

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

March 21-22, 1989

The Institute of Paper Chemistry

Appleton, Wisconsin

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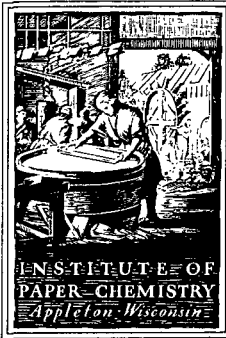
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Your advice and suggestions on any of the projects will be most welcome.



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March 3, 1989

TO: Members of the Pulping Processes Project Advisory Committee

The next meeting of the Pulping Processes PAC will be held in Appleton on March 21 and 22, 1989. The meeting will convene Tuesday morning at 8:30 in the Seminar Room of the Continuing Education Center at The Institute of Paper Chemistry. Accommodations are available for committee members at the Continuing Education Center. Enclosed is a pink "security card" which has instructions for entering the CEC building in the event you find it locked when you arrive. Please confirm that you will attend this meeting at your earliest convenience.

The information enclosed with this letter is for your review for the upcoming meeting. Included are:

- (A) a list of current committee members,
- (B) the agenda for the March meeting,
- (C) a table of 1989-90 dues-funded projects for the Chemical Sciences Division,
- (D) a list of current M.S. and Ph.D. student work,
- (E) minutes from the October 1988 meeting, and
- (F) the status reports for the individual funded projects.

As is customary for the spring meeting, the status reports are summary in nature.

TO: Members of the PPPAC

March 3, 1989

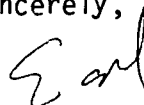
Page 2

The agenda is similar to previous meetings. We will set aside roughly 10 minutes after each presentation for committee discussion. This should expedite discussions held at the committee meeting the following morning.

Two items will be reviewed at the evening session. First, the technical program for the upcoming year (July 1989 to June 1990) will be discussed, with emphasis on what can be done against the background of our move to Atlanta. Second, the status of our July 1989 move to Atlanta will also be discussed.

See you in Appleton!

Sincerely,



Earl W. Malcolm  
Director  
Chemical Sciences Division

EWM/gmk  
Enclosures

## PULPING PROCESSES PROJECT ADVISORY COMMITTEE

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AGENDA

PULPING PROCESSES PAC MEETING  
 March 21-22, 1989

The Institute of Paper Chemistry  
 Continuing Education Center  
 Appleton, Wisconsin

Tuesday, March 21

- |            |  |                                  |
|------------|--|----------------------------------|
| 7:00 a.m.  | BREAKFAST  |                                  |
| 8:30       | OPENING REMARKS  | D. Johnson                       |
| 8:35       | RESEARCH OVERVIEW  | E. Malcolm                       |
| 8:50       | PROJECT PRESENTATIONS  |                                  |
|            | KRAFT CHEMICAL RECOVERY PRESENTATIONS  |                                  |
|            | Fundamental Processes in Alkali Recovery Furnaces<br>(Project 3473-1)                        | J. Empie<br>T. Adams<br>C. Brown |
|            | Black Liquor Combustion (DOE supported)<br>(Project 3473-6)                                  | T. Grace<br>K. Nichols           |
|            | Kraft Black Liquor Delivery Systems (DOE supported)<br>(Project 3657-2)                      |                                  |
| 10:45      | BREAK/TOUR   |                                  |
|            | Computer Model of Recovery Furnace<br>(Project 3605)   |                                  |
|            | CHEMICAL PULPING   |                                  |
|            | Fundamentals of Selectivity in Pulping and Bleaching<br>(Project 3475)                       | D. Dimmel                        |
| 12:00 noon | LUNCH  |                                  |
| 1:00 p.m.  | PROJECT PRESENTATIONS (continued)  |                                  |
|            | Sulfur-Free Selective Pulping Process<br>(Project 3661)                                      | H. Chum<br>D. Dimmel             |
|            | Improved Processes for Bleached Pulp<br>(Project 3474)                                       | T. McDonough                     |
|            | Mechanisms of Dioxin Formation in Pulp Production<br>(API/NCASI supported)<br>(Project 3667) | D. Dimmel                        |
| 3:00       | BREAK  |                                  |

## PROJECT PRESENTATIONS (continued)

Fine Structure of Wood Pulp Fibers  
(Projects 3288 and 3521 [IPC/DOE])

R. Atalla

Raman-Based Lignin Sensor  
(FKBG/DOE/IPC)

R. Atalla

## HIGH YIELD PULPS

Fundamentals of Brightness Stability  
(Project 3524)

U. Agarwal

Development and Application of Analytical Techniques  
(Project 3477)

E. Malcolm  
S. Berben

5:00 SOCIAL HOUR

6:00 DINNER

7:00 EVENING DISCUSSIONS

Research Program for 1989-1990

E. Malcolm

Atlanta Move

Wednesday, March 22

7:00 a.m. BREAKFAST (CEC)

8:00 COMMITTEE MEETING (KRANNERT - Rooms K108-109)

12:00 noon LUNCH (CEC) END OF WEDNESDAY SESSION

Next Meeting: October 17-18, 1989IN ATLANTA

DUES--FUNDED PROJECTS

20	3288	Fine Structure of Wood Pulp Fibers	70	65	70	70
20	3473	Fundamental Processes in Alkali Recovery Furnaces	250	250	280	280
20	3474	Improved Process for Bleached Pulp	60	150	250	250
20	3475	Fundamentals of Selectivity in Pulping and Bleaching	150	90	120	120
20	3477	Development of Analytical Techniques	60	45	30	15
20	3521	Raman Microprobe ... Woody Tissue	45	50	50	50
20	3524	Fundamentals of Brightness Stability	140	170	190	155
20	3524	Exploratory Research	60	60	60	60
20	3566	Strong, Intact, High Yield Fibers	175	150	50	50
20	3605	Computer Model of Recovery Furnace	40	80	80	80
			1,050	1,110	1,180	1,130
		Division 20 Totals				



A190

MASTERS

## INDEPENDENT STUDY

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
Aloisi	Dynamic simulation with MAPPS.	Waterhouse
Burkhead	A study of sheet bulk development during impulse drying.	Lindsay
Connor	Effects of particle orientation on the fluid mechanics of coatings.	Lindsay
Dudek	Preliminary experiments on the encapsulation of zygotic and somatic embryos of Norway spruce.	Rangaswamy
Ebert	An investigation of the compression/expansion mechanisms of a porous layer in a press nip.	Aidun
Exarhos	Electron microscopy study of ultrastructure of <u>Picea abies</u> plants obtained through somatic embryogenesis.	Conners
Flood	Effects of warm black liquor impregnation on kraft selectivity.	Malcolm
Gao	Monitoring the aging of paper nondestructively.	Waterhouse
Gaudette	The use of flash x-ray radiography in imaging black liquor sprays from flat spray nozzles.	Grace
Hagen	Sample preparation techniques for metal analysis by inductively coupled plasma spectrometry.	Easty
Horstmann	Influence of sizing and refining on the edge penetration of paper by an aqueous solution.	Stratton
Huhn	The effects of metal chlorides on corrosion fatigue of suction roll alloys.	Ahlers
Hull	The quantitative determination of formaldehyde in paper.	Easty

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
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
Logsdon	Patterns of and changes in gene expression associated with maturing and germinating seed.	Dinus
Lynde-Maas	Fructose utilization by embryogenic and nonembryogenic callus cultures of Norway spruce.	Johnson
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
Myers	The use of acoustic attenuation in tissue to determine air permeability.	Habeger
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
Rosik	Modeling end use performance characteristics.	Jones
Ross	Statistical geometric study of the molecular structure of water.	Etzler
Sachs	Dependence of charge density on the flexibility of a polyelectrolyte.	Stratton
Santkuy1	Delamination in impulse drying.	Sprague
Schwantes	Alkaline degradation of a polymer supported cellulose model.	Dimmel

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
Tembreull	A case study of the application of ultra-sonic measurements of moduli and shear for online control of paper properties.	Jones
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
Wadsworth	Two-sided impulse drying.	Sprague
Wallace	The effects of extraneous substances on the colloid titration technique	Stratton
Walker	Culture of somatic embryos in bioreactors.	Becwar
Waren	Transport of anthraquinone model compounds in kraft pulping.	Malcolm
Weber	Expert system modeling of pulping parameters effectd by chip dimension.	Malcolm
Wood	The effect of cold-shocking on cultures of <u>Larix decidua</u>	Dinus
Zavaglia	Flash x-ray investigation of the impulse drying process.	Lindsay
Zheng	The effect of lignin precursors on bacterial cellulose.	Atalla

A490

Ph.D.

## THESES IN PROGRESS

<u>Student</u>	<u>Passed to Thesis Candidacy Approval</u>		<u>Subject</u>	<u>Committee</u>	<u>Room</u>
Biasca, J.	1/4/84	2/24/84	Oriented fiber refining: application of individual modes of mechanical action to single pulp fibers.	Habeger, chr. (Baum) McDonough Michael Jackson (Weyerhaeuser) [adjunct member]	71 K27
Bither	9/10/85	1/27/86	Strength development through internal fibrillation and wet pressing.	Waterhouse, chr. Habeger Stratton	203A
Barkhau	12/6/85	12/16/85	Anthraquinone inhibited lignin condensation.	Dimmel, chr. Malcolm	K206
Kulas, G.	3/25/86	4/16/86	An investigation of the fire- side sulfidization of kraft recovery furnace waterwall tubes.	Grace, (co- Yeske chr.)	Cor. Lab., Rec. Lab.
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
Kulas, K. (Not in residence summer 1986)	6/13/86	12/2/86	An overall model for the com- bustion of a single droplet of kraft black liquor.	Grace, chr. Clay Atalla	69
Harper (Not in residence summer 1986)	6/13/86	11/24/86	Sulfur release during black liquor burning.	Grace, chr. Clay McDonough	K115
Burns, B.	6/27/86	10/6/86	A kinetic study of medium consistency chlorination.	McDonough, chr. Lindsay Malcolm	168 and 49

<u>Student</u>	<u>Passed to Thesis Candidacy Approval</u>		<u>Subject</u>	<u>Committee</u>	<u>Room</u>
Goulet (Not in residence summer 1986)	6/27/86	12/2/86	The effect of pulping, bleaching, and refining processes on the electrokinetic properties of wood fibers.	Stratton, chr. Conners Easty	1225
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
Sumnicht	9/23/86	11/24/86	Computer model of a char bed.	Grace, chr. Nichols (Farrington)	312
Biasca, K.	11/7/86	12/11/86	A study of delignification kinetics during alkaline sulfite anthraquinone pulping.	McDonough, chr. Clay Malcolm	67
Goerg	11/7/86	12/18/86	A study of fume particle deposition.	Grace, chr. Orloff Cameron (Farrington)	SR17
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

<u>Student</u>	<u>Passed to Thesis Candidacy Approval</u>		<u>Subject</u>	<u>Committee</u>	<u>Room</u>
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
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
Verrill (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
Bunker (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.	Conners, 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



Tacoma, Washington 98477  
Tel (206) 924 2345

February 21, 1989

Dr. Earl Malcolm  
Director, Chemical Sciences Division  
The Institute of Paper Chemistry  
P.O. Box 1039  
Appleton WI 54912

Dear Earl:

Re: Pulping Processes Project Advisory Committee (PPPAC) Report for the  
October 1988 Meeting

The committee provided many comments about the October meeting as part of our report to RAC on November 9, 1988. I am very grateful to Doug Armstrong for presenting the report to RAC in my absence. The following comments are intended to be a somewhat more complete account of the committee's views concerning IPC's programs in the pulping processes area.

Project 3473-1: Fundamental Processes in Alkali Recovery Furnaces

Project 3473-6: Black Liquor Combustion (DOE Project)

The committee felt that good progress has been made in spite of the substantial personnel changes. Concern was expressed over the ability to maintain stated completion schedules for the reports due to the part-time status of the authors. Also, it is hoped that, as the technical results are brought together, these authors can maintain the high level of enthusiasm of the past so that they can assimilate the data as a whole and recombine the information into meaningful relationships for the control of recovery boilers.

The committee encourages IPC to press on with restaffing this area so that the momentum can be regained in what has been an exceptionally well organized and highly productive program for the past several years.

Project 3605: Computer Model of Recovery Furnace

Results on the progress of the development of the overall computer model developed much interest and considerable discussion took place relative to future work. It was noted that the present requirements of four months of computer time to close, based on 50,000 cells, would impair its practicality of use even when much larger, much faster computers were to become available in the future. Current plans include expansion of the model to 250,000 cells so that tangential flow can be handled. With this expansion and with the use of faster, dedicated computers, it is estimated that closure would still require weeks rather than months. Therefore, it was felt that it will be necessary to have the efficiency of the programming improved by professional programmers. It is possible that the model might be presented in several levels of complexity in order to better serve the different requirements of

the industry and to promote greater use of the model. Such reductions in the size of the model cannot be properly done until the full model is tested against operating boilers to determine the significance of the detail now being incorporated.

The committee agreed that strong consideration be given to seeking DOE funding for further development of the model. It was noted that DOE has long had a goal of supporting technologies leading to improved process control.

Project 3475: Fundamentals of Selectivity in Pulping and Bleaching

Progress has continued in four main areas, as discussed below.

A. Amorphous/Crystalline Cellulose Studies

Excellent progress is being made in this area now that a method has been developed to reproducibly make a high viscosity, stabilized amorphous cellulose. The work being done to directly examine the effects of oxidative attack on cellulose will provide an excellent tool to use to further understand how bleaching process modifications affect pulp properties. The initial work done showing how various metal ions protect and/or accelerate carbohydrate degradation is very interesting and needs to be explored in depth.

In terms of future work in this area, molecular weight distributions need to be generated to confirm that viscosity measurements are correctly reflecting losses in DP. It was also pointed out that introduction of metal ions into experiments designed to study  $H_2O_2$  attack on cellulose should be reviewed in terms of peroxide degradation due to interactions with the metal ions.

B. Polymer-Supported Insoluble Model Compound Work

The methodologies being used to link cellulose model compounds to polystyrene appear to give the desired end product for use in experimental work. Determination of the exact extent of compound uptake and/or desorption from the polymer substrate, however, has proven to be a difficult task and additional work is needed on the preparation methods to get around this problem. The committee agrees that no further work should be done in this area unless it can be incorporated into student work.

C. Electrochemical Studies

The development of an electrochemical cell that allows direct observations of the action of a catalyst on pulping reactions continues to generate excitement. Unfortunately, mechanical problems with the cell and electrode systems are continuing and much of the technical efforts on the project have to be directed at solving these mechanical problems. We are hopeful that the now formal association with SERI will allow their considerable electrochemical experience to be applied to the problems so that the IPC effort can be directed to fundamental research using the cell.



D. Sulfur-Free Pulping Processes

This project is now a DOE-funded joint IPC-SERI project and, as such, requires a major manpower commitment on the part of IPC. The electrochemical cell project is now incorporated into this work. In addition, research aimed at developing a process to make cheap pulping catalysts from lignin (from the thesis work of John Wozniak) is also to be covered by this grant. We are expecting SERI to be reporting on the progress of this project at the next PAC meeting jointly with the IPC staff.

Project 3474: Improved Processes for Bleached Pulp

The committee enthusiastically endorsed the program and complimented progress to date on this project and encouraged further activity as planned. The preliminary results demonstrating the effectiveness of oxygen delignification, high dioxide substitution and oxygen/peroxide reinforced extraction on the reduction of TCDD and TCDF was most promising.

The IPC staff pointed out that the API/NCASI sponsored work, although significant in itself, could really serve as the basis for identifying the fundamental factors involved in TCDD and TCDF formation and thereby be the initiating point for future programs. The committee agreed and listed the following questions as germane examples:

- . Why were certain results obtained? For example, is the indicated pulp strength loss a necessary result?
- . What is the effect of additional chlorate/chlorite concentrations in the effluent on the environment?
- . What is the effect of black liquor carry-over?
- . What is the effect of chlorination filtrate recycle?
- . Should toxic effects, as such, be evaluated?
- . What is the effect of including secondary treatments such as aerobic/anaerobic treatment on AOX generation?

The committee questioned why an effort was being expended on studying the patented PreNox process. When the staff explained that the interest was to understand the principals so that potential alternatives could be developed, the committee endorsed the effort.

A few additional comments from a committee member follow:

1. AOX measurements should be carefully qualified to avoid confusion; regulations in Sweden and Germany are on final effluent levels, most of which are untreated, or perhaps treated in an aerated lagoon. Their values should roughly correspond to our influent levels to secondary treatment plants.

2. There is no accepted method for "AOX on pulp." This could be a major contribution if a standard method could be developed, since it is well known by now that much of the chlorinated dioxins and furans stay with the pulp and are not easily removed by washing.
3. It seems likely that high substitution of  $\text{ClO}_2$  will be used more widely to reduce the use of  $\text{Cl}_2$ . There is still much to be learned in the area of optimizing for best bleaching results and for minimum environmental effects. The chemical reactions of lignin with  $\text{Cl}_2$  after treatment with  $\text{ClO}_2$  are not well defined, and could improve our understanding of the system, leading eventually to additional modifications. These fundamental studies may be of interest to researchers at IPC as part of the overall dioxin study.

#### Project 3524: Fundamentals of Brightness Stability

This project is the only one currently active at IPC in the area of high yield pulping. It is important that IPC maintain a capability to work in the high yield pulping area, and work on brightness stability should receive priority when staffing needs are considered.

U. P. Agarwal has confirmed the presence of ferulic acid in photoyellowed sheets using GC-MC. There is also some chromatographic evidence for the presence of cis-ferulic acid, possibly formed by photoisomerization of trans-ferulic acid. Though cis-ferulic acid is yellow, the degree to which it contributes to the yellowness of photoreverted sheets is not yet clear.

The immediate priorities in this project should be to quantify the contribution of cis-ferulic acid to the yellowness of photoreverted sheets in comparison to the contribution of quinone structures. Kinetic experiments might help establish whether ferulic acid is formed early in the brightness reversion mechanism, or whether it is a terminal byproduct of one photoreversion pathway.

Work of this type is useful as it contributes to our knowledge of photoreversion mechanisms. Efforts should be made to obtain the staff levels necessary to maintain critical mass in this area.

#### Project 3477: Development and Application of Analytical Techniques

Progress reported included the development of methodology for bleaching effluent analyses, developing a method for determination of volatile components in paper and an assessment of near infrared spectrometry for lignin analysis. The committee was again pleased with the quality of this work.

#### Project 3288: Fine Structure of Wood Fibers

#### Project 3521: Native State of Woody Tissue

A variety of physical methods are being used to probe fine structure and valuable insight has been provided into how patterns of molecular chain aggregation in pulp fibers are affected by process operations. Examples from recent work include the identification of structural differences arising from: a) repeated drying cycles; b) kraft vs. acid chlorite pulping, and; c) steam explosion at different temperatures.

Dr. Earl Malcolm  
February 21, 1989  
Page 5

Attachment E-5

Improvements have been demonstrated in obtaining Raman spectra of high yield pulps. This could be of value as a method for an on-line lignin sensor.

The committee views the methodology being developed and applied here as important to the long-term goal of improved high yield pulps.

Best regards,



D. C. Johnson, Chairman  
Pulping Processes Project Advisory Committee

DCJ:dcw/b113/0221

STATUS REPORTS

TO THE

PULPING PROCESSES PROJECT ADVISORY COMMITTEE

March 21-22, 1989

The Institute of Paper Chemistry  
Appleton, Wisconsin

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PROJECT SUMMARY FORM

DATE: February 8, 1989

PROJECT NO. 3288: FINE STRUCTURE OF WOOD PULP FIBERS

PROJECT LEADER: R. H. Atalla

IPC GOAL:

Develop relationships between the critical paper and board property parameters and the way they are achieved as a combination of raw materials selection, principles of sheet design and processing.

OBJECTIVE:

Define the structure of wood pulp fibers and relate to ultimate web properties.

CURRENT FISCAL YEAR BUDGET (JULY 1988 TO JUNE 1989): \$65,000

PRIOR RESULTS:

The solid state  $^{13}\text{C}$  NMR spectra have shown differences between the core crystalline domains of kraft and acid chlorite pulps. Similar differences were also observed between low temperature holopulps and holopulps annealed at higher temperatures.

Studies of the effects of biosynthetic environment on native fiber structure have revealed a correlation between the nature of the synthesizing complexes that occur on the surface of the membrane of the cell producing the cellulose, and the relative amounts of the  $I_{\alpha}$  and  $I_{\beta}$  forms in the particular cellulose.

The studies of biosynthesis of cellulose by *Acetobacter xylinum* provided new insights concerning the different types of interactions which determine the manner of aggregation of cellulose during the earliest stages of its formation.

SUMMARY OF RESULTS SINCE LAST REPORT:

Additional solid state  $^{13}\text{C}$  NMR studies of the effects of isolation procedures on core crystalline domains in pulp fibers have shown differences between kraft and sulfite fibers, as well as confirming the effects of annealing reported previously. In the comparison of kraft and sulfite pulps, all isolated from the same latewood of the same annual ring of a southern pine log, the  $^{13}\text{C}$  NMR spectra showed that the crystalline domains in the sulfite fibers were fully relaxed significantly more rapidly than the kraft fibers. This observation implies that the mobility of molecular chains is higher in the sulfite pulps, and conversely, that the kraft pulps have more tightly aggregated crystalline domains. The annealing studies indicated subtle but real increases in relaxation times for the crystalline domains with higher annealing temperatures; these in turn indicate progressively higher crystallinity.

In the studies of aggregation of cellulose during biogenesis, we continue to observe that associations with both hemicelluloses and lignin precursors inhibit the crystallization of nascent cellulose fibrils. The pattern which emerges for the hemicelluloses is that those hemicelluloses which have a  $\beta$ -1,4 backbone with

very limited substitution or branching are the most effective at blocking the crystallization of bacterial cellulose grown in their presence. Extraction of the hemicelluloses does allow crystallization of the cellulose, though not necessarily to the same extent as would have been observed in the absence of the hemicelluloses.

In studies of the effects of lignin precursors, the most striking effect we have observed so far, occurs in the case of coniferin; its structure consists of coniferyl alcohol with a glucose unit attached at the phenoxy oxygen on C4 of the aromatic ring. The presence of coniferin during the biogenesis seems to inhibit the assembly of nascent cellulose fibrils to the extent that the x-ray pattern is that of an essentially amorphous cellulose. Extraction of the coniferin in 0.2% NaOH solution results in aggregation of the cellulose to crystalline domains very similar in crystallinity to those produced by the microorganisms under normal conditions.

Information from the different subprograms of this project and related academic studies is helping us to develop a better understanding of the patterns of molecular aggregation in native woody tissue, and the manner in which these patterns are changed during pulping; the patterns of aggregation are the primary determinants of mechanical properties of the resulting pulps.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

The primary focus of effort in the short term will be on bringing the current phase of these programs to conclusion and preparing a comprehensive report to the membership. In parallel, detailed plans for moving the laboratory to the Atlanta facility will need to be prepared. Effort on this project will be limited in the short term by manpower considerations.

#### POTENTIAL FUTURE ACTIVITY:

Progress on several projects, including the new areas of high-yield pulping and moisture tolerant webs, will benefit from a better understanding of the relation between fiber structure and product properties. New information on the fine structure of cellulose and fibers will be helpful in guiding activities in those areas. Future work will focus on the structure of native wood fibers and its modification in both conventional chemical and high yield pulping processes.

#### RELATED STUDENT RESEARCH:

Erin Byers, Ph.D.-1988; Ingegerd Uhlin, Ph.D.-1989 (Gunnar Nicholson Fellow); Tan Zheng, special student from China.

PROJECT SUMMARY FORM

DATE: February 8, 1989

PROJECT NO. 3521-2: RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE

PROJECT LEADER: R. H. Atalla

IPC GOAL:

Develop relationships between the critical paper and board property parameters and the way they are achieved as a combination of raw materials selection, principles of sheet design and processing.

OBJECTIVE:

Develop a better understanding of wood fiber structure through the use of Raman microprobe spectroscopy. Establish the molecular structure present in cell walls of native woody fibers, including cellulose, hemicelluloses, and lignin. Determine the response of structure to process variables.

CURRENT FISCAL YEAR BUDGET: \$50,000\*

PRIOR RESULTS:

The Microprobe system was transferred to a vibration isolation table; this eliminated the residual minor mechanical instabilities which continued to occur occasionally after prior modifications.

Studies of luminescence led us to the conclusion that stable free radicals generated during the mechanical fiberization or sectioning of samples may be responsible for the fluorescence. It also appeared that such radicals may contribute to enhancement of the  $1600\text{ cm}^{-1}$  band in untreated woody samples.

The system for time resolved spectroscopy was used to acquire a spectrum of ethylene glycol that had a fluorescing dye dissolved in it. By proper gating it was possible to discriminate against the fluorescence from the dye. This is the procedure which we believe will result in spectra from kraft pulps. The ultra-fast laser was modified to include a Q-switch system which, in conjunction with the mode locker, will allow us to select pulses of much higher energy for excitation. This will allow us to generate Raman spectra of pulps more efficiently.

Two studies related to assignment of the spectra of lignins were completed. One focused on the changes in the spectra during the early stages of acid chlorite delignification, the other was concerned with a lignin model compound. Both have enhanced our ability to interpret the spectra of lignins in pulp fibers.

\*This work will also be supported by a DOE grant in fiscal year 1989/90.



SUMMARY OF RESULTS SINCE LAST REPORT:

The work undertaken in the current period was in two categories: (a) the further optimization of the microprobe, the spectrometers, and the ultrafast laser systems, and (b) the exploration of cell wall structures using both the microprobe and other investigative techniques.

The optimization of the instrumental systems included installing a motorized and microprocessor controlled stage, and mounting on a vibration free platform. These modifications provide stability of samples on the stage for periods of hours, as well as the capacity to scan cell wall domains reproducibly. The detectors were cooled so that diode arrays now operate at  $-20^{\circ}\text{C}$ . Procedures for operating the diode array systems have been established; it is now possible to obtain spectra equal in quality to those which were possible in the older scanning spectrometer which has a thermoelectrically cooled photomultiplier tube as a detector. The gating electronics have also been improved to allow more precise cutoff of the action of the intensifier on the gated diode array. A Q-switch has been added to the YAG laser to allow operation in this mode; together with a pulse picker, the Q-switch allows operation with much higher power level pulses at the frequency doubled wavelength of 532 nm. The remaining modification to the system will be interfacing of the ultrafast laser to the microscope to permit time resolved studies with the microprobe.

In investigations of the cell walls we have encountered a number of interesting phenomena which we are pursuing further. We have observed a transient component in the intensity of the  $1600\text{ cm}^{-1}$  peak associated with lignin. We believe that it is due to the presence of two types of structures within the lignin. These are structures which have a double bond conjugated with the aromatic ring (between the alpha and beta carbons of the propane sidegroup), or structures which include a stable free radical. Both classes of structures are expected to have higher Raman scattering coefficients than the more usual structural units in the lignin. These structures appear to be modified by action of the laser light in such a way that their scattering coefficients are reduced. Other studies had earlier shown that treatments that can modify these entities result in early decline in the intensities of the Raman bands well before any significant reductions in the lignin contents are observed.

Our preliminary mapping studies confirm our earlier findings that the aromatic rings of the lignin within the cell walls are indeed oriented predominantly parallel to the plane of the cell walls. This confirmation of earlier results is particularly important in view of the observation of the transients mentioned above.

Some of our samples were investigated at the National Biomedical ESR Center in Milwaukee, in search of evidence for free radicals. It is clear that stable free radicals occur in our samples. Though no doubt some of these are generated in the course of mechanical division, it is clear that many of the radicals are generated during biogenesis and are inherently stable within the cell wall system.

In related studies we have investigated some patterns of association between lignin precursors and the polysaccharide components in the cell wall. In the presence of coniferin we find that the assembly of cellulose into crystalline domains is interrupted so that a relatively amorphous cellulose is produced. When the coniferin is extracted a highly crystalline cellulose is produced.

Finally, on the basis of our earlier evidence that lignin is oriented in the cell walls, and the knowledge that the separation between aromatic centers is sufficiently small to allow charge transfer, we have speculated that the cell wall system would be photoconductive. We have carried out the appropriate experiments to test this hypothesis, and have indeed observed photoconductive effects when the woody tissue is illuminated at frequencies absorbed by lignin!

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

The primary emphasis in the microprobe program will be on completing at least one mapping program prior to disassembly of the microprobe system for transportation to the Atlanta facility. The work with the ultrafast laser system will focus on the requirements of the on-line lignin sensor program we are undertaking for FKBG. We will seek more precise gating of the detector by improving the responsiveness of the intensifier switching system. We will also be experimenting with a fiber optic system for transmission of the exciting laser pulses to the sample, and for carrying the Raman scattered light from the samples to the entrance slit of the spectrometer. The safe transfer of the systems to Atlanta will be a high priority.

#### POTENTIAL FUTURE ACTIVITY:

Continuation of the program in conjunction with the DOE supported effort is anticipated through Fiscal 1989/90. The methods developed under this program will be adapted to explore the effects of mechanical and chemical treatments on structure and organization in high yield pulps. Some of these methods will also be incorporated into the program, directed at development of an on-line lignin sensor.

#### RELATED STUDENT RESEARCH:

J. Wiley, Ph.D.-1986; J. Bond, Ph.D.-1990.

PROJECT SUMMARY FORM

DATE: February 6, 1989

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

PROJECT LEADERS: H. L. (Jeff) Empie

IPC GOAL: Increase the 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:

The important reactions for reduction of sulfate and the factors governing reduction rates are understood. This information has been reported and the results used in practice.

Char burning via the sulfate-sulfide cycle has been conclusively established. The research and its implications have been reported. Recent work has indicated that direct carbon oxidation may occur in parallel with the sulfate-sulfide cycle, but the implications to operations are not changed. An advanced model has been developed which predicts char burning rates which are consistent with representative burning temperatures.

The cause of intense fume formation during oxidative processes in black liquor combustion has been determined and the work has been reported. This phenomenon had not been recognized prior to our research. Our work suggests that this phenomenon is responsible for most of the fume formed in the recovery boiler.

The main mechanism for deposition of fume particles on cooled surfaces has been shown to be thermophoresis, where deposition rates are directly proportional to thermal gradients near the cool surface. A study of reactions of  $\text{SO}_2$  with  $\text{Na}_2\text{CO}_3$  fume particles has shown that sulfitation can lead to chemical sintering of particles and may be important in dust hardening.

The experimental part and analysis of the phenomenological study of black liquor burning behavior using the single-particle reactor has been completed. The data on single-particle burning behavior include data from testing of random samples of mill liquor as well as liquors produced in controlled laboratory experiments. Extensive data analysis is in progress, and the collaborative effort with Professor Mikko Hupa of Abo Akademi in Finland on this problem is continuing.

Initial studies of the reaction of  $\text{H}_2$  gas with  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  under high temperature conditions have been completed. The implications of this work are being pursued.

Data have been acquired on the release of sulfur gases as a function of temperature and heating rate as well as a function of the nature of sulfur compounds present in the liquor. Sulfate and sulfite sulfur are not volatilized during black liquor pyrolysis, while sulfide and thiosulfate sulfur are. A model using these results is being formulated.

Experimental studies have started on the corrosion of mild steel in molten smelt under conditions where a frozen smelt layer adheres to the metal surface. Getting reproducible data has been difficult; work is continuing.

The experimental data on drying of black liquor droplets in high temperature environments show higher drying rates than theoretical predictions based upon external heat transfer control. These rates can be explained by the increase in effective heat transfer surface area when the droplets expand. In addition, pyrolysis and volatile burning can be initiated before the drop is completely dry, resulting in an apparent shortening of the drying period.

A spray test facility has been constructed to test spray nozzles using real black liquor at temperatures, pressures, and solids contents that are representative of commercial practice. By use of a flash x-ray procedure to "photograph" spray patterns, image analysis techniques are employed to determine spray size distributions and the angular distribution of the liquor coming from the nozzle. Initial tests have indicated the need to reduce environmental impacts through equipment modification.

Ph.D. theses on swelling during pyrolysis, drying of black liquor drops, char burning under an impinging jet, and recovery furnace models of the combustion zone and gas flow trajectories have been completed.

#### SUMMARY OF RESULTS SINCE LAST REPORT:

##### Sulfur Release

Frank Harper has extended his data base on sulfur release to include the effects of intraparticle heat transfer rates, particle size, and black liquor solids content. Models to describe the time-temperature history of the sulfide and thiosulfate release data and the rate of heat transfer within and from the liquor particle are being developed. Recent experiments looking at the possible interaction of sulfide with thiosulfate have given puzzling results; namely, kraft liquor shows the sulfur release from these two ionic species to be additive whereas it is not for soda liquor spiked with sulfide and thiosulfate. An explanation is being sought.

##### Fume Formation/Deposition

Chris Verrill is studying fume formation during single droplet combustion. He has completed the laboratory reactor/furnace assembly and is constructing the mechanism for capturing fume particles on a moving filter tape, thus providing a time history of fume production during a particle burn. Analytical techniques for measuring, and characterizing the fume collected are being evaluated. Kristin Goerg is studying the deposition of fume particles on cooled surfaces.

She has found that the main mechanism for particle deposition is thermophoresis; i.e., deposition due to a thermal gradient near the cool surface. Particle deposition rates are proportional to particle size and particle concentration in the gas phase and are independent of gas flow rate. Also, the rates are highly dependent on the chemical composition of the particles.

#### Char Burning ✓

The major effort on char burning is being carried out under the DOE-sponsored black liquor combustion project and is described in that report. The DOE char burning data have been correlated into an empirical mass transfer coefficient which was incorporated into Dan Sumnicht's computer model of the char bed. The model predicts that a large fraction of char combustion can occur on the char bed. The model also predicts the importance of the C/CO<sub>2</sub> and C/H<sub>2</sub>O reactions, and the significant influence that the bed shape has on flow patterns and other variables important to furnace operation.

Work has continued on the measurement of pure gases (CO and CO<sub>2</sub>) above a burning black liquor char bed. A reference cell which permits the determination of these gases at elevated temperatures (1000°C) has been completed and successfully tested. Preliminary results indicate that a more rigorous approach to the temperature calculations than has been done by previous workers in the field is required to achieve improved accuracy.

#### Single-Particle Burning

Experimental burning studies have continued using the two-color pyrometer technique developed by NIST for measuring the particle surface temperature during burning. Kathy Kulas has measured drying rates and developed a model for particle drying. She is also studying the sulfate-sulfide cycle and its influence on char burning. Jim Frederick and Mikko Hupa at Abo Akademi in Finland have been analyzing all of the single-particle data with the goal of developing a cohesive overall model. They have been able to correlate liquor drying rate with particle swelling behavior and have established that the combustion rate is mass transfer controlled and therefore related to particle surface area. The pyrolysis and smelt oxidation rate data still have to be reconciled.

#### Corrosion

Polysulfide is a sulfur species suspected of being involved in the sulfidation of recovery boiler waterwall tubes. The direct addition of polysulfide to a smelt containing carbonate, sulfide, and sulfate has shown the polysulfide to be unstable, reacting with the carbonate to form sulfide, sulfate, and carbon dioxide. This suggested that the existence of carbon dioxide in the gas above the melt might stabilize polysulfide. Greg Kulas bubbled carbon dioxide through a smelt containing carbonate, sulfide, and sulfate and found that an equilibrium level of polysulfide of about 1% is established. Corrosion tests have been made with a 15% sodium sulfide/15% sodium sulfate/70% sodium carbonate smelt with and without carbon dioxide bubbling. The corrosion product formed without carbon dioxide bubbling is iron oxide. When carbon dioxide is bubbled so that the melt contains polysulfide, the corrosion product is iron sulfide. The corrosion rate is somewhat higher when the iron sulfide product is formed. This sulfidation corrosion process will be investigated further.

### DOE Combustion Report

The major emphasis for the past six months has been in the area of char bed burning. A study has been completed on the effect of gas jet velocity and oxygen concentration on burning rates for completely pyrolyzed char beds. The results confirm the hypothesis that the burning rate is mass transfer limited. The initial results indicate a linear correlation with oxygen concentration and gas jet velocity. Additional testing over a greater velocity range has been completed to determine if the correlation is actually less than first order, as predicted by theoretical calculations of mass transfer.

The addition of CO<sub>2</sub> and H<sub>2</sub>O to the gas jet have shown that a reaction of the form  $CO_2 + C = 2CO$  makes a significant contribution to the char burning rate (15 - 25% increase in the carbon flux). The addition of H<sub>2</sub>O does not seem to increase the rate of carbon consumption, but it definitely promotes the conversion of CO to CO<sub>2</sub>, increasing the oxygen consumption rate.

This work is discussed in a separate project summary for Project 3473-6.

### DOE Liquor Delivery Systems Project

Initial trials of the black liquor spray facility have been carried out on a southern mill liquor. This includes shakedown of the flow loop, spray booth, and flash x-ray system, and has provided a start on the data base on black liquor sprays. Several system weaknesses and limitations have been identified which will require modification and improvement. Included are unsteady flow control, containment of the liquor spray by the tank enclosure, and containment of odor released by reduced sulfur compounds. One important observation was made which confirmed the industry belief that liquor temperature can dramatically affect spray stability. For the CE hollow-cone nozzle, three distinct spray patterns were observed for one liquor flow rate within a temperature range of 10°F. Two of the patterns would have been unacceptable in mill operation. Further tests will be required to confirm this result and compare it to results for the B&W nozzle.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

#### Sulfur Release

Frank Harper will complete data collection on sulfur release during pyrolysis, including resolution of the observed interaction of sulfide and thiosulfate. He will finish developing a cohesive model which is consistent with the results and begin writing his thesis.

#### Fume Formation and Deposition

Chris Verrill will complete installation of equipment to study fume formation during single-particle burning (including initial troubleshooting runs), define the limits of its operation, and establish what analytical techniques he will use to quantify his results. Kris Goerg will finish data reduction on her fume deposition work and complete writing her thesis. Postdoctoral Fellow Paul Ku will determine the feasibility of using a fiber optic method for measuring mean size and number density of fume particles in the region close to a smelt bed.

### Char Burning

To improve the signal quality and hence the accuracy of the high temperature absorption measurements for CO and CO<sub>2</sub>, Pat Medvecz will modify the reference cell and make more rigorous the calculation procedure.

### Single-Particle Burning

Kathy Kulas will continue her study of the impact of the sulfate-sulfide cycle on char burning by doping soda liquors with different amounts of Na<sub>2</sub>SO<sub>4</sub>) and measuring rate differences. Results will be incorporated into a model for particle combustion. Jim Frederick, working with Mikko Hupa, will analyze the pyrolysis and smelt oxidation rate data and incorporate their results into the overall particle burning model.

### Corrosion

Greg Kulas will make some minor changes in operating procedures in an attempt to improve the reproducibility in his data. Additional runs are planned to elucidate the corrosion mechanism and the role of polysulfide as the corrosive species.

### DOE Liquor Delivery Systems Project

After modifications to the system are made to eliminate the problems identified during the initial liquor spray trials, testing will proceed to characterize performance of a B&W splashplate type nozzle and a CE swirl cone nozzle. A third nozzle of new design will also be studied. For each type performance will be determined as a function of pressure-flow characteristics, spray stability, and impact of velocity-viscosity interactions on spray mass median diameter.

#### POTENTIAL FUTURE ACTIVITY:

Apply results of fundamental studies to improve recovery boiler operation.

Develop a recovery boiler probe technique which can obtain operating data to verify the models characterizing recovery boiler performance.

Summarize and publish overall program results, including experimental and modeling, in a form readily understood and used by mill operating personnel.

#### RELATED 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; 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.

PROJECT SUMMARY FORM

DATE: February 6, 1989

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

PROJECT LEADER: T. M. Grace  
NBS Subcontractor - Dr. A. Macek

IPC 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 ANNUAL BUDGET: \$264,000

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 will be reported in Progress Report Three, the draft of which is nearly complete.

The NBS two-color temperature probe was successfully used to measure single-particle burning surface temperatures. This probe has been adopted as an integral part of Kathy Kulas' single-particle burning work.

An experimental char bed furnace was designed, installed, and made operational.



SUMMARY OF RESULTS SINCE LAST REPORT:

A systematic set of char bed burning experiments has been successfully carried out and the data analyzed. Burning rates were determined as a function of oxygen concentration and gas flow rate (velocity). All test conditions were replicated. The data are consistent with oxygen mass transfer as the rate limiting step. The experimental mass transfer coefficients correlated to the average gas velocity raised to a power between 0.8 and 1 with  $R^2$  greater than 94%. Measured mass transfer coefficients were 2 to 3 times higher than coefficients calculated for turbulent flow over a smooth flat plate. This difference is attributed to the surface roughness and porosity which enhances the reacting surface area. Temperature measurements indicate that the depth of the active burning area is only 3 to 7 cm deep. Recent experiments with  $CO_2$  added to the bed air supply showed that carbon burnup rates were increased. Further studies of the effect of carbon gasification reactions on char bed burning rates are underway.

Work on the laser polarization ratio technique to determine fume particle size and concentration has continued. The technique appears to be effective if the fume source/sample is brought to the optical table and the laser beam has uninterrupted access to the fume cloud. Difficulties have been encountered when trying to make measurements in close environments. In particular, initial attempts to use fiber optics to transmit the beam were not successful.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Work on char bed burning on beds of prepyrolyzed char will be completed. This will focus on extending the range of gas velocities and verifying the actual velocity profiles within the experimental reactor. Additional studies of gasification by  $CO_2$  and  $H_2$  occurring concurrently with char burning will be carried out.

The major focus of the fume measurement study will be to adapt the technique to allow measurements in closed systems, in particular, the DOE flow reactor. We will attempt to overcome earlier difficulties with fiber optic light guides.

Relocation of the Institute to Atlanta will occur during the next reporting period and this will have a serious impact on short term productivity. We will try to take advantage of this disruption to redesign and change the flow reactor, prior to its reconstruction, to overcome some of the current drawbacks. One objective of this redesign is to be able to carry out steady-state bed burns with continuous liquor feed.

Phase 4 efforts on recovery furnace simulation will make extensive use of the 3-D furnace model, developed under Project 3605, to evaluate operating and control strategies.

Progress Report 4 covering the work completed on char bed burning and fume formation processes is targeted for completion in June. A summary report on the entire project is targeted for the end of 1989.

Project 3473-6

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POTENTIAL FUTURE ACTIVITY:

A comprehensive summary report on all of the work will be written at the end of the project.

Opportunities to apply the results of this work to commercial practice will be sought.

PROJECT SUMMARY FORM

DATE: February 9, 1989

PROJECT NO. 3474: IMPROVED PROCESS FOR BLEACHED PULP

PROJECT LEADER: T. J. McDonough

IPC 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:

Bleaching Effluent Control

- \* Implementation of precise analytical methods for determination of adsorbable organic halogens (AOX) and investigation of the effects of storage conditions and inorganic chloride content on the analysis.
- \* Development of a protocol for laboratory bleaching to generate effluents for analysis of dioxins and other chlorinated organic materials.
- \* Evaluation of a softwood kraft pulping and bleaching sequence incorporating extensive modifications designed to limit production of dioxins and AOX. Reductions of about 95% in both were demonstrated, but pulp strength was adversely affected.

Bleaching

- \* Elucidation of the harmful effects of reactive oxygen-derived intermediates on pulp carbohydrates and evaluation of a variety of candidate control methods.
- \* Extensive characterization of the behavior of nitrogen dioxide as a selectivity-improving pretreatment for oxygen bleaching. It was shown to be both a carbohydrate protector and a delignification accelerator, prompting efforts to learn more about the mechanisms involved.
- \* Initiation of studies of NO<sub>2</sub> pretreatment mechanisms. In-situ analysis of lignin structure indicates that promotion of lignin removal is not primarily the result of introduction of free phenolic hydroxyl groups. Pretreatment was shown to introduce nitro or nitroso, carboxylic acid and quinonoid groups.

- \* Investigation of other pretreatments and identification of bromine as a superior pretreatment agent. Relative to either nitrogen dioxide or chlorine, bromine gave better delignification and equivalent viscosity protection.
- \* Demonstration of metal ion catalysis of peroxide delignification and of the possibility of favorably affecting the balance between delignification and peroxide decomposition.
- \* Development of a new mechanistic hypothesis, and the corresponding mathematical model, for kraft pulp chlorination.
- \* Initiation of Ph.D. thesis research on the mechanism of kraft pulp chlorination at medium consistency in a high shear mixer.

#### Pulping

- \* Development of empirical models of kraft and kraft anthraquinone pulping that allow economic and environmental assessment of a variety of strategies for reducing unbleached kappa number.
- \* Identification of conditions that allow selective pulping to extremely low unbleached kappa numbers in alkaline sulfite anthraquinone (ASAQ) systems.
- \* Establishment of kinetics of the bulk and residual phases of ASAQ pulping, as a first step towards a kinetic model that will allow a new low lignin pulping process to be defined.
- \* Initiation of Ph.D. thesis research to elucidate the kinetics of the initial phase of ASAQ pulping, to allow completion of the delignification component of the kinetic model.

#### SUMMARY OF RESULTS SINCE LAST REPORT:

##### Bleaching Effluent Control

IPC effort on control of chlorinated organics in bleaching effluents has been divided between this project (Project 3474) and Project 3664, a project funded by the American Paper Institute through the National Council of the Paper Industry for Air and Stream Improvement (NCASI). No conflict is seen here, since IPC and NCASI have many members in common and both have expressed their willingness to share information en route to the common goal of a solution to the chlorinated organics problem.

Work completed or initiated in the period since the last report has included:

- \* an experiment to determine the effect of solvent extraction of unbleached pulp on the production of dioxins in a subsequent conventional CEDED bleaching sequence,

- \* dibenzodioxin (DBD) and dibenzofuran (DBF) spiking and extraction experiments, with NCASI, to assess the degree to which these precursors are responsible for formation of dioxins during chlorination,
- \* experiments, also with NCASI, to identify the source of unchlorinated dioxin precursors, and
- \* investigation of the cause and point of origin of the pulp strength loss observed when a variety of measures designed to reduce chlorine usage were combined in a single modified bleach sequence.

Effect of Pulp Preextraction on Dioxins in Combined CEDED Effluents and Bleached Pulp. Southern pine kraft pulp of kappa number about 30 was bleached in the CEDED sequence, with and without exhaustive preextraction. In each case, the effluents from all five stages were combined and submitted for analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF, together with the corresponding bleached pulps and combined solvent rinsates of all equipment contacted by the pulp or effluent in every stage.

The pulping and bleaching conditions and experimental procedures were identical to those reported earlier, when the CEDED sequence on conventional pulp was compared to a modified sequence on low-lignin pulp. In the present case, however, the samples were submitted to Triangle Laboratories for analysis; the earlier samples were sent to Wright State University. This afforded an opportunity to compare the results obtained by the two laboratories.

The data are shown in the attached table. A discrepancy was noted between the two laboratories. Triangle found little or no dioxin and much more furan than was found by Wright State. The furan/dioxin ratio from Triangle is more typical of those found in the literature. An as yet unanswered question concerns the possible role of fines in the effluent in explaining this discrepancy.

The effect of extracting before bleaching was to reduce, but not eliminate, furan generation. The generation of furan from extracted pulp does not rule out the precursor hypothesis because we were unable to demonstrate that the extraction was exhaustive. Also, the possibility of atmospheric contamination of the extracted pulp with precursors cannot be ruled out. Such contamination has been a problem at PAPRICAN and NCASI.

The samples sent to Triangle included the Kapak bags used for the chlorination and extraction stages. The bags contained no detectable 2,3,7,8-TCDD and 14% of the total 2,3,7,8-TCDF generated in a control bleach. On the basis of this observation and the known relatively low rate of generation of dioxins and furans in the stages downstream of the first caustic extraction, it seems safe to use such bags as D-stage containers in future work.

Results of Analyses for  
2,3,7,8-Tetrachlorodibenzodioxin/furan, µg/tonne (ppt)  
Laboratory Comparison and Effect of Brownstock Solvent Extraction

		Experiment 2 (Triangle Labs)	Experiment 1 (Wright State)	
			1	2
2,3,7,8-TCDD:				
Control	Effluent	<2.0	24.0	17.5
	Pulp	<0.5	<1.6	2.0
	Ethanol	0.9	n.d.	<0.1
	Toluene	0.5	0.7	0.5
	Bags	<1.4	n.d.	n.d.
	Total	<5.3	26.3	20.0
Extracted	Effluent	5.5		
	Pulp	<0.8		
	Ethanol	0.8		
	Toluene	1.2		
	Bags	n.d.		
	Total	<8.3		
2,3,7,8-TCDF:				
Control	Effluent	15.0	12.0	7.3
	Pulp	8.0	3.7	1.7
	Ethanol	18.4	n.d.	<0.1
	Toluene	1.6	1.1	0.5
	Bags	6.8	n.d.	n.d.
	Total	49.8	16.8	9.6
Extracted	Effluent	10.4		
	Pulp	<2.5		
	Ethanol	1.3		
	Toluene	2.9		
	Bags	n.d.		
	Total	17.1		

n.d. = not determined; nondetects are shown as detection limits following the symbol "<".

DBD and DBF as Precursors. Mill jack pine brownstock was bleached by chlorination and caustic extraction stages. The unbleached, chlorinated and caustic extracted pulps were sent to NCASI's Corvallis laboratory for determinations of DBD, DBF, and chlorinated dioxins and furans. For comparison, an additional sample of unbleached pulp was exhaustively extracted to remove DBD and DBF before bleaching, and another was artificially enriched in these precursors by adding measured amounts of the pure compounds. Analysis of all of the resulting effluents and pulps is in progress.

Source of DBD and DBF. Also in progress are experiments to determine the extent to which these precursors occur in unpulped wood and whether they are formed during pulping. Pulping runs have been carried out on unextracted wood and on wood that was exhaustively extracted with ultrapure solvents prior to pulping. Wood, pulps and extracts will be analyzed for DBD and DBF.

Strength Loss in Low Chlorine Bleaching. The last status report contained data to show that pulps prepared according to a combination of strategies that minimize chlorine use were weaker than the corresponding conventionally prepared pulps. Since interest in such strategies is growing, we have begun experiments to determine the reason for the strength loss and the point at which it occurs. They involve interrupting both types of sequence at various points and determination of viscosity, ultrasonic in-plane and out-of-plane moduli, and other network and fiber properties.

#### Bleaching

Progress in understanding the mechanism of oxygen bleaching selectivity improvement by pretreatment with nitrogen dioxide and other compounds depends on being able to reproducibly delignify very small pulp samples. It is necessary to work with small samples because the chemical tools needed, such as methylation with diazomethane, would otherwise become dangerous and prohibitively expensive. We have therefore developed equipment and procedures for simultaneously delignifying up to 13 samples of pulp, each weighing 0.5-4 g. The reproducibility of the method has been experimentally demonstrated.

One hypothesis for the mechanism of action of nitrogen dioxide is that nitro groups introduced into the aromatic rings of nonphenolic lignin units promote ether cleavage in alkali, which in turn creates new phenolic hydroxyl groups to serve as oxygen delignification initiation sites. To test this, we are comparing the effects of methylation on oxygen bleaching response of untreated and NO<sub>2</sub> pretreated pulps. The latter should have the ability to generate new phenolic hydroxyl groups during oxygen bleaching after methylation. Their bleaching rate should therefore be relatively unaffected by methylation. Oxygen bleaching after methylation of the untreated pulps, on the other hand, is expected to be severely retarded. This experiment also provides an opportunity to characterize structural changes associated with the pretreatment and subsequent bleaching by methods not heretofore employed, such as <sup>13</sup>C NMR and laser Raman spectroscopy. In addition, it provides an opportunity to compare the effects of bromine pretreatment, which we have shown to be effective, with those of nitrogen dioxide. The pretreated and methylated pulps have been prepared and oxygen bleached in duplicate. Analysis of the samples is in progress.

Ph.D. thesis research by Barbara Burns is progressing toward the objective of elucidating the mechanisms that are important in medium consistency chlorination. Mass transfer coefficients for chlorine dissolution have been estimated as a function of consistency and temperature at low consistency, as a basis for extrapolation to medium consistency conditions. The extrapolated values will be verified by experiments in the flow-through high shear mixer. The residence time distribution of that mixer is being determined in a series of tracer experiments now in progress. Subsequent work will assess the importance of chlorine dissolution as a rate limiting step.

Master's research by Deborah Mallat will investigate the effect of peroxyacid dissociation constant on the efficacy of pulp bleaching with peroxyacids. Previous research has suggested the possibility that more weakly acidic peroxyacids than peracetic acid may be very effective bleaching agents.

### Pulping

Experimental work on the Ph.D. thesis of Karyn Biasca is virtually complete. She has employed a flow reactor to define the kinetics of the initial phase of sulfite-anthraquinone pulping. Earlier work suggested that the key to pulping to very low lignin contents with this process may lie in the initial phase.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Experiments aimed at determination of the significance and source of DBD and DBF as PCDD/PCDF precursors will be concluded. Additional work will be contingent on the outcome.

A study of effects of chlorination stage variables on dioxins production will be undertaken, with API/NCASI funding and collaboration. This will include mixing studies at medium consistency in a batch mixer soon to be acquired.

Pulp quality will continue to be examined in relation to environmentally prompted process changes, with emphasis on understanding the mechanisms of strength losses.

Dioxins generation in hardwood bleaching, both conventional and low chlorine, will be examined, together with effects of the latter on pulp quality.

The role of quinonoid and carboxylic acid group formation in oxygen bleaching pretreatments will be experimentally assessed.

#### POTENTIAL FUTURE ACTIVITY:

In-depth studies of effects of isolated process changes on dioxins generation may be undertaken. Examples are oxygen bleaching and chlorination stage filtrate recycle.

#### RELATED STUDENT RESEARCH:

S. Pugliese, Ph.D.-1988; B. Burns, M.S.-1986, Ph.D.-1989; M. Breinging, M.S.-1986; J. Fisker, M.S.-1986; J. Rogers, M.S.-1986; K. Biasca (Sime) M.S.-1986, Ph.D.-1989; D. Boyle, M.S.-1987; T. Stroh, M.S.-1987; S. Graf, M.S.-1988, W. Tracey, M.S.-1988, M. Flood (Best)-M.S.-1989.



PROJECT SUMMARY FORM

DATE: February 20, 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 high selectivity of anthraquinone (AQ) pulping is probably associated with its ability to promote single electron transfer (SET) reactions. We have used a variety of experimental probes to establish that anthrahydroquinone (AHQ) a reduced form of AQ, can transfer electrons to quinonemethides; the latter are important intermediates in lignin reactions. The electrons which are accepted by appropriately substituted quinonemethides can cause fragmentation of the structures; these fragmentation reactions are synonymous with delignification.

An electrochemical technique known as cyclic voltammetry has been used to establish the feasibility of SET delignification reactions. These studies were done in cooperation with Dr. Helena Chum and coworkers at the Solar Energy Research Institute (SERI) in Golden, CO. After substantial design modifications, an electrochemical cell has been developed at IPC which can function at high temperatures (165°C) in aqueous alkali. Cyclic voltammograms of mixtures of AQ with bleached kraft pulp and wood meal show the catalytic action of AQ/AHQ during simulated pulping.

The sensitivity of our measurements when observing the AQ/AHQ catalytic redox pulping reactions by electrochemical means were quite low; therefore, attempts were made to develop a more sensitive electrochemical cell, one which would also allow the measurement of the internal cell temperature and pressure and allow sampling of the cell's contents. Work was centered on achieving stable potentials between the working and reference electrodes, examining sensitivity improvements associated with the use of microelectrodes, and using pulse voltammetry techniques. The new approaches were partially successful. While distinct improvements in stability and sensitivity were observed with some of the changes, the electrode materials did not function well at high temperatures in caustic and with repeated use.

Carbohydrate chain cleavage reactions are a common occurrence during alkaline pulping and bleaching operations. 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.

Amylose, a water soluble,  $\alpha$ -linked glucose polymer, is severely degraded by the action of hot (100°C) alkali containing AQ. In contrast, cotton linters cellulose (a crystalline, water insoluble,  $\beta$ -linked glucose polymer) appears relatively unaffected by AQ at high (150°C) temperatures. Similarly, little differences in viscosity and molecular weight distributions have been seen for the carbohydrate fraction obtained from the pulping of wood by the soda and soda/AQ or kraft and kraft/AQ processes. Specific model studies have indicated that the reactivity difference between amylose and cellulose toward AQ is not related to the  $\alpha$ - or  $\beta$ -linkage difference, but to solubility differences.

It was of interest to compare the reactivity differences of amorphous and crystalline 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 (NaBH<sub>4</sub>) to prevent "peeling" losses in monomer units when heated in alkali. The viscosity losses as a function of time of heating at 150°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 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  $\mu$ 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. Some exploratory peroxide studies indicate that rather severe viscosity losses are associated with treating amorphous cellulose with hydrogen peroxide at pH 11 at 50-60°C; a combination of magnesium sulfate and sodium silicate was stabilizing.

Another way to study physical effects related to DP losses is to examine the reactions of an insoluble carbohydrate model which is chemically modified to prevent competing peeling reactions. Such an insoluble model has been produced by coupling a carbohydrate unit to a polymer. Two solvents, DMF and THF, have been employed in the coupling step; each led to a different degree of loading and distribution of model onto the polymer. Several new techniques have been developed to characterize the polymer supported carbohydrate models and it is now clear that some of the carbohydrate units in the DMF-produced model polymer are inaccessible with certain solvents. The polymer model degraded much slower in alkali at 170-195°C than the corresponding soluble model carbohydrate. Again, the results suggested that "physical" effects play a significant role in the rate of carbohydrate chain cleavage reactions.

SUMMARY OF RESULTS SINCE LAST REPORT:

Metals can have profound effect on the course of oxygen-alkali and peroxide reactions; therefore, the cotton linter sample, which was used to prepare amorphous cellulose samples, was analyzed for metals. Also, the typical caustic solutions were analyzed. Both showed quite low levels of the active (harmful) metals. Treatment of cotton linters and amorphous cellulose with  $\text{SO}_2$  to remove metals must be done with extensive care to keep the solution from becoming too acidic. We found that  $\text{SO}_2$  solutions at pH 2.3 caused no loss of viscosities for linters or amorphous samples; however, at pH values below 2.3, large viscosity losses were observed.

The molecular weight distribution of samples of amorphous and crystalline cellulose which had been heated in  $\text{NaCl}$  or  $\text{NaOH/AQ}$  at  $150^\circ\text{C}$  were determined by GPC techniques. The results were inconclusive with regard to AQ causing DP losses.

A sample of cotton linters (12% consistency) was treated with 0.2% hydrogen peroxide at  $50^\circ\text{C}$  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.

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  $\text{NaBH}_4$ . Samples were then exposed to  $\text{O}_2/\text{NaOH}$  and low levels of cobalt at  $100^\circ\text{C}$  for various time periods. The acid-treated linters showed severe viscosity drops with reaction time. The corresponding  $\text{NaBH}_4$  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.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

A detailed oxygen-alkali/cobalt study of viscosity changes with crystalline, amorphous, and kraft celluloses will be performed to confirm earlier results. Efforts will be made to publish the large backlog of results which exists from past carbohydrate research. This should be completed before anticipated changes in personnel occur.

POTENTIAL FUTURE ACTIVITY:

The extent of future activities will depend on how rapidly the new Georgia support personnel can be assimilated into the project activities following the move to Atlanta. 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.

PROJECT SUMMARY FORM

DATE: February 6, 1989

PROJECT NO. 3477: DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES

PROJECT LEADER: D. B. Easty

IPC GOAL: N/A

OBJECTIVE:

Evaluate and/or develop analytical techniques which are required to meet demands of both Institute and member company activity.

CURRENT FISCAL YEAR BUDGET: \$45,000

PRIOR RESULTS:

Consistent with the stated objective of this project, analytical method developments and evaluations have been directed at meeting a wide range of Institute and member company needs. Principal accomplishments since the start of this project are listed below:

Developed a method for estimation of pulping yield in continuous digesters from carbohydrate and lignin determinations.

Developed a gas chromatographic method for determination of elemental and polysulfide sulfur in kraft pulping liquors.

Discovered and evaluated several sources of error in the amalgam method for determining polysulfide in kraft white liquor.

Evaluated and validated the use of ion chromatography for analysis of pulping liquors.

Demonstrated the utility of the UV detector for sulfide in the ion chromatograph and the importance of diluting samples with oxygen-free water.

Evaluated ion chromatography for analysis of bleaching liquors. Discovered that ion chromatography could be used to determine chlorine dioxide.

Developed a method for estimation of lignin in pulp by diffuse reflectance Fourier transform infrared spectrometry.

Developed a method for reduction of paper interference in the identification of polymers in paper by pyrolysis-gas chromatography.

Revised the TAPPI Test Methods on ion chromatographic analysis of pulping and bleaching liquors.

Developed a method for detecting rosin size and alkyl ketene dimer in paper involving silylation of the paper and GC/MS analysis of the products.

SUMMARY OF RESULTS SINCE LAST REPORT:

Determination of Total Organic Chlorine in Pulp

A method has been developed for the determination of total organic chlorine (TOCl) in pulp samples. After the pulp is formed into a column in the stem of a funnel, potassium nitrate solution is passed through the column to remove chloride. The pulp is then pyrolyzed, and chloride produced by combustion of organic chlorine compounds is determined by coulometric titration. Pyrolysis and coulometric titration are performed in an adsorbed organic halogen (AOX) analyzer. Repeatability of the procedure is about 8%, and the detection limit is 5-10 ppm.

Pulps from which chloride had been removed yielded comparable results by this method and by neutron activation analysis. In addition, values for pulps analyzed by the new procedure and by an independent method in a member company laboratory were essentially identical.

A report describing the new procedure for TOCl in pulp has been issued to the membership (IPC Technical Paper Series 323) and submitted to Tappi Journal.

Analysis of Pulp by Near Infrared Spectrometry

The near infrared (NIR) spectrometer, on loan from Pacific Scientific, was started up in November. Studies have been conducted on use of NIR to quantify hardwood/softwood percentages in pulp blends and to estimate the lignin content of unbleached pulps.

Quantification of hardwood percentage in pulp blends by NIR was tested on six bleached pulps from a variety of sources. Percent hardwood, ranging from 5 to 95%, had been determined by microscopy in the IPC Fiber Science Laboratory. For these limited samples, NIR was able to estimate percent hardwood within about 2%; this precision is comparable to that of microscopy. The ability of NIR to distinguish between bleached hardwood and softwood is apparently due to differences in the pulps' carbohydrate composition. Effects of physical differences between the pulps are minimized by use of second derivative NIR spectra for the measurements. More samples must be run to confirm the validity of this technique.

Comparisons of second derivative NIR spectra of lignin (Indulin) and bleached pulps have revealed bands which should be useful for lignin estimation. However, because NIR bands from lignin are broad and overlap those from carbohydrates, the sensitivity of lignin estimations is influenced by the variability of the carbohydrate substrate. Spectral differences between species provide the basis for hardwood/softwood ratio measurements, but they add to the complexity of lignin content estimations. Thus, it seems unlikely that a single NIR calibration can be developed for estimation of lignin in all types of pulps.

A calibration line was prepared from laboratory-pulped aspen and oak with lignin contents between 1.4 and 6.9%; lignin values estimated by NIR were within about 0.1% of measured Klason lignin. Softwood (larch) pulps formed a line with a different slope. The ability of these separate lines to estimate lignin in a range of pulps from many hardwood and softwood species must be tested by analysis of more samples.

Pulps used for this study have been air dried and fluffed in an Abbe mill. Sampling errors were prohibitive when NIR measurements were attempted on pieces of dry pulp. Fluffed pulps with moisture contents of 10 and 15% exhibited differences in their NIR spectra. A way to correct for moisture will need to be developed in order to use NIR for estimating lignin in pulps with different moisture levels.

#### Student Research

Second year student M.S. research will be completed in March. The work of Bill Hagen will yield a rapid, microwave oven procedure for wet digestion of wood, pulp, and black liquor for metals analysis. A study by Ken Hull should reveal that the chromotropic acid method for free formaldehyde in paper produces erroneously high results.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Development of additional methods needed to support studies of chlorinated organics in bleaching effluents will continue to receive high priority. Variables in the European "AOX in pulp" method are presently under study. The European procedure is designed to estimate the sum of the chlorine compounds extracted from pulp during papermaking.

More samples will be analyzed to confirm earlier findings on uses of NIR for pulp characterization. The Fiber Science Laboratory will provide known hardwood/softwood mixtures for NIR testing. Pulps from different wood species cooked to varying lignin contents will also be needed for analysis by NIR. Development of a correction for pulp moisture content on lignin estimation will be attempted. Progress in this work will be dependent on the availability of personnel.

A paper on our NIR studies has been accepted for presentation at a workshop on Modern Methods of Analysis of Wood, Annual Plants and Bleach Effluents in Myrtle Beach, SC, May 19-21. This workshop will precede the Fifth International Symposium on Wood & Pulping Chemistry. The thrust of our current NIR work is to acquire data for that presentation.

#### POTENTIAL FUTURE ACTIVITY:

Future work will involve continued studies of pulp, paper, and liquors by chromatographic and spectrometric techniques.

Application of near infrared spectrometry for determination of coatings and additives in paper should be fully evaluated. Paper is, within a grade, a much more uniform substrate than pulp. This property should minimize sampling errors and enhance the ability of NIR to quantify coatings and additives.

PROJECT SUMMARY FORM

DATE: February 8, 1989

PROJECT NO. 3524: FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT LEADER: U. P. Agarwal

IPC GOAL:

A significant increase in yield of useful fibers

OBJECTIVE:

Establish mechanism for brightness loss in high yield pulps.

CURRENT FISCAL YEAR BUDGET: \$170,000

PRIOR RESULTS:

Optical equipment has been put in place to evaluate both color development and photobleaching. This has been used to arrive at a comprehensive theory for color change on exposure to light. The kinetics of the yellowing reaction have been established and comparisons made between bleached and unbleached, hardwood and softwood sheets. Laboratory results have been verified by outdoor exposure to sunlight.

Bleached sheets yellow at a faster rate than unbleached. Heavy metals do not have a major effect on light-induced yellowing. Direct reaction with singlet oxygen suggests that singlet oxygen is not directly involved in the yellowing reaction. We have support, but no positive proof, that photobleaching is a result of triplet oxygen interaction with the quinone triplet state. ESR work has confirmed the presence of radicals generated in the sheet on exposure to light. An IPC Ph.D. thesis by S. Lebo entitled "Formation of ortho-quinonoid structures in high-yield pulp lignins" has been completed. The contribution of ortho-quinonoid lignin structures to the absorbance of yellowed spruce pulp has been quantified. A novel method based on formation of the phosphite ester and subsequent  $^{31}\text{P}$  NMR analysis was developed to aid in the quantification. While the o-quinonoid lignin structures are a major reason for color development on exposure to light, other colored structures are present. These may originate in the carbohydrate component of the pulp. Acetylation has been used to give sheets with greatly reduced yellowing. Mechanistic implications are being considered.

The Raman equipment necessary to study the initial photochemical reactions is installed. Equipment evaluation trials are in progress. Preliminary model compound studies aimed at establishing the initial photochemical pathway for yellowing have been completed. The relative occurrence of fluorescence vs. phosphorescence is being investigated. Ferulic acid has been shown to be formed during the photoyellowing of white spruce handsheets. Raman spectroscopic studies as well as GC mass spectroscopic analyses were used to obtain direct evidence in its detection. FTIR data were found to be in agreement. Mechanistic implications are being considered.

#### SUMMARY OF RESULTS SINCE LAST REPORT:

Further analyses of the sheet extracts by GC/MS have clearly established the presence of cis and trans ferulic acids in the photoyellowed handsheets. In view of these findings, a number of studies were initiated in order to investigate the role of cis ferulic acid in the yellowing process. Although some of these studies are ongoing, results obtained recently are reported in the following.

#### Ferulic Acid Detection by HPLC

High performance liquid chromatography was applied and further developed in order to achieve good separation between the peaks of ferulic acid isomers. The technique was then used to isolate small quantities of pure cis ferulic acid. Moreover, when yellowed handsheet extract was analysed by HPLC, peaks corresponding to cis and trans ferulic acid were detected. In our work with liquid chromatography, we have noted that the values of the molar extinction coefficients of the two isomers are solvent & pH dependent.

#### Isolation and Spectroscopic Studies of cis Ferulic Acid

In order to make better utilization of the spectral data, individual contributions from the ferulic acid isomers need to be sorted out. This would also be useful if one of these techniques were to be used for quantification purposes. In view of this, we decided to study cis ferulic acid spectroscopically. Commercially obtained ferulic acid is predominantly trans and cis isomer needed to be prepared. In order to obtain pure cis isomer, a mixture of cis/trans ferulic acid was produced by UV light exposure and was separated by HPLC. Several eluting fractions containing cis ferulic acid were collected and from these cis isomer was recovered. The obtained sample was studied by UV/Vis, FTIR, and Raman techniques. Such results not only support our earlier conclusions, but make possible spectral data assignments in terms of specific isomers.

#### Laser Irradiation (514.5nm) of cis Ferulic Acid

Ar ion laser induced changes in the cis ferulic acid needed to be studied in order to look at the individual contributions of the isomers to the yellowed handsheet Raman spectrum. Cis ferulic acid at the fiber surface, when laser exposed, is thought to undergo similar changes. Two observations were made on the basis of the behaviour of cis isomer in the laser beam. One, significant fluorescence levels were present in the spectrum due to this sample. Secondly, upon continued laser exposure Raman signal-to-background ratio improved considerably. The latter resulted from thermally induced cis to trans transformation, as was evident by the before and after the Raman experiment analyses of the sample by HPLC. We think that the Raman features in the spectrum are solely due to trans ferulic acid and the cis conformer is primarily responsible for the fluorescence. This interpretation provides us insights in to what actually happens when spectra are obtained from the yellowed handsheets.



### Reaction of 1-thioglycerol with Ferulic Acid

1-thioglycerol is known to stabilize high-yield pulps against photoinduced color reversion. We wanted to see how it affects trans/cis ferulic acid isomerization reaction. To study this, 1-thioglycerol was mixed with trans ferulic acid solution and UV irradiated for several hours. The photoirradiated solution was then analysed by HPLC along with the irradiated control. The solution containing the stabilizer was found to have depleted in ferulic acid. This result is interesting as it provides one mechanistic pathway for the stabilizing action of 1-thioglycerol. Further studies are, however, needed.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Research activity is planned to bring together several aspects of the ferulic acid research.

We will proceed on the topic of quantification of ferulic acid in pulps. We have begun the process of comparing suitability of various analytical techniques for this purpose. If ferulic acid can not be quantified directly in the handsheets and is to be isolated, role of prevailing conditions under which such an isolation occurs may have to be studied.

Another topic of interest is the study of cis/trans ferulic acid isomerization reaction. This isomerization reaction is sensitive to factors like pH, solvent and solute concentration. In addition, of relevance to us will be the effect of microenvironment at the fiber surface.

An M.S. thesis is aimed at looking in to the possibility of ferulic acid - trimethyl phosphite reactions. Now we know that ferulic acid is present in the yellowed handsheets, however, its fate upon TMP treatment needs to be determined. Moreover, such information will be helpful in order to quantify various chromophoric contributions to yellowing.

Investigations focused on the mechanisms of photoformation of ferulic acid will be started. To begin with, photochemistry of coniferyl alcohol in a number of environments will be looked at.

Thermally-yellowed pulps, treated pulps, and hardwood-based pulps will be analysed for ferulic acid and other chromophores.

#### POTENTIAL FUTURE ACTIVITY:

Several interesting topics are presently seen as targets of potential research. A number of them are briefly mentioned in the following; priorities will be assigned in the near future.

A need exists for assigning contributions to yellowing by the two types of chromophores, namely cis ferulic acid and ortho-quinonoids. Research activity will be directed at this point.

Work on the topic of time resolved studies at the macro as well as higher temporal resolution levels will be started at once. Such an endeavor will help

define the dynamical aspects of lignin photobehavior in the wood pulps. Moreover, overall photoyellowing reaction will be defined at several levels of detail. Such detailed knowledge is indeed desirable for designing reaction schemes that will succeed in stopping color reversion of high-yield pulps.

Finally, as one becomes knowledgeable in these matters, and opportunities arise for application of such information to block unwanted pathways, attempts will be made to solve yellowing problems.

RELATED STUDENT RESEARCH:

G. Furman, Ph.D.-1986; D. Dallow, M.S.-1986; S. Lebo, Ph.D.-1987;  
P. Medvecz, M.S.-1987; C. Stoffler, M.S.-1987; D. Meyer, M.S.-1990.

PROJECT SUMMARY FORM

DATE: February 17, 1989

PROJECT NO. 3566: STRONG, INTACT HIGH YIELD FIBERS

PROJECT LEADERS: T. J. McDonough, S. Aziz

IPC 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 and physical form of the resulting fibers. The mechanical properties should be as good as or better than those possessed by the fiber as it existed in the original wood, and the geometrical form of the original fibers should either be preserved or altered in controlled directions. Develop bonding methods applicable to strong, high lignin fibers that will translate fiber characteristics to desired paper and board properties.

CURRENT FISCAL YEAR BUDGET: \$150,000

PRIOR RESULTS:

Chemimechanical pulps have been prepared with sheet strength approaching that of kraft and containing fibers having a higher breaking load than kraft fibers. Fibers sampled from high yield pulps have been shown to be stronger than corresponding wood sections, indicating that at least some of the fibers in the pulp have retained much or all of their native strength. On the other hand, measurements of the strengths of classified fibers have shown that strength and length are correlated, suggesting that events that shorten fibers also reduce their strength.

Batch laboratory fiberizations have provided information on the fiber separation mechanism and its implications. Thermal softening was shown to have important effects only at short retention times and only for wood which had not been chemically pretreated. Increasing temperature had a negative effect on the efficiency of fiber separation from pretreated pulps.

A series of trials were run in a member company's thermomechanical pulping pilot plant to establish the effect of fiberization temperature on fiber strength retention. The results show that fiberization at 160°C gives stronger fibers than at 120°C, and that fiber fragments tend to be weaker than intact fibers. These findings suggest that fiber strength is reduced during fiber separation, and that the extent of the damage increases with increasing resistance to separation. This, in turn, implies that conventional thermomechanical pulping sacrifices strength for surface development by separating fibers at less than the optimum temperature for fiber strength retention.

Efforts to cause strong, intact chemimechanical pulp fibers to form a sheet with kraftlike strength have continued. Chemical treatment followed by refining has given sheets of tensile strength in excess of 8 km breaking length; hot pressing and artificial bonding were less successful (6 and 5 km respectively). Addition of kraft fines has given promising initial results with unrefined samples; work is in progress to assess the combined effects of fines addition and refining.

In related student research the distribution of bound sulfur in the cell walls of chemically pretreated wood has been investigated, in view of its implications for chemimechanical pulp properties. A gradient within the S<sub>2</sub> layer was observed under all treatment conditions. The distribution can be manipulated to a limited extent by varying liquor pH and Na<sub>2</sub>SO<sub>3</sub> concentration. In addition, a study of prehydrolysis as a pretreatment in chemimechanical pulping has revealed beneficial effects that may lead to a new pulping process.

SUMMARY OF RESULTS SINCE LAST REPORT:

There was no activity on this project during the past six months.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Because of staff limitation, no work is planned in the upcoming period.

POTENTIAL FUTURE ACTIVITY:

Emphasis will be placed on understanding the factors that limit the contribution of fiber strength to sheet strength. This will include studies of the mechanism of failure of sheets made from strong, high-yield fibers. The relationship of cell wall composition and component distribution to fiber and bond properties will also be explored.

PROJECT SUMMARY FORM

DATE: February 6, 1989

PROJECT NO. 3605: COMPUTER MODEL OF RECOVERY FURNACE

PROJECT LEADER: T. M. Grace

IPC GOAL: Increase the capacity potential of processes

OBJECTIVE:

Develop a comprehensive, three-dimensional, mathematical model of the fireside processes in a kraft recovery furnace. The model would be based on first principles and would incorporate and integrate the results of ongoing fundamental studies of black liquor combustion.

CURRENT FISCAL YEAR BUDGET: \$80,000

PRIOR RESULTS:

This project was initiated in the Fall of 1986 as three concurrent Ph.D. theses. The concept is a three-dimensional model of the processes going on in the furnace cavity (up to the entrance into the screen or superheater section). This model is envisioned as an effective way of translating the fundamental knowledge of black liquor combustion being obtained in other research programs into improvements in recovery boiler performance. The modeling effort is divided into three distinct parts (each a thesis):

1. a model of the char bed,
2. a model of liquor supply and in-flight behavior,
3. an overall model integrating the other two models along with air/flue gas flow patterns, gaseous reactions, and heat transfer.

The overall model provides the core and structure for the entire effort. It is formulated in an Eulerian coordinate frame using a cellular description of the furnace space. After a period of examining different options, we have decided to base the furnace model on the FLUENT software package. This is basically a finite difference package for modeling fluid flows. Additional features of FLUENT include a six-flux radiation model, the PSI-CELL model for two-phase flow, a combustion model, and a number of turbulence models. The initial modeling effort was directed toward predicting cold-flow behavior in recovery boiler geometries. This was done for two reasons: first it is the least complicated situation we need to deal with, and second, data were available from cold-flow tests on scale-model furnaces to check the model predictions. A 10,000 node version of the FLUENT program was used for this stage of the effort. In general, the bulk flow behavior, particularly in the upper furnace, matched the experimental data reasonably well. It is clear, however, that 10,000 nodes is insufficient for a proper description, particularly near the bed and when focusing on individual air jet behavior. A 50,000 node version of the program was obtained and was found to be adequate. The source code was also made available to us to allow modifications for our purposes.

The liquor supply and in-flight model is formulated partially in a Lagrangian reference frame (moving with the particle). Trajectory equations are formulated based on Newtons Law and include mass changes, gravity and aerodynamic drag. For each particle, drying, pyrolysis and volatiles burning, char burning and smelt reoxidation are modeled in a Lagrangian frame. The PSI-CELL (Particle Source in Cell) subprogram is used to transform the information from the Lagrangian frame to the Eulerian frame required by the main model. This part of the effort is highly coupled with the overall model, because gas flow patterns and temperatures have a major influence on droplet trajectories and behavior. At the time of the last report, we were in the process of integrating the particle and gas flow models. The bed model was in the process of being developed and had not yet been integrated into the rest of the model. We were expecting to begin the convergence of the first base case in late spring.

#### SUMMARY OF RESULTS SINCE LAST REPORT:

FLUENT/RFM is a fundamental 3-dimensional model of a kraft recovery furnace based on a finite-volume solution of the governing equations for mass, momentum, energy and species concentration for the gas phase. In-flight burning of liquor drop/particles and bed burning are included and affect the gas phase through source and sink terms. The core of the model, FLUENT, is a commercially available computational fluid dynamics code marketed by Create, Inc.

A converged solution of a recovery furnace simulation using all the features in FLUENT/RFM was obtained. Convergence involved a certain amount of operator interaction as it proceeded and required 3500 iterations and some twelve trillion math operations. Approximately 3-4 months of continuous CPU time on a MicroVAX II is required to converge a simulation starting from scratch.

The base case simulation gave results which were consistent with experience. A large central core of hot, oxygen-deficient, high upward velocity gas formed from the convergence of primary and secondary air in the lower furnace. The tertiary air did not break up this core. A substantial amount of in-flight burning occurred and the solids reaching the bed tend to arrive around the perimeter of the furnace. Simulations of the char bed have demonstrated the importance of carbon gasification reactions in bed burning. The critical influence of bed shape on gas flow patterns was also demonstrated.

Two of the Ph.D. students, Walsh and Jones, who developed the model have defended their theses and left. The third Ph.D. student, Sumnicht, will finish in March/April. That will close the initial development phase of the model. An M.S. student, Tom Kindler, has started working on the model. The initial focus of his work is familiarization and documentation.

#### PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

There are two main short term activities; documentation of the current model and planning for further development aimed at greatly reducing the time for a solution and at validating the model.

A proposal for funding model speedup and validation is being prepared. Speeding up convergence involves two aspects: modifying the code to increase the speed of the solution algorithms and running the model on an intrinsically faster machine. Both avenues are being addressed. Code modifications of the type envisioned would probably best be done at Creare, Inc.

In the meantime, further simulations and model sensitivity tests will be carried out.

POTENTIAL FUTURE ACTIVITY:

There are some clear areas where the model needs further development. It would be very desirable to use a 250,000 node version which would get rid of the symmetry assumption and which would permit greater detail around the bed and the air entry regions. It would also allow the elimination of nodes where one dimension is much larger (or smaller) than the other two. For this to be feasible, the code would have to be developed to run on a faster machine than the one currently being used.

It is also necessary to add sulfur release and recapture chemistry and fume production to the model. Since these processes are not expected to have a large effect on gas flow patterns and the general combustion process, they could be put into an auxiliary program that would use an already converged solution from the current model as an input.

Great insight can be obtained with the current model. We will have just scratched the surface of understanding what is going on inside the furnace when the current students are finished. An object code version of the model that could be used by others would be quite useful, provided it is realized that this model's prediction cannot be taken literally and quantitatively.

RELATED STUDENT RESEARCH:

This entire effort is being done through student research. The three Ph.D. students are:

Andy Jones	- overall model	- finished
Allan Walsh	- in-flight model	- finished
Dan Sumnicht	- char bed model	- finished March/April
Tom Kindler	- M.S. student	- continuity

PROJECT SUMMARY FORM

DATE: February 10, 1989

PROJECT NO. 3657-2: KRAFT BLACK LIQUOR DELIVERY SYSTEMS  
(DOE FUNDED PROJECT)

PROJECT LEADER: T. N. Adams

IPC GOAL: Increase the capacity of existing systems

OBJECTIVE:

Optimize black liquor spray systems for decreased carryover and improved furnace combustion.

CURRENT ANNUAL BUDGET: \$300,000

PRIOR RESULTS:

This is the first report on the project. Previous contract work on black liquor sprays resulted in a small data base of droplet size distribution from both types of commercial black liquor spray nozzles.

SUMMARY OF RESULTS SINCE LAST REPORT:

A second set of black liquor spray trials increased our data base on droplet size distribution. It also resulted in the identification of spray stability as a crucially important feature of these sprays. As well, the limiting resolution of the flash x-ray technique for black liquor sprays was determined.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

Following calibration tests, the extent of spray instability will be mapped for both of the commercial black liquor spray nozzles. An alternative high speed video camera will be acquired for laboratory and field testing.

POTENTIAL FUTURE ACTIVITY:

Initial feasibility for direct observation of sprays in operating recovery boilers with high speed video seems very promising. If this is confirmed, field trials could be carried out during the period when IPC is moved to Atlanta.

RELATED STUDENT RESEARCH:

Ph.D. research is being carried out by Tom Spielbauer on black liquor spray size distribution. His topic deals with the fundamental mechanism of droplet formation from liquid sheets.



PROJECT SUMMARY FORM

DATE: February 20, 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: \$161,000

PRIOR RESULTS:

The research 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 can be oxidized to benzoquinones, which in turn can be modified by Diels-Alder reactions into anthraquinone type pulping catalysts. The synthetic yields are respectable and the Diels-Alder products have moderate to excellent pulping activity. The process (lignin  $\longrightarrow$  catalysts) has potential for providing an inexpensive, selective, sulfur-free pulping process.

SUMMARY OF RESULTS SINCE LAST REPORT:

The oxidative procedures developed by Wozniak were reexamined to familiarize present personnel and 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 have been 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. At the present time we suspect that the products are over-oxidizing.

Wozniak had to estimate some product yields because authentic samples were not available. We have now synthesized these samples and have attempted to obtain reproducible gas chromatography (GC) response factors. Straight analysis and analysis after derivatization (reductive acetylation and methylation) have been examined. Water solubility and high volatility make the analysis difficult.

The Fremi salt oxidation of lignin models has also been extensively studied. The analysis of products here is also complicated. The stability of benzoquinone and hydroquinones on the GC columns is a concern. Analysis by UV and by reductive acetylation has been applied here. 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 organosolv aspen lignin pulping liquor extracts (EtOAc). Supercritical fluid extracted aspen kraft black liquors and steam exploded lignin are presently being evaluated.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

We will continue to assess the suitability of different substrates as starting materials for the synthesis of pulping catalysts from lignin. The generation of benzoquinones from lignin by electrochemical techniques will be more thoroughly explored. Other oxidization agents for quinone generation from lignin will be pursued. The possibility of performing Diels-Alder reactions in supercritical solvents will be examined. Direct ways of producing multi-ring quinones with specific substituted dienes will be investigated.

POTENTIAL FUTURE ACTIVITY:

The following areas would appear to be suitable research goals:

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

PROJECT SUMMARY FORM

DATE: February 20, 1989

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

IPC GOAL:

Eliminate, or minimize, dioxins in pulp production

OBJECTIVE:

The proposed research involves developing a fundamental understanding of the chemistries associated with dioxin production and degradation during wood pulping and bleaching operations. Dioxin levels appear to be closely related to the levels of dibenzo-p-dioxane (DBD) and dibenzofuran (DBF) in the pulp and liquors. Therefore, understanding the reactivities of the DBD/F compounds appears critical. The goal is to prevent the conversion of DBD/F, or any other precursor, to chlorinated DBD/F derivatives (the dioxins) or to destroy dioxins that may be present in bleached pulps and liquors.

CURRENT FISCAL YEAR BUDGET: \$25,000

PRIOR RESULTS:

This is a new project.

SUMMARY OF RESULTS SINCE LAST REPORT:

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 eightly closely related compounds. The literature contains few reports of reactions of DBD/F, other than chlorination and nitration. The information is being gathered into a report, together with suggestions for research areas which should be pursued to understand dioxin formation.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1989:

A proposal will be submitted to API/NCASI for funding future research at the Institute aimed at developing a fundamental understanding of DBD/F and dioxin reactivities, especially related to reactions of the type encountered in pulping and bleaching systems.

POTENTIAL FUTURE ACTIVITY:

The extent of future activity in this project will be related to the extent of research funds which become available. The anticipated level of activity would be a principal investigator (D. Dimmel) part-time, a postdoctoral fellow full-time, a technician half-time, and personnel at an outside laboratory, as needed, to perform toxic chemical reactions and analyses.