. This will cause particles to be deposited on surfaces that are colder than the gas phase. The controlling parameters are flue gas temperature, tube surface temperature, particle composition and size, particle concentration, and (to some extent) gas flow rate.

The following equation was derived:

$$\text{Dep. rate (g/min/cm}^2\text{)} = 0.047 \alpha_T d_p C \frac{T_e - T_w}{T_w}$$

where:

$\alpha_T$  = thermal diffusion factor, dimensionless

$d_p$  = particle diameter,

$C$  = fume concentration in flue gas, g/l

$T_e$  = bulk flue gas temperature, absolute

$T_w$  = tube surface temperature, absolute

This equation applies the Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl, and simultaneous Na<sub>2</sub>SO<sub>4</sub>/NaCl fume deposition and is similar in form to thermophoretic

equations derived by other authors.

For fume deposition under the following experimental conditions:

1. Fume particle sizes from 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$  in diameter.
2. Flue gas temperatures from 250° C to 580° C.
3. Reynolds numbers less than 3 (based on cooled tube diameter).

the following equations were derived:

$$\text{Na}_2\text{CO}_3 \text{ dep. rate (g/min/cm}^2 = 0.00440 \text{ C } \frac{\Delta T}{T_w}$$

$$\text{Na}_2\text{SO}_4 \text{ dep. rate (g/min/cm}^2) = 0.00419 \text{ C } \frac{\Delta T}{T_w}$$

$$\text{NaCl dep. rate (g/min/cm}^2 = 0.0146 \text{ C } \frac{\Delta T}{T_w}$$

$$\text{Na}_2\text{SO}_4/\text{NaCl dep. rate (g/min/cm}^2 = 0.00279 \text{ C } \frac{\Delta T}{T_w}$$

where:

C[=] g/l

T[=] °K

It was also found that, during simultaneous Na<sub>2</sub>SO<sub>4</sub>/NaCl generation, the generation of Na<sub>2</sub>SO<sub>4</sub> and the generation of NaCl were additive and independent. The simultaneous deposition of the two compounds, however, were not independent of each other.

Other important results are:

1. Gas flow rate has little effect on the deposition rate.
2. The fume deposition rate is the same on the upstream and downstream side of the cooled cylinder.
3. No fume deposition occurs when no temperature gradient is present.
4. The accumulation of collected fume does not influence the deposition rate.

The results are directly applicable to fume deposition in the generating bank and the economizer section in recovery boilers, where flue gas temperatures range from 200° C to 700° C. The Reynolds number in a boiler bank is between 3000 and 5000; however, once the difference in flow rate between the experimental system and the recovery boiler is taken into account, the experimental results show close agreement with actual recovery boiler data.

Water vapor in the system was found to affect the fume composition; fume composition was less  $\text{Na}_2\text{CO}_3$  and more  $\text{Na}_2\text{SO}_4$  when water vapor was present.

Two future research possibilities arise as a result of this study. First, determine, in greater detail, the reactions of water vapor and fume. This is important because the composition of the fume has an effect on the deposition rate.

Second, repeat the experiments at a Reynolds number closer to that found in a recovery boiler (approximately 5000). This will experimentally determine the effects of boundary layer regimes. Changes would have to be made to the apparatus, because the present construction of this apparatus limits the gas flow rates. Changes may be difficult to accomplish. Adding fans above the melt but below the cooled tube would increase the gas flow rate but would drastically decrease the fume concentration; increasing the gas flow through the melt would result in much bubbling and splashing from the smelt.

### 3. Overall Model of the Combustion of a Single Droplet of Kraft Black Liquor (K. A. Kulas)

Kraft black liquor burns through four distinct stages - drying, volatiles burning, char burning, and inorganic reactions. Three models, one for each of the first three burning stages, have been developed to run sequentially. Two of the models, drying and volatiles burning, combine mass and energy balances around the drop to predict the mass and temperature of the particle at any time during the stage, and to predict the completion time of the stage. The third model, char burning, predicts the completion time from the kinetics of the competing carbon burnup reactions and the rate of oxygen mass transfer to the char surface.

Each model was verified with data obtained from the convective single particle reactor (SPR). Two types of single particle reactors were used for these studies - suspended and flowing. Individual drops are held stationary throughout combustion on wires in the suspended type reactors. Drops are sprayed into the flowing reactors, and burn while passing from one end of the reactor to the other. The advantage of studying captive single particles, as opposed to moving particles, is that changes in particle mass, temperature, and size can be observed

throughout combustion for the same particle. The observations (drop mass, temperature, and size) can then be correlated.

The model was tested with three liquors, kraft, soda, and soda loaded with sulfate. The soda liquor tested was a lab cook concentrated to 59.2% solids for the pure soda, and 61.2% solids for the loaded soda. The drops were dried and pyrolyzed at 800° C in the SPR under nitrogen prior to char burning. The gas was switched to air when pyrolysis was complete. The kraft liquor studied was a mill liquor from Weyerhaeuser Paper Co. concentrated to 68% solids. Combustion conditions in the SPR were 2% - 8% oxygen in the gas stream and 800° C - 910° C gas temperature. The conclusions are as follows.

1. The model of the drying stage of single particle combustion is based on external heat transfer and predicts the drop moisture and temperature as functions of time. The predicted temperature was within 10% of the measured temperature for drops drying in air at temperatures between 550° C and 650° C, in a non-convective environment. The low temperatures were used to slow down drying, and are not indicative of actual boiler temperatures. The predicted drying time was compared with measured times for small drops (.7 - 1.1 mm initial diameter) drying in air at 800° C, in a non-convective environment. A regression between the predicted and measured times had an  $r^2$  of 0.9.

2. Volatiles burning was also modeled as an external heat transfer limited process. The particle mass, temperature, and diameter are predicted as functions of time. An empirical correlation was developed to predict the maximum swollen diameter as a function of the initial drop mass. Gas conditions, temperature (800° C - 910° C) and oxygen concentration (2% - 8%), did not influence the maximum swollen diameter. Volatilization was assumed to be complete when the particle reached its maximum swollen diameter. Volatiles burning in most of the furnace is without a distinctive flame sheet surrounding the particle, based on observations of flame characteristics in the SPR.

The predicted rate of volatilization and the time to maximum volume were compared to the measured rate and time for particles combusted under a wide range of conditions. The gas temperature range was 666° C to 910° C, the gas oxygen concentration was 0% to 21% with the balance nitrogen, and the initial size was 4 mg to 60 mg.

The regression between the predicted and measured rate of volatilization had an  $r^2$  of 0.72. The test to determine if there is significant lack of fit in the model yielded the result that there was no significant lack of fit and the low  $r^2$  was due to experimental error. The time to maximum volume is a combination of the drying time and the volatiles burning time. The measured time is the time it takes the drop to swell to its maximum volume. The regression between the predicted and observed time had an  $r^2$  of 0.82. Again there was no significant lack of fit between the model and the data.

3. The model of the char burning stage predicts the mass, reduction ratio, and the mass of CO and CO<sub>2</sub> in the boundary layer around the particle. The time for burning pure soda liquor was accurately predicted by the model without the sulfate/sulfide cycle. Sulfur was shown, through tests with pure soda liquor and soda loaded with sulfate, to influence the char burn time in single particles. The sulfate/sulfide cycle applies to single particle char burning. The model accurately predicted the char burn time for kraft liquor (gas temperature 800° C - 910° C, oxygen concentration 2% -8% in nitrogen). The oxygen concentration had a large influence on the char burn time. The influence of initial char mass and gas temperature decreased as the oxygen concentration increased from 2% to 8%.

The reduction ratio was predicted to be zero throughout char burning, even with the sulfide oxidation kinetics included in the model. The reason is the high surface area to mass ratio in the highly swollen char particles and slow carbon/sulfate kinetics. Previous work used pellets with a low surface area to mass ratio and the reduction ratio was predicted to be high throughout most of char burning.<sup>8</sup> When those conditions used were put into the char burn model, similar predictions for the mass and reduction ratio resulted.

4. A two-color pyrometer was constructed and accurately measured the surface temperature of a combusting particle to within 10°C at 500°C. The pyrometer was used to measure the surface temperature of the char particle during char burning.

The three models developed in this work are an improvement over previous models in the literature because they are more fundamental. However, each of the three models contain empiricism due to a lack of information in several areas which were beyond the scope of the project.

Particle swelling in less than 10% oxygen with the balance nitrogen has not been investigated in any detail. The swelling during drying was assumed constant in the present model, the value of the diameter increase relative to the initial diameter was a parameter used to fit the model to data. A prediction for the average amount of swelling during drying is needed to relate the swelling factor used in the model to the furnace conditions.

The swelling during volatiles burning was predicted from an empirical equation relating the maximum diameter to the initial mass of solids. This was a liquor specific relation, and only one data set was available for the correlation. The diameter increase with time was assumed to be a function of the fraction of total volatiles to evolve. A better understanding of the chemical and physical factors which drive swelling in less than 10% oxygen, and the dynamic diameter during volatiles burning is needed for a less empirical representation of the swelling process in the volatiles burning model. It is

apparent from this work that the maximum diameter can be predicted from the initial test conditions. Swelling at low oxygen concentrations does not appear to be as random an event as swelling in nitrogen. This could be due to volatiles combustion, which reduces swelling.

The kinetic mechanism for volatiles evolution is not quantified for volatiles evolution from single particles in low concentrations of oxygen. This was an area of major simplification in the present volatiles burning model. The kinetic expression used in the model treated all the volatile evolution reactions as one Arrhenius type reaction with overall kinetic constants. The constants were obtained from pyrolysis tests in the SPR.

During volatiles burning the black liquor particle was assumed to be isothermal. A temperature gradient should be included inside the particle during this stage. Volatiles evolution is an endothermic process causing the particle to act as a heat sink. The center of the particle is therefore cooler than the surface, creating a temperature gradient across the particle. The experimental techniques now available are not able to track the front of volatilization through the particle, or even to estimate the thermal conductivity, density, porosity, or heat capacity as functions of time.

The char burning model contains two major simplifications. The first is the char temperature profile in time, and the second is the relative rates of CO and CO<sub>2</sub> production from the C/SO<sub>4</sub> reactions,  $f_{CS}$ , and from the C/O<sub>2</sub> reaction,  $f_{OX}$ . The char temperature can be measured experimentally with an optical pyrometer. However, this does not make the model useful in practical situations where the char surface temperature is not known. The equation used to predict the maximum temperature for kraft char burning as a function of gas temperature and concentration is an empirical correlation obtained from char bed studies. The solution to the temperature question is to incorporate an energy balance into the char burn model.

Relative rates of CO and CO<sub>2</sub> production are difficult to measure with the experimental techniques now available. Off gas analysis of the reaction products also include gas phase oxidation of CO and CO<sub>2</sub>. Ongoing research in FTIR analysis of the gases immediately above the char bed at IPST will hopefully be able to measure relative rate values as functions of combustion gas composition.

The carbon/sulfate reaction needs to be studied in a system which allows a high loading of kraft char in the smelt pool.

Three models need to be integrated into one overall model which can then be inserted into a recovery boiler simulation. Each individual model accurately describes its respective stage of black liquor combustion. The disadvantage of three separate models lies in manually feeding the results of one model into the next model.

4. Char Gasification/Burning (P. J. Medvecz, S. R. Lee)

The goal of this study is to contribute to the quantitative understanding of the char burning process. Although char burning is only part of the complex process of black liquor combustion, knowledge of char burning is valuable in itself. Such knowledge provides a basis for informed decisions on how to meet recovery boiler operating objectives such as improved reduction, optimum fume production, bed control and blackout prevention. The greatest potential benefit would be the ability to achieve enhanced burning rates of liquor, which would result in capacity improvement.

In-Situ Co/CO<sub>2</sub>/Temp Measurements using FT-IR (P. J. Medvecz)

Since the previous PAC report, work has continued on the determination of gas temperatures from carbon monoxide infrared absorption spectra. The spectra are recorded at high temperatures, 250-1000° C, using Fourier Transform Infrared Absorption Spectroscopy (FT-IR). This work is just one part of a three part thesis which consists of the following: the determination of gas temperatures from high temperature pure carbon monoxide infrared absorption spectra, the determination of concentrations of carbon monoxide and carbon dioxide from their high temperature pure gas absorption spectra, and finally the quantification of carbon monoxide and carbon dioxide concentrations and the determination of temperatures in the gas phase above a burning black liquor char bed. The ultimate objective of the project is to develop a spectroscopic technique which can be used for gas analysis of char burning experiments in the DOE supported char combustion reactor.

Significant progress has been made since March of 1989 in developing techniques which will aid in determining temperatures from infrared absorption spectra of carbon monoxide. In March, it was first realized that the application of mathematical techniques developed by previous workers in the field would be inadequate to making reliable temperature measurements. It was further identified that more rigorous efforts in temperature determinations would involve a thorough understanding of the absorption characteristics of carbon monoxide at high temperatures coupled with a mathematical knowledge of the distortions a FT-IR instrument imparts upon spectra as a result of its limited resolution. A more complete knowledge of each of these events has been developed and incorporated into a Turbo Pascal program.

This program is capable of determining the temperature of a carbon monoxide gas sample from its FT-IR absorption spectrum. It accomplishes this objective by the following: first, a temperature for the gas sample is guessed and the experimental absorption peak heights are corrected for instrument distortions, second, gas temperature calculations are performed using these corrected peak heights

based upon a knowledge of fundamental infrared absorption theory of diatomic gases, third, the calculated temperature is used as the next guessed temperature and an iterative procedure begins, finally, the iterative procedure is stopped when the calculated temperature and the guessed temperature are nearly identical.

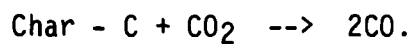
The application of this program to carbon monoxide absorption spectra has yielded good results, particularly of low temperature spectra, 25-500° C. Application of the program to higher temperature spectra has been partly hampered by our present inability to obtain high quality, high temperature absorption spectra in the 800-1000° C temperature range. Upcoming modifications in the existing FT-IR equipment, however, should circumvent most of the present difficulties.

In order to verify the temperature measurements calculated from absorption spectra, a second, simultaneous, means of temperature determination must be made while the absorption spectra are being recorded. In the months ahead efforts will be directed towards accomplishing this objective which will most probably result in the use shielded thermocouples or by making radiation corrections for convention thermocouples.

#### Char Gasification Rate Measurement (S. R. Lee)

The kinetics of the gasification reaction of kraft char-carbon with carbon dioxide are being determined. The effects of temperature, carbon dioxide, carbon monoxide, char particle size, and reactant mixing are being investigated in order to develop a reliable rate equation.

The most specific objective of this study is to understand how the rate of char burning is related to the concentration of carbon dioxide. The reaction of char-carbon with carbon dioxide is as follows:



This reaction leads to the gasification of black liquor char. The kinetic results from this study can be related to other gasification results and to the direct oxidation of kraft char with oxygen. Through such relationships, a global rate of reaction for black liquor can be obtained. The gasification reaction may be rate limiting steps in char burning. Through determination of these reaction rates, the throughput of a recovery furnace may be influenced.

The experimental system used to study the kraft char gasification with carbon dioxide has been designed and constructed, and initial performance testing completed. The system is shown in Figure 1. The system consists of gas cylinders, mass flow meters, a temperature controlled furnace, CO and CO<sub>2</sub> IR analyzers and a computer data acquisition system. Initial performance tests showed that temperature

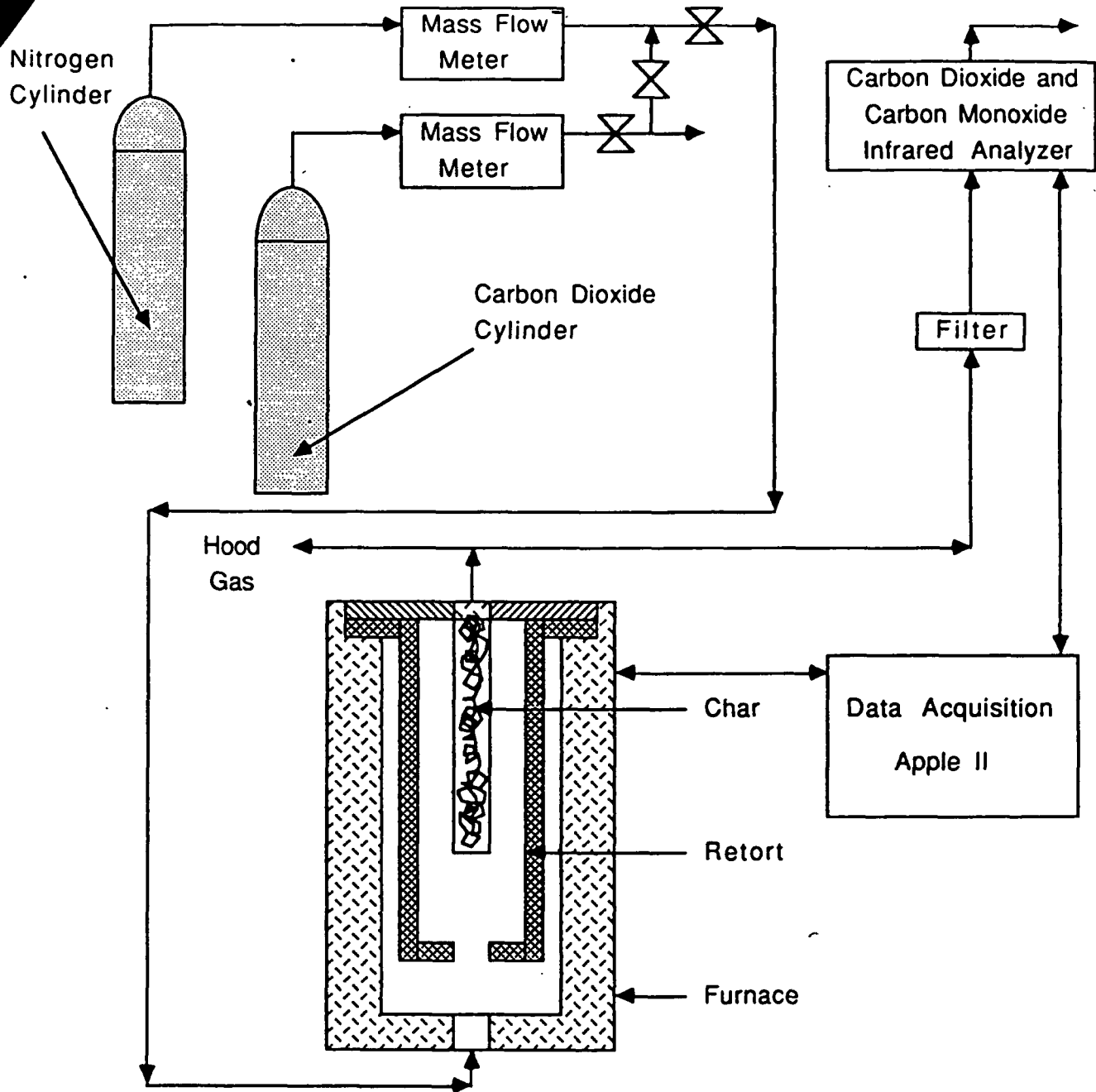


Figure 1

Experimental System

could be controlled, and that time resolved CO and CO<sub>2</sub> concentration data could be obtained during the burning of the sample char. At the conclusion of the performance testing, the reactor and equipment was disassembled and shipped from Appleton to Atlanta.

Throughout this study, the char burning stage of black liquor combustion will be examined. Data from studies with other forms of char, such as coal char-carbon, suggest rates for the respective systems. However, no substantial data has been collected to lead to a significant rate for a kraft char.

#### 6. Investigation of Factors Affecting Corrosion of Carbon Steel

##### Boiler Tube Material Exposed to Simulated Kraft Smelt (G. Kulas)

The lower portions of waterwall tubes in kraft recovery boilers are covered with a layer of frozen smelt composed primarily of sodium sulfide, sodium sulfate, and sodium carbonate. The effect of this smelt on the corrosion of the tubes has not been investigated. The objective of this work was to investigate the corrosion of carbon steel boiler tube material exposed to frozen smelt under heat transfer conditions, when the metal temperature is 600-700° F. This is the temperature regime in which accelerated corrosion is reported to occur in recovery boilers. Iron sulfide corrosion products are associated with accelerated waterwall corrosion in kraft recovery boilers. For a frozen smelt composition resulting in the generation of iron sulfide corrosion products, the mechanism of the corrosion process was investigated to determine whether the limiting step in the corrosion process is transport of the corrosive species through the frozen smelt layer, transport of either metal or the oxidant through the corrosion product layer, or the reaction kinetics. Additional objectives included developing corrosion rate expression, based on the rate limiting process in the corrosion mechanism and relating the results of this work to the problem of kraft recovery furnace waterwall corrosion.

The conclusions of this work are:

1. An experimental apparatus was consisting of an air-cooled probe was developed for studying the corrosion which occurs beneath a layer of frozen smelt under heat transfer conditions.
2. Frozen smelt containing sulfide, sulfate, and carbonate does not result in significant corrosion of carbon steel in the temperature range of 600-700° F. The corrosion rate is a logarithmic function of time with the long term corrosion rate being less than 1 mpy. The corrosion products are iron oxides.
3. Thiosulfate, elemental sulfur, and polysulfide are not stable in

molten smelt containing carbonate. However, an equilibrium polysulfide content can be established in the molten smelt by bubbling CO<sub>2</sub> through the melt. When a small amount of polysulfide (0.5-1.0%) exists in the frozen smelt, the corrosion of carbon steel is accelerated over that observed for sulfide/sulfate/carbonate smelt. The corrosion products are observed to be crystalline iron sulfide (FeS).

4. The corrosion occurring with a smelt containing polysulfide is due to transport of the polysulfide sulfur through the frozen smelt to the metal surface. The frozen smelt is only in direct contact with 15-20% of the metal surface. Over the remaining area, a gap exists between the metal and the smelt. In these areas of direct contact, the polysulfide is reduced to sulfide. This results in oxidation of iron. In the regions of smelt/metal contact, the oxidized iron ions dissolve in the frozen smelt layer. In the regions where there is a gap between the iron and the smelt, an iron sulfide forms. Apparently, sulfide ions are capable of migrating over the metal surface from the zones of smelt metal contact to the regions where the iron sulfide is formed. There is a very small sulfur vapor pressure associated with frozen smelt of this composition at this temperature, and this has no effect on the corrosion of carbon steel.

5. The corrosion rate occurring with smelt containing 0.5-1.0% polysulfide, with a metal temperature of 650° F, can be described by the equation:

$$\text{corr} = C_0(1 - \exp(-k_1*t)) + k_2 * C_0 * t$$

where C<sub>0</sub> is the bulk smelt polysulfide content

k<sub>1</sub> is the kinetic reaction rate constant

k<sub>2</sub> is the mass transfer coefficient for polysulfide transport through the frozen smelt layer

The first term accounts for the initial high rate of corrosion due to the high polysulfide content at the metal/smelt interface, and the second term describes the diffusion of polysulfide through the frozen smelt. The first term rapidly goes to zero, so the corrosion becomes a linear function of time, depending on the transfer of polysulfide sulfur to the smelt/metal interface. The linear portion of this curve corresponds to a corrosion rate of 6.6 mpy. This equation indicates that the corrosion rate is directly proportional to the bulk polysulfide content of the smelt.

#### 7. Computer Model of a Kraft Char Bed (D. W. Sumnicht)

A computer model of a kraft char bed has been developed as part of a three-dimensional model of the recovery furnace. The char bed model

calculates mass and energy exchange between the char bed surface and the gases in the furnace. The three-dimensional distribution of temperatures, gas velocities, and gas concentrations is used to calculate both local and global bed burning rates. The sulfate/sulfide cycle theory of char burning is used as a basis for calculating reduction efficiency.

The results of model calculations suggest that the bed influences gas flow patterns as well as playing an important role in overall char combustion. Most of the char combustion can occur on the bed surface, and  $C/CO_2$  and  $C/H_2O$  reactions make a significant contribution to bed burning. The reduction efficiency is not threatened by a large oxygen supply except around the periphery of the bed where cool, oxygen-rich air lowers the reduction efficiency. Three bed shapes - a high bed, a crater-shaped bed, and a low bed - resulted in different flow patterns in the lower furnace for each case. The high bed forced the secondary jets upward while the crater bed and low bed resulted in the development of gas recirculation patterns above the bed. The low bed case appeared to have the lowest carryover although solution convergence issues make this conclusion tentative.

The conclusions related to recovery furnace operation are as follows:

1. Most of the char combustion can take place on the bed. The case using the experimental IPC correlation had bed burning rates which were 119% of the char entering the furnace. A firing strategy which seeks to maximize bed burning would permit coarser sprays to be used, and larger drops are less likely to be carried out of the furnace. Pluggage problems would decrease as a result, and energy efficiency would be improved due to less sootblowing steam usage and cleaner heat transfer surfaces.
2. Heat release in the lower furnace is desirable from the standpoint of keeping a high bed surface temperature which in turn promotes rapid burning rates and a high reduction efficiency. The  $C/CO_2$ ,  $C/H_2O$ , and  $C/Na_2SO_4$  reactions are endothermic reactions which will tend to cool the bed surface, but gas phase oxidation of CO and volatiles above the bed is a means of providing heat to the surface to keep the endothermic reaction rates high.
3. The bed shape influences the flow patterns in the lower furnace. There appears to be a difference in carryover caused by different bed shapes, but this conclusion is very tentative since cases used to draw this conclusion were not completely converged.
4. A large oxygen supply should not jeopardize the reduction efficiency provided there is sufficient carbon and high temperatures. The model predicts that the sulfate/sulfide cycle is mass transfer limited in oxygen except around the perimeter of the bed. The reduction efficiency is in general not threatened by a large oxygen supply, but

smelt leaving the furnace should be isolated from cool, oxygen-rich air. Oxygen from the primary ports is rapidly consumed by combustibles above the bed. Oxygen in the combustion air is a significant oxidant on the char bed surface, but gas-phase oxygen consumers, such as pyrolysis gases and CO, reduce the amount of oxygen that can make it to the surface. On the other hand, oxygen gets to the surface indirectly via oxidation of gases to CO<sub>2</sub> and H<sub>2</sub>O which in turn react with the char bed surface. A sufficient oxygen supply in the lower furnace is therefore essential to fast bed burning rates.

The conclusions associated with modeling issues are as follows:

1. The fact that the gasification reactions are important on the char bed makes the in-flight char particle combustion model deficient. The gasification reactions are included in the bed model, but they are not included in the in-flight char combustion model. Walsh concluded that particles which are swept into a hot, oxygen-deficient core of upward-flowing gases are carried out of the furnace because they remain in a low density form<sup>32</sup>. This conclusion may be modified if the gasification reactions are included in the in-flight char particle combustion model. CO<sub>2</sub> and H<sub>2</sub>O in the oxygen deficient core could burn out some particles in an oxygen deficient core.
2. There is a problem with unreasonably high temperatures in some gas cells close to the char bed. The problem is caused by excessive fuel released near cells with high oxygen contents and a high degree of turbulence. The k- $\epsilon$  turbulence model apparently overpredicts mixing in regions of high shear rate near the primary ports. Fuel from the bed entering these cells reacts as far as stoichiometry allows. Unrealistic reaction rates lead to unreasonably high temperatures which tend to be propagated over the bed region. The resulting high temperatures above the bed cause a high radiant heat flux back to the bed. The bed energy balance is heavily influenced by radiation. The predicted surface temperatures are higher than expected, but the combustion rate is not overestimated if burning is mass transfer controlled. The problem of artificially high temperatures is moderated by spreading pyrolysis gases over more cells to reduce the heat release in individual cells.
3. There is no way currently to construct a model which solves for the bed shape without introducing a high degree of arbitrariness. The bed shape must be arbitrarily specified in the current version of FLUENT/RFM, and there is no mechanism for closing the mass balance in individual cells. Individual cells can grow or shrink, and the global bed mass balance can likewise be out of closure. The bed shape suggested by the bed cell mass balances is not likely to be the same as the specified bed shape, but an algorithm to determine the bed shape must be physically realistic or the end result will be no better (and perhaps worse) than specifying an arbitrary bed shape. A preferable approach to trying to solve for a steady-state bed shape is to

investigate the influence of bed shape in a given furnace simulation to determine the extent to which bed shape influences overall furnace behavior.

4. A pseudo-steady-state bed is valid in a steady-state model, since the time constant for changes in bed shape are much longer than the time constant for changes in the flow patterns.

5. Allowing certain particles hitting the bed to remain in the gas phase is more physically realistic than arbitrarily trapping particles where they strike the bed. Some particles may be in a low-density state when they reach the bed, and the force of the primary jets would sweep these particles across the surface of the bed if the model allows it. The high-temperature problem would be reduced since the volatiles would be more evenly distributed. Spreading the volatiles this way is more physically realistic than arbitrarily specifying a certain fraction of bed pyrolysis in the cells above the bed.

Future work should focus on issues pertaining to char burning in general and bed burning in particular.

A more comprehensive mass transfer correlation is desirable. The IPST correlation is the best available for char burning on the bed at present, but its range of applicability is limited to no more than 6 m/s. Extrapolation to higher velocities gives substantially different mass transfer coefficients depending the assumed power dependence of velocity. A larger velocity range is necessary to determine the power dependence of velocity with statistical significance if possible.

Data on the C/CO<sub>2</sub> reaction rate is required to clear up the ambiguities involved in Li's rate expression. Data on the C/H<sub>2</sub>O rate is also required since the form of Li's expression was used in the model rather than actual data for the C/H<sub>2</sub>O reaction.

Some of the methods of redistributing the mass discussed above could be investigated and expanded. Any redistribution done to determine a bed shape should at least be physically realistic or nothing more will be gained by arbitrarily specifying a bed shape.

A fuming model and a sulfur release model would be useful for investigating their effects on recovery boiler operation. A bed fuming model and particle fuming model could be incorporated into FLUENT/RFM as soon as more computer memory and rate data for fume generation and deposition become available. At present, the furnace simulation requires all 16 Mbytes in the MicroVax II station used in this work. Fume modeling would require one more chemical species, and a sulfur model would require a reduced-sulfur species and an oxidized-sulfur species in FLUENT/RFM.

Little useful information could be gained from a subsurface model. Current modeling techniques are insufficient to accurately handle all the processes occurring beneath the surface of the char bed. A subsurface model would need to handle simultaneous endothermic chemical

reaction, heat transfer, and three-phase flow through porous media with possible phase change. The main output of the model would be the final reduction efficiency of the smelt leaving the furnace. It has been shown earlier, however, that most of the reduction can occur near the surface. Thus, the additional information gained from a detailed subsurface model would not be very useful.

The particle combustion model should be modified to include the gasification reactions. This modification could have a substantial impact on predicted in-flight combustion and carryover.

The parameters used to determine  $k$  and  $\epsilon$  in the turbulence model should be investigated to see to what extent they contribute to unrealistic combustion rates in the gas phase.