

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

March 22-23, 1988

The Institute of Paper Chemistry

Appleton, WI 54912



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Institute of Paper Science and Technology
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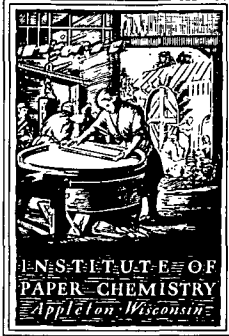
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Your advice and suggestions on any of the projects will be most welcome.



THE INSTITUTE OF PAPER CHEMISTRY
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February 26, 1988

TO: Members of the Pulping Processes Project Advisory Committee

The next meeting of the Pulping Processes PAC will be held in Appleton on March 22 and 23, 1988. The meeting will convene Tuesday morning at 8:30 a.m. 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) preliminary project forms for the next fiscal year (July 1988 through June 1989),
- (D) information on the IPC midrange plan,
- (E) a list of current M.S. and Ph.D. student work,
- (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

February 26, 1988
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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 planning items will be reviewed at the evening session. First, the technical program for the upcoming year (July 1988 to June 1989) will be discussed, with emphasis on objectives and research plans for each project. Second, IPC's longer range project plans will be summarized in the context of the IPC midrange plans.

The evening session will consist of a brief summary of our upcoming research program plus a discussion of a recent RAC survey concerning the research needs of the paper industry. We are planning to put together a revised long range plan for IPC research in the next few months. We will discuss mechanisms for getting your input at the meeting.

See you in Appleton!

Sincerely,



Earl W. Malcolm
Director
Chemical Sciences Division

EWM/gmk
Enclosures

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AGENDA

PULPING PROCESSES PAC MEETING
March 22-23, 1988The Institute of Paper Chemistry
Continuing Education Center
Appleton, WisconsinTuesday, March 22

7:00 a.m.	BREAKFAST	
8:30	CONVENE	D. Johnson
8:35	RESEARCH OVERVIEW	E. Malcolm
8:50	PROJECT PRESENTATIONS	
	KRAFT CHEMICAL RECOVERY	T. Grace
	Fundamental Processes in Alkali Recovery Furnaces (Project 3473-1)	J. Cameron
	Black Liquor Combustion (DOE supported)	D. Clay
	Black Liquor Sprays (DOE supported)	T. Spielbauer
	Computer Model of Recovery Furnace (Project 3605)	K. Goerg
10:45	BREAK/TOUR	
	CHEMICAL PULPING	
	Fundamentals of Selectivity in Pulping and Bleaching (Project 3475)	D. Dimmel
	Development and Application of Analytical Techniques (Project 3477)	J. Wozniak
		D. Easty
12:00 noon	LUNCH	
1:00 p.m.	PROJECT PRESENTATIONS (continued)	
	Improved Processes for Bleached Pulp (Project 3474)	T. McDonough
	Fine Structure of Wood Pulp Fibers (Projects 3288 and 3521 [IPC/DOE])	R. Atalla
	Raman-Based Lignin Sensor (FKBG/DOE/IPC)	R. Atalla

3:00	BREAK		
	HIGH YIELD PULPS		
	Strong, Intact High Yield Fibers (Project 3566)		T. McDonough
	Fundamentals of Brightness Stability (Project 3524)		E. Malcolm U. Agarwal
5:00	SOCIAL HOUR		
6:00	DINNER		
7:00	EVENING DISCUSSIONS		
	Research Program for July 1988 to June 1989		E. Malcolm
	IPC Midrange Plan		

Wednesday, March 23

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 18-19, 1988

PRELIMINARY RESEARCH BUDGETS (1988-1989) - CHEMICAL SCIENCES DIVISION (\$1000)

<u>IPC FUNDED</u>	<u>88/89</u>	<u>87/88</u>	<u>Difference</u>	<u>% +/-</u>
<u>Chemical Pulping</u>				
3288 - Fine Structure of Wood Pulp Fibers	65	70		
3475 - Fundamentals of Selectivity in Pulping and Bleaching	90	150		
3474 - Improved Processes for Bleached Pulp	150	60		
3477*- Development and Application of Analytical Techniques	<u>15</u>	<u>13</u>		
	320	293	+ 27	+ 9
<u>Recovery</u>				
3473-1-Fundamental Processes in Alkali Recovery Furnaces	250	250		
3456-2-Smelt-Water Explosions	20	20		
3477* -Development and Application of Analytical Techniques	10	13		
3605 -Computer Model of Recovery Furnace	<u>80</u>	<u>40</u>		
	360	323	+ 37	+ 11
<u>High Yield Pulping</u>				
3566 - Separation of Strong, Intact Fibers	150	175		
3524 - Fundamentals of Brightness Stability	170	140		
3521-2-Molecular Structure of Woody Tissue - Raman Microprobe	50	45		
3477*- Development and Application of Analytical Techniques	<u>10</u>	<u>13</u>		
	380	373	+ 7	+ 2
<u>Other</u>				
3477*- Analytical (Paper)	10	21		
3534 - Exploratory Research	<u>60</u>	<u>60</u>		
	70	81	- 11	- 14
	<u>70</u>	<u>81</u>		
TOTAL IPC FUNDED	1,130	1,070	+ 60	+ 6
<u>CONTRACT RESEARCH</u>				
<u>Government Funded</u>				
3473-6-Fundamental Studies of Black Liquor Combustion				
	IPC	182	230	
	NBS	50	135	
3521-3-Molecular Structure of Woody Tissue - Raman Microprobe	72	102		
New-Lignin Sensor (DOE)	75	-		
New-Improved Pulping Process (DOE/SERI)	93	-		
New-Black Liquor Spray (DOE)	<u>500</u>	<u>-</u>		
	972	467	+505	+ 108
<u>Nongovernment Funded</u>				
Pulping/Bleaching	100	-		
Analytical Services	200	200		
FKBG (lignin sensor)	60	50		
Environmental	300	200		
Other	<u>50</u>	<u>100</u>		
	710	550	+160	+ 29
TOTAL GOVERNMENT AND NON-GOVERNMENT RESEARCH	1,682	1,017	+665	+ 65
TOTAL FUNDED AND CONTRACT-----	2,812	2,087	+725	+ 35
	(60% Contract)	(49% Contract)		
	(40% Funded)	(51% Funded)		

* Portion of project assigned to this area

EWM/gmk
2/8/88

PROJECT TITLE: FINE STRUCTURE OF WOOD PULP FIBERS

PROJECT STAFF: R. H. Atalla

PRIMARY AREA OF INDUSTRY NEED: Properties related to
End Use

PROGRAM AREA: Performance and Properties of Paper
and Board

Date: 2/8/88

Budget: \$65,000

Period Ends: 6/30/89

Project No.: 3288

Approved by VP:

PROGRAM 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.

PROJECT OBJECTIVE:

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

PROJECT RATIONALE:

The properties of a paper web depend on the properties of the fiber used in its manufacture. Fundamental relationships between fiber and paper properties are being addressed in other IPC projects. Fiber properties are, in turn, determined by the fine structure of the fiber, from the microscopic down to the molecular level. Relationships at this level are the subject of the present project. Two classes of questions are addressed: (1) the degree to which the composite character of native cellulose (coexistence of the I_{α} and I_{β} forms) expresses itself in fibers from woody tissue, and (2) the degree to which the linear hemicelluloses as well as oligomers of lignin, which coexist with cellulose in wood fibers, are integrated into the cellulose in a mixed semicrystalline lattice. An indirect expression of these questions is the hypothesis that the physical structure of cellulose in wood pulp fibers is determined as much by the sequence of events during isolation, as by its native state. We are testing the hypothesis and addressing the structural questions. We are also continuing the effort to develop quantitative measures of the variability of structure so that the structural information can be correlated with fiber properties.

RESULTS TO DATE:

Relaxation and spin diffusion studies utilizing solid state ^{13}C NMR, have confirmed the presence of the two crystalline forms I_{α} and I_{β} and indicate that the I_{α} component in celluloses from higher plants may be as low as 10%. The results also indicate that the I_{α} component is more susceptible to degradation, and generally more reactive than the I_{β} component. Particularly significant are recent results showing differences in this respect between celluloses isolated from the same wood source utilizing different pulping procedures.

Raman spectral studies on water immersed cellulosic samples continue to provide valuable new information on differences between the structures of different celluloses that may be obscured during drying. Studies on a series of never dried, dried, and rewetted celluloses provide clear evidence that drying causes sufficient stresses at the fibrillar level to result in lattice distortions. Some irreversibility in drying effects has also been detected at the molecular level, and provide some insight concerning difficulties in hydration of recycled fibers.

Studies of aggregation of other β -1,4 linked polysaccharides, as well as some lignin precursors, with cellulose, continue to support the hypothesis that they may indeed be integrated into the cellulose lattice in native woody celluloses.

PLANNED ACTIVITY FOR THE PERIOD:

Continue the work using Solid State ^{13}C NMR, x-ray diffraction and Raman spectroscopy to define cellulose and hemicellulose structure in native materials. Relate variations in structure to differences in mechanical properties, chemical reactivities and process response.

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.

STUDENT RELATED RESEARCH:

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

PROJECT TITLE: SMELT-WATER EXPLOSIONS

PROJECT STAFF: T. M. Grace

PRIMARY AREA OF INDUSTRY NEED: Capital Effectiveness:
Improvement of capital productivity for existing
processes

PROGRAM AREA: Recovery Systems

PROGRAM GOAL: Increase the capacity potential of processes

PROJECT OBJECTIVE:

Decrease in frequency (and ultimately elimination) of destructive explosions in recovery boilers. Continual evaluation of underlying causes of recovery boiler explosions and dissemination of that information to operating personnel. An increased understanding of the phenomena of smelt-water explosions and the application of that knowledge to reduce the hazard of smelt-water contacts.

PROJECT RATIONALE:

Recovery boilers are subject to the special hazard of smelt-water explosions as well as the normal hazards of all combustion equipment. The costs of this problem are borne through reduced unit availability and high insurance premiums. Recently there is much concern about the continued insurability of recovery boilers and a greater fraction of the risk of a major outage is being borne by the mills. A better understanding of the underlying causes of explosions and the dissemination of this information to the operations side of the industry can lead to a reduction in the number of serious explosions. In the long range, knowledge of the nature of smelt-water explosions can permit the development of means for reducing the level of violence when a smelt-water contact occurs.

RESULTS TO DATE:

The experiences in the industry on explosions and recovery boiler safety continue to be monitored. In the past few years we have played a major role in identifying combustible gas explosions originating from black liquor pyrolysis as a distinct hazard and getting the industry to recognize this hazard by working with the API Recovery Boiler Committee and BLRBAC. Our analysis of past incidents also identified that over two-thirds of the recent recovery boiler explosions involved a failure to follow generally recognized safe practices to some extent. This has helped to focus attention on the role of management and operator training in this continuing problem.

We carried out on-site investigations of four major recovery boiler explosions in 1987, either under the auspices of API Recovery Boiler Committee or consultation contracts. We have kept abreast of regulatory and insurability issues and are serving as a member of API's task force on recovery boiler safety.

A separate project (3575) funded by the Nuclear Regulatory Commission has been completed. The first phase determined the energy released from a number of actual explosions and compared this with thermodynamic estimates of the maximum potential energy release based on the amounts of smelt and water present. The second phase dealt with scaling criteria for this type of explosion based on models of the explosion process. This analysis provided a convincing rationale that smelt-water explosions in recovery boilers are inherently low efficiency events.

Date: 2/8/88

Budget: \$20,000

Period Ends: 6/30/89

Project No.: 3456-2

Approved by VP-R:

We continue to keep abreast of the state of knowledge concerning the physical phenomena involved in smelt-water explosions as it is developed at other universities and laboratories.

PLANNED ACTIVITY FOR THE PERIOD:

Remain active in API Recovery Boiler Committee and BLRBAC.

Pursue opportunities defined by API Safety Task Force.

Pursue implications of the explosion energetics results from the NRC study.

POTENTIAL FUTURE ACTIVITIES:

Greater involvement in safety education and audit activities.

PROJECT TITLE: FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES

PROJECT STAFF: T. M. Grace, J. H. Cameron, D. T. Clay

PRIMARY AREA OF INDUSTRY NEED: Capital Effectiveness: Improvement in productivity from existing units

PROGRAM AREA: Recovery Systems

PROGRAM GOAL: Increase the capacity of existing systems

PROJECT 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 production, and fume formation. The final goal is a comprehensive theory of black liquor combustion.

PROJECT RATIONALE:

Current recovery boilers have undergone an evolutionary development with little basic knowledge of the black liquor burning process available for guiding design or operation. Significant increases in capacity or thermal efficiency of existing recovery boilers will require major process changes which are unlikely to be found by simple empirical optimization methods. A much better understanding of black liquor combustion fundamentals is needed to guide optimization strategies.

RESULTS TO DATE:

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.

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 experimental part and analysis of the phenomenological study of black liquor burning behavior using the single-particle reactor has been completed. A report on all of this work is in preparation. The collaborative effort with Prof. Mikko Hupa of Abo Akademi in Finland on this problem is continuing.

Initial studies of the reaction of H₂ gas with Na₂SO₄ and Na₂CO₃ under high temperature conditions have been completed. The implications of this work are being pursued.

Date: 2/8/88

Budget: \$250,000 *

Period Ends: 6/30/89

Project No.: 3473-1

Approved by VP:

* Additional support through DOE under Project 3473-6.

Ph.D. theses on swelling during pyrolysis, drying of black liquor drops, and char burning under an impinging jet have been completed. Student research is also underway on single-particle combustion, fume formation during particle burning, fume condensation/deposition, sulfur release during pyrolysis and burning, corrosion of steel by smelt, and liquor spray characteristics.

PLANNED ACTIVITY FOR THE PERIOD:

A substantial part of the effort will be support of two large DOE sponsored projects, the existing black liquor combustion project and a new black liquor spray study using flash radiography for quantitative characterization of existing spray nozzles and testing of novel nozzle designs. The combustion project will focus on completing char bed burning work and preparing a summary report. The spray project will focus on characterization of standard nozzles.

Work on fuming will continue primarily through student research on fume formation during single-particle burning and on condensation behavior. There will be increased emphasis on the role that fume particles play in boiler plugging.

Work on reactions between smelt constituents and hydrogen will continue.

Work on sulfur release during pyrolysis and liquor burning will continue as a student thesis.

The phenomenological burning study will be completed.

A comprehensive, quantitative model of single-particle burning will be developed.

Studies of corrosion reactions will be carried out in cooperation with the IPC Corrosion Group, partially through student theses.

POTENTIAL FUTURE ACTIVITIES:

Expanded corrosion studies in cooperation with the Corrosion Group.

Simulation of new black liquor combustion process concepts on the DOE Continuous Flow Reactor.

Work with individual companies, trade associations and manufacturers in applying results for improved recovery boiler operation.

Initiate studies of the burning behavior of spent liquor from high yield pulping processes.

Initiate studies of burning behavior of chlorine-containing effluents.

STUDENT RELATED RESEARCH:

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

PROJECT TITLE: IMPROVED PROCESS FOR BLEACHED PULP

Date: 2/8/88

PROJECT STAFF: T. J. McDonough, B. Bihani

Budget: \$150,000

PRIMARY AREA OF INDUSTRY NEED: Capital Effectiveness:
Reduction of capital intensity of new units

Period Ends: 6/30/89

PROGRAM AREA: Reduction of Process Complexity

Project No.: 3474

PROGRAM GOAL: To improve the process for production of bleached chemical pulp

Approved by VP:

PROJECT OBJECTIVE:

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

PROJECT RATIONALE:

Conventional multistage bleaching of standard kraft pulps requires complex bleach plants of high capital cost and produces an effluent that represents a major problem for the industry. These problems can be attacked by modifying the pulping process to allow easier bleaching and by the development of nonchlorine bleaching processes.

The pulping process modifications should result in a reduction in the amount of residual lignin and should change the structure of this lignin to render it easier to remove. Ideally, the bleaching process should produce an effluent which can be recycled to a standard recovery boiler. At the very least, it should not contain significant amounts of chlorinated organics such as dioxin that can cause environmental problems. In practice, this means a nonchlorine bleaching process, likely based on oxygen. This could turn the effluent problem into an advantage, in the form of increased energy recovery. Combined improvements in pulping and bleaching technology may lead to fewer, smaller bleaching stages, with reduced needs for effluent treatment, thereby reducing the capital needs for a bleached kraft mill. In addition, elimination of corrosive chlorine-containing bleaching agents would allow the use of cheaper materials in the construction of the bleach plant.

RESULTS TO DATE:

Kraft and kraft-anthraquinone pulping were systematically studied under conditions that give pulps of unusually low lignin content. The results were incorporated into an empirical model that allows assessment of the economic and environmental impacts of reducing unbleached kappa number in a variety of situations. Alkaline sulfite anthraquinone systems were also evaluated as low-lignin pulping alternatives. Conditions were found that gave extremely low kappa numbers at acceptable viscosity and yield levels. Further improvements will require an understanding of the kinetics of delignification and carbohydrate degradation. An appropriate investigation was therefore undertaken, and estimates of some of the important parameters were obtained. This study is being continued as Ph.D. thesis research.

In other student research related to low-lignin pulping, the impact of pulping variables and unbleached kappa number on response to subsequent CED and OC/DED bleaching has been quantified and a new dynamic model of the kraft and kraft-AQ processes has been developed. Current work on the kinetics of chlorination at both low and medium consistencies also has implications for improved bleached chemical pulp processes.

Research on nonchlorine bleaching was first aimed at identifying effective cellulose protectors by understanding the action of harmful radicals on pulp carbohydrates during oxygen bleaching. An improved understanding was achieved but it has not yet resulted in the identification of effective control methods. Emphasis was subsequently shifted to improving selectivity by accelerating delignification instead of retarding carbohydrate degradation. Pretreatments with nitrogen oxides and peracetic acid have been investigated in considerable detail. (The former was shown to play the dual role of delignification catalyst and carbohydrate protector, prompting efforts to learn more about the mechanism of its action.) Experiments in model systems have provided evidence for the hypothesis that lignin modified with NO_2 limits carbohydrate attack by oxygen by serving as a free radical scavenger. (In situ analysis of lignin structure indicates that promotion of lignin removal is not a result of the introduction of free phenolic hydroxyl groups; current research is designed to clarify the role of carboxyl groups and to assign NO_2 -induced changes in the FTIR spectrum of kraft pulp to specific structural changes.)

Pretreatment with halogens has also been investigated, mainly to provide mechanistic information but also to test the feasibility of sequences based on them. Relative to the sequence nitrogen dioxide-oxygen, the sequence bromine-oxygen gave better delignification and equivalent viscosity protection. Bromine was superior to chlorine (on either a weight or molar basis) by both criteria.

An alternative approach to reduced chlorine usage, hydrogen peroxide delignification, has also been investigated. An evaluation of several transition metal ions as potential catalysts showed that copper accelerates delignification but also reduces viscosity. Manganese was shown to be an effective carbohydrate protector, while slightly retarding delignification.

PLANNED ACTIVITY FOR THE PERIOD:

Effort will continue to be directed towards pretreatments that facilitate lignin removal by oxygen, hydrogen peroxide, ozone and other chlorine-free delignifying agents. Fundamental concepts will be pursued in addition to conceptual development of new process technology. In addition, we will investigate known pulping and bleaching sequences that minimize the generation of chlorinated organics to define what sacrifices in pulp properties must be made if environmental regulations force usage of this technology.

POTENTIAL FUTURE ACTIVITIES:

We will continue to expand our understanding of the kinetics of pulping and bleaching reactions, with a view to achieving more selective delignification.

STUDENT RELATED RESEARCH:

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

PROJECT TITLE: FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

PROJECT STAFF: D. R. Dimmel

PRIMARY AREA OF INDUSTRY NEED: Capital Effectiveness:
Reduction of capital intensity of new units

PROGRAM AREA: Reduction of process complexity

PROGRAM GOAL:

Improved process for bleached chemical pulps

PROJECT 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.

PROJECT RATIONALE:

A better understanding of the chemistry and structures will lead to the development of processes which require less energy, conserve resources, increase productivity, and lower air and water emission problems.

RESULTS TO DATE:

Lignin Reactions

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. After substantial design modifications, an electrochemical cell has been developed which can function at high temperatures (165°C) in aqueous alkali. Cyclic voltammetry studies of mixtures of AQ with bleached kraft pulp and wood meal have allowed us to observe the catalytic action of AQ/AHQ during simulated pulping. A new version of our electrochemical cell is now being tested. We expect improved sensitivity of the electrochemical signal, a more accurate measure of the internal temperature of the cell, and the ability to sample directly from the solution.

Most studies directed at establishing the nature of lignin reaction pathways have involved soluble lignin models. Studying the chemistry of insoluble lignin models will help establish the validity of soluble model conclusions and help define the importance of physical effects during delignification reactions. Several types of insoluble lignin model compounds have been synthesized. The insoluble models having trityl model-to-polystyrene linkages were not stable to pulping conditions; the benzyl bound models appear suitable.

Date: 2/8/88

Budget: \$90,000

Period Ends: 6/30/89

Project No.: 3475

Approved by VP:

Carbohydrate Reactions

The main thrust of the research in this area concerns understanding the chemistry and factors associated with polymer carbohydrate chain cleavage reactions. 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; the latter can be determined by gel permeation chromatography (GPC). Earlier work in this project involved developing the GPC method.

Recent work has been directed at preparing a high viscosity, stabilized amorphous cellulose sample and comparing its reactions to those of a crystalline cellulose sample. We find that under the same high temperature alkaline conditions the amorphous sample exhibits a much more rapid loss of DP (as determined by viscosity measurements) than does the crystalline sample. This result implies that "physical" effects are important in chain cleavage reactions.

Because of its higher reactivity, amorphous cellulose should be an excellent substrate for studying chemically induced chain cleavage reactions. For example, numerous experiments with AQ and either crystalline or amorphous cellulose provide data which indicates that AQ does not cause DP losses.

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. The thesis work of M. Bovee has produced such an insoluble model. Additional amounts of this polymer bound cellulose model have been prepared by us. In a step which couples the carbohydrate unit to the polymer, we employed a DMF, rather than THF, as the solvent. This led to a different degree of loading and distribution of model onto the polymer than what Bovee observed. Some parts of the latest sample have carbohydrate units which are bound to regions of the polymer which are not accessible with certain solvents. Several new techniques have been developed to characterize these polymer supported carbohydrate models.

PLANNED ACTIVITY FOR THE PERIOD:

Our electrochemical studies will focus primarily on improving the cell sensitivity, correlating electrochemical behavior with delignification rates, and assessing the potential of these techniques. Selected mechanistic studies aimed at better understanding delignification chemistry will be used to fill in the time gaps during electrochemical cell development.

Emphasis will be placed on the reactions of bleaching chemicals with crystalline and amorphous cellulose. An investigation of the effects of oxygen will serve as a starting point. The amount of carbohydrate model that is "accessible" to reaction in water at 170°C will be determined for the polymer bound carbohydrate model. Proper model degradation conditions will be assessed and preliminary product characterization will commence.

POTENTIAL FUTURE ACTIVITIES:

The high temperature electrochemical studies will be expanded into evaluating methods to monitor pulping and promoting (probably indirectly) beneficial pulping reactions. As new information on SET reactions becomes available, we will examine novel ways to promote these reactions in an economical manner.

The thesis work of J. Wozniak, concerning generating pulping catalysts from lignin, will be pursued in a joint project with the Solar Energy Research Institute. The research will be aimed at developing a sulfur-free selective pulping process.

Methods which have been developed for determining cellulose molecular weight distribution will be applied to assess the effect of carbohydrate physical structure (crystalline vs. amorphous) on the extent of chain cleavage reactions. A systematic study as to how changes in pulping and bleaching conditions affect carbohydrate chain cleavage reactions will be pursued. Such studies will involve the reactions of oxygen (with and without metals present), nitrogen dioxide, peroxide, ozone, etc., and the effects of "dead load" (increased ionic strength) on cellulose samples. The aim will be to develop a fundamental understanding of bleaching chemistry which may lead to better nonchlorine bleaching systems.

The reactions of appropriate insoluble lignin and carbohydrate model compounds will be investigated; a comparison of the chemistries of soluble and insoluble model reactions will (1) clarify the suitability of the former model studies and (2) provide data on "physical effects."

STUDENT RELATED RESEARCH:

P. Apfeld, Ph.D.-1986; D. Smith, Ph.D.-1986; M. Henderson, Ph.D.-1986; D. Geddes Ph.D.-1987; M. Bovee, Ph.D.-1987; V. Gentile, Ph.D.-1986; G. Reed, Ph.D.-1987; W. Molinarolo, Ph.D.-1987; J. Leege, M.S.-1987; P. Medvecz, M.S.-1987; P. Sands, M.S.-1987; R. Barkhau, Ph.D.-1988; J. Wozniak, Ph.D.-1988.

PROJECT TITLE: DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES

Date:	2/8/88
Budget:	\$45,000
Period Ends:	6/30/89
Project No.:	3477
Approved by VP:	

PROJECT STAFF: D. B. Easty, Analytical Staff

PRIMARY AREA OF INDUSTRY NEED: Various

PROGRAM AREA: N/A

PROGRAM GOAL: N/A

PROJECT OBJECTIVE:

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

PROJECT RATIONALE:

Significant progress in most technical areas demands quantification of information. Often analytical techniques are not available to provide the required data. Ongoing activity is required to investigate potential applications of newer analytical techniques. Development of totally new analytical methods may be needed.

RESULTS TO DATE:

The following research findings and method developments resulting from this project have been published in the past year:

A method for estimating lignin in unbleached pulps using diffuse reflectance Fourier transform infrared spectrometry was developed. The method is nondestructive and may be used on samples as small as 0.5 mg.

Based on findings in this project, TAPPI Test Methods for ion chromatographic analysis of pulping and bleaching liquors were revised. Included in the methods were recommendations regarding use of a UV detector for sulfide and deoxygenated dilution water for sulfate.

An improved pyrolysis - gas chromatographic method for identifying polymers in polymer - paper combinations was developed by a student working in close collaboration with staff. Sequential pyrolysis removed cellulose interference from the programs of other polymers.

Studies were recently initiated to evaluate near-infrared spectrometry (NIR) for measuring lignin in pulp and paper. Preliminary results have indicated that NIR possesses considerable potential for lignin estimation.

PLANNED ACTIVITY FOR THE PERIOD:

The thrust of this work will continue to be the development of improved techniques for analysis of pulp, paper, and relevant process streams.

Discussions with an instrument manufacturer may lead to placement of a near-infrared spectrometer at the Institute on consignment. The instrument would be used to demonstrate the feasibility of NIR for lignin monitoring. Studies will emphasize measurements on wet samples and sample pretreatments to increase data precision.

An inductively coupled plasma (ICP) spectrometer has been purchased. An early use of this instrument will be the development of optimized procedures for determination of metals in pulping liquors. This work was prompted by discordant data obtained on samples submitted to instrument vendors.

Student research will be performed on the following topics: (a) quantitative determination of volatiles in paper by headspace analysis, (b) use of CIRCLE cell for infrared analysis of aqueous solutions, (c) sample preparation for inductively coupled plasma spectrometry, (d) determination of formaldehyde in paper.

POTENTIAL FUTURE ACTIVITIES:

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

STUDENT RELATED RESEARCH:

L. Christensen, M.S. - 1988; M. Lundberg, M.S. - 1988; B. Hagen, M.S.- 1989;
K. Hull, M.S. - 1989.

PROJECT TITLE: RAMAN MICROPROBE INVESTIGATION OF
MOLECULAR STRUCTURE AND ORGANIZATION
IN THE NATIVE STATE OF WOODY TISSUE

Date: 2/8/88

Budget: \$50,000 *

PROJECT STAFF: R. H. Atalla

Period Ends: 6/30/89

PRIMARY AREA OF INDUSTRY NEED: Properties related
to End Use

Project No.: 3521-2

Approved by VP:

PROGRAM AREA: Performance and Properties of Paper and Board

PROGRAM 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.

PROJECT 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 reponse of structure to process variables.

PROJECT RATIONALE:

With the Raman microprobe, spectra can be recorded for very small areas. Many points on a given wood fiber cross-section can be evaluated. This permits investigation of the variability of lignin distribution and orientation across cell walls, between adjacent cells, and between cells in different tissue types. These results will reveal information about the integration of lignin into the cell walls which has not been hitherto available. In time, this information will provide a basis for further exploration of the effects of pulping, bleaching and refining in which lignin is disrupted or removed.

The response of woody tissue to laser excitation will also be examined as part of the program. This will add to fundamental understanding of the photochemistry of lignin which is important in a number of other programs.

RESULTS TO DATE:

A substantial component of our effort has been dedicated to the assembly of the new Raman microprobe system with multichannel detection. A major redesign of the microscope-spectrometer interface was necessary before the system became operational. The system is now assembled and we continue to optimize our procedures for its use. Preliminary results will be reported at the upcoming PAC meeting.

In the course of studies utilizing the older system we have investigated the quenching effects of molecular oxygen on laser induced fluorescence. We believe the effect may be related to the same class of interactions between lignin, oxygen, and light that may be responsible for color reversion.

* This work will also be supported by a DOE grant in fiscal year 88/89.

The system for time resolved spectroscopy has been installed. The ultrafast laser is operational. The gated detection system has also been installed. Preliminary tests are in progress. Our first studies will be directed at establishing the basic parameters necessary for lignin detection. We are currently designing the coupling optics, and we expect the system to be operational by summertime. This system will allow us to obtain a Raman spectrum before significant fluorescence develops.

PLANNED ACTIVITY FOR THE PERIOD:

Exploration of the spectra of different woods and native fibers will be continued. The effects of chemical treatments on the architecture of the cell walls will also be investigated.

A preliminary assessment of the photophysical processes in lignin will be undertaken. Lignins, chemically modified lignins, and lignin model compounds will be examined.

POTENTIAL FUTURE ACTIVITIES:

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.

STUDENT RELATED RESEARCH:

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

PROJECT TITLE: FUNDAMENTALS OF BRIGHTNESS STABILITY

Date: 2/5/88

PROJECT STAFF: U. P. Agarwal

Budget: \$170,000

PRIMARY AREA OF INDUSTRY NEED: Raw Materials

Period Ends: 6/30/89

PROGRAM AREA: Much Higher Yield Pulps for Conventional Product Lines

Project No.: 3524

PROGRAM GOAL: A significant increase in yield of useful fibers

Approved by VP:

PROJECT OBJECTIVE:

Establish mechanism for brightness loss in high-yield pulps

PROJECT RATIONALE:

One of the major drawbacks to high-yield pulps is poor brightness stability. As high-yield pulps will contain considerable amounts of lignin, the problem must be solved if high-yield pulps are to replace kraft pulps.

RESULTS TO DATE:

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-quinoid lignin structures to the absorbance of yellowed spruce pulp has been quantified. A novel method based on formation of the phosphite ester and subsequent ³¹P NMR analysis was developed to aid in the quantification. While the o-quinoid 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.

PLANNED ACTIVITY FOR THE PERIOD:

Additional professional support to this project will enable more rapid progress to be made. This will include both theoretical and applied research. From the mechanistic point, we need to establish the isomeric nature of the ferulic acid and investigate its role as a chromophore in yellowing. Work aimed at understanding the elementary mechanistic steps in yellowing will be started. The applied work will center on ways to interrupt the yellowing sequence. Acetylation will be considered in the initial stage of this research.

POTENTIAL FUTURE ACTIVITIES:

Once mechanism of color reversion is known, efforts will be directed to modify and/or block the undesirable reaction pathways.

STUDENT RELATED RESEARCH:

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

PROJECT TITLE: EXPLORATORY RESEARCH
(Chemical Sciences Division)

Date: 2/8/88

PROJECT STAFF: Division 20

Budget: \$60,000

PRIMARY AREA OF INDUSTRY NEED: Open

Period Ends: 6/30/89

PROGRAM AREA: N/A

Project No.: 3534

PROGRAM GOAL: N/A

Approved by VP:

PROJECT OBJECTIVE:

Investigate novel ideas and develop supporting information to justify formal funded projects.

PROJECT RATIONALE:

Scientists at IPC are urged to devote a portion of their time to developing novel ideas leading to new research projects. Many of these new ideas require preliminary experimentation and review to see if further research is indeed warranted. This project serves to support exploratory work on new research concepts in the Chemical Sciences area. Most of the ideas will fall into the pulping, bleaching, and recovery areas; however, some will not.

RESULTS TO DATE:

During the past year research activity has included: quantification of paper size, Tamarack pulping, low consistency oxygen bleaching, and algal cellulose.

PLANNED ACTIVITY FOR THE PERIOD:

Small, exploratory projects will be opened as required to encourage development of novel research concepts.

PROJECT TITLE: STRONG, INTACT HIGH YIELD FIBERS

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

PRIMARY AREA OF INDUSTRY NEED: Raw Materials

PROGRAM AREA: Much Higher Yields for Conventional Product Lines

PROGRAM GOAL: A significant increase in the yield of useful fibers

Date: 2/8/88

Budget: \$150,000

Period Ends: 6/30/89

Project No.: 3566

Approved by VP:

PROJECT 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.

PROJECT RATIONALE:

Most high strength, high brightness pulp is now made by the kraft process at yields of about 40%. One approach to solving wood cost and supply problems is to develop a capability for replacing bleached kraft with ultrahigh yield pulps at adequate product performance levels. This implies the need to develop a workable process for making pulps in the 80 to 90% yield range that possess high strength, high brightness and good brightness stability.

The magnitude of this task demands that it be broken down into approachable component problems. The present project is directed at solving one of these. Attainment of the ultimate program objectives will require a fiberization process that is capable of retaining, and preferably enhancing, the strength of the fibers in the original wood and offer some degree of control over changes in fiber geometry. It must also perform equally well on different wood species. Once fiber separation without damage is achieved, a means will be sought to efficiently bond the resulting strong, high yield fibers.

Selective chemical modification of the fiber wall components and structural elements, offers the possibility of enhanced fiber strength, and control over other mechanical properties of the fiber, such as those that determine the degree of bonding and other important network properties.

RESULTS TO DATE:

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 S₂ layer was observed under all treatment conditions. The distribution can be manipulated to a limited extent by varying liquor pH and Na₂SO₃ 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.

PLANNED ACTIVITY FOR THE PERIOD:

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.

POTENTIAL FUTURE ACTIVITIES:

Identification of wood properties that correlate with subsequent fiberization behavior and determination of the effects of various chemical, solvent, and biological treatments on these properties.

Identification of alternative fiber separation techniques.

STUDENT RELATED RESEARCH:

T. Cornbower, M.S.-1987; H. C. Dundore, M.S.-1987; T. Heazel, Ph.D.-1988.

PROJECT TITLE: COMPUTER MODEL OF RECOVERY FURNACE
PROJECT STAFF: T. M. Grace
PRIMARY AREA OF INDUSTRY NEED: Capital Effectiveness:
Improvement of capital productivity for existing units
PROGRAM AREA: Recovery Systems
PROGRAM GOAL: Increase the capacity potential of processes

Date:	2/8/88
Budget:	\$80,000
Period Ends:	6/30/89
Project No.:	3605
Approved by VP:	

PROJECT OBJECTIVE:

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

PROJECT RATIONALE:

A valid, comprehensive recovery boiler model can serve as a bridging tool between the acquisition of knowledge about black liquor combustion from laboratory-scale studies and the application of that knowledge to recovery boilers. The model would allow quantitative evaluation of methods for increasing capacity of recovery boilers rather than the qualitative estimates now available. In addition, the costs and risks of making major modifications to recovery boilers requires a methodology for assessing the potential benefits and problems before undertaking the modifications.

RESULTS TO DATE:

This model is being developed by three Ph.D. students who began in the fall of 1986. The effort is divided into three parts:

1. A model of liquor spray and in-flight behavior,
2. a model of the char bed, and
3. an overall model integrating the other two models and also incorporating air/flue-gas flow patterns and heat transfer.

After examining options, it was decided to base the model on the FLUENT software package. This is a finite difference package for modeling fluid flows. It also includes a six-flux radiation model, the PSI-CELL model for two-phase flow (gas-particles), a combustion model and a number of turbulence models. The source code has been obtained to allow modification for our purposes. Initial model development was done with a 10,000 node version of the program. We now have a 50,000 node version and machines that are adequate for the development of the model. The model development is proceeding at a timely pace.

PLANNED ACTIVITY FOR THE PERIOD:

The initial converged base case solution should be in hand by July 1988. The remainder of 1988 will be devoted to model refinement, documentation and the development of graphical display methods. Two of the students should complete their theses by the end of 1988. The third student, working on the bed model, should finish in early 1989. During 1989 we will exercise the model to study variable sensitivity and explore different firing methods.

POTENTIAL FUTURE ACTIVITIES:

When the model is completed, it will be used for the following purposes:

1. Sensitivity analyses of variables and variable combinations,
2. exploration of radically different methods for introducing liquor or air into the furnace, and
3. reduction and interpretation of field data from recovery boilers.

STUDENT RESEARCH:

A. Jones, Ph.D.-1988, A. Walsh, Ph.D.-1988, D. Sumnicht, Ph.D.-1989.

EXCERPTS FROM
MIDRANGE PLAN FOR

THE INSTITUTE OF PAPER CHEMISTRY

R. A. Yeske
December 1987

DRAFT

IV.B Critical Needs in IPC Research

Although each research project proposed for study in this mid-range plan is a free-standing project focused on a specific industry problem, it is useful to group projects by their applicability to selected areas of broad industry need. These areas have been discussed in Section III.C as areas of critical industry need for current IPC projects. In this section, the proposed IPC research projects for FY 88-93 are described in terms of six areas of industry need where cooperative research is needed to address a broad industry concerns.

These six areas of research focus are derived from those presently in use. Feedback from the RAC survey and conversations with member company representatives indicate that the current research thrusts in terms of critical industry needs are more or less appropriate descriptors for the Institute research program. In some cases, however, the areas of critical industry need have been revised and/or renamed to reflect the changing needs of the industry or evolutionary changes in the research projects themselves. Furthermore, the area of industry need relating to environmental needs has been restored in view of current industry concerns in this area.

The six areas of critical industry need which describe Institute research proposed for the coming period are:

- * Capital Effectiveness
- * Properties Related to End Use
- * Raw Materials
- * Environmental Impact
- * Reduced Operating Cost

Each of these areas is described briefly in the following paragraphs:

Capital Effectiveness. The manufacture of pulp and paper products is a very capital intensive industry. In the present era, the cost of a new, integrated, greenfield mill may exceed one billion dollars, corresponding to a capital cost of one million dollars per daily ton of production. This high capital cost degrades the profitability of the entire industry and inhibits the replacement of existing production equipment with new equipment incorporating current technology.

High capital costs arise from several sources. Processes for pulping, bleaching, papermaking, and chemical recovery are complex and require sophisticated process equipment. Large mill installations are required to achieve economies of scale. For many mills, extensive woodlands are held to assure future supplies of fiber, which adds to the capital required for production. Corrosive process conditions sap the life from existing equipment and require fabrication of new facilities from exotic and expensive materials of construction.

Options for reducing the capital expense of the industry are easily identified:

- * Reduce process complexity, thereby reducing the size and expense of production equipment. An example is the substitution of mechanical pulp for chemical pulp with attendant savings in processing equipment costs.
- * Improve productivity of existing production equipment. For example, raising the throughput of an existing recovery boiler that is a production bottleneck may eliminate the need for an expensive boiler replacement.
- * Improve fiber production and utilization. Examples include the use of higher yield pulp to replace chemical pulp in furnishes, and forest productivity improvements which reduce the woodland acreage needed to assure fiber supplies.

- * Extend the lifetime of existing production facilities. For example, eliminating suction roll failures would remove an expensive capital cost from papermaking processes.

In many cases, the implementation of measures that reduce capital demands is prevented by technological limitations, which limitations constitute fertile areas for cost-effective cooperative research. For example, replacement of chemical pulp by less capital-intensive mechanical pulp is limited by questions regarding strength, hardwood utilization, and brightness reversion. Increasing recovery boiler throughput requires solutions to problems arising from carryover, pluggage, and related concerns. Resolution of these and similar concerns through cooperative research will encourage a reduction in the capital cost of production of pulp and paper.

Properties Related to End Use. Paper and board products provide unique attributes in terms of stiffness, strength, opacity, liquid receptivity, etc. that allow these products to compete effectively in the marketplace. In contrast to some other materials, the characteristics of fiber-based products are highly sensitive to the exact raw materials used to manufacture the product and the processing subsequently applied to these materials. Each producer has evolved an empirical understanding of the broad relationship between his raw materials, processing, and product performance, but this understanding usually is quite specific to a given product.

The strong dependence of performance on selection of raw materials and subsequent processing provides interesting research opportunities for two reasons. First, research is needed to provide reliable quantitative relationships between raw materials selection, processing methods, and the resultant properties of paper and board. Second, research is needed to identify ways to control the product variability introduced through the strong sensitivity to raw materials and processing which affects the uniformity of fiber-based products.

A better understanding of the relationship between raw materials selection, processing conditions, and eventual product performance would provide many benefits to the industry. If quantitative relationships between

raw materials, processing, and performance were known, the properties of fiber-based products could be better tailored to individual customer needs without the empirical, trial-and-error approach now common in product development. Complicated inter-relationships between wood species pulped, pulping methods, refining, paper machine draws, etc. now dictate product performance, but such relationships are known only on a qualitative basis. The situation with more complex products, such as multi-ply laminates, is even more complicated and obscure. An improved understanding of the materials/processes/performance relationship offers many opportunities for reduced costs and optimized products.

Research is also needed to control the variability inherent in the production of paper and board products. Uniformity of product properties from reel to reel and from day to day has been difficult to achieve because of the strong sensitivity to inherent variations in raw materials and processing conditions. Two research opportunities are evident. The first is the development of sensors and process control strategies that detect and compensate for product variations related to raw materials and processing. The second is development of an enhanced understanding of those paper and board properties that are critical for routine converting and ultimate performance of the product.

Raw Materials. The recent expansion of eucalyptus pulp usage in the United States and elsewhere has underscored the importance of adequate production and utilization of the wood resource on which the industry depends. Fiber cost constitutes a large fraction of the cost of production of pulp and paper products. In a global marketplace, mills in countries with long growing seasons and high woodland productivity will enjoy a significant competitive edge unless improvements are made in the availability and use of the wood resource in the United States. In the long term, there are concerns about the ability of the industry to secure the domestic fiber necessary for continued growth in production.

Two approaches for improved use of the wood resource appear tenable. The first involves increased productivity of woodlands through genetic or clonal propagation of superior trees with significantly higher growth rates

and improved resistance to pests, frost, drought, etc. The second approach involves utilization of a larger fraction of the pulpwood in paper and board products through broader use of higher yield pulps. Both of these approaches face technological obstacles to implementation.

Research is clearly needed to expand the productivity of the wood resource. Regeneration of an improved wood resource through controlled breeding programs has a long economic payback period and offers only limited improvements in fiber production and/or quality. On the other hand, clonal techniques for regeneration are in an embryonic state of development, especially for conifers. Clonal propagation from mature trees remains an elusive goal, and questions remain whether the clones will exhibit the superior characteristics of the parent trees. Cost-effective methods for production of the millions of seedlings needed for regeneration must also be developed. In spite of these obstacles, the need for an improved raw material resource is apparent as a critical industry need that will impact not only those who maintain woodlands, but will ultimately touch all fiber users.

Increased reliance on high yield pulps for more and different products is an attractive concept, but the retention of lignin in the furnish introduces several well-known problems which have defied years of study. Residual lignin in high yield pulps introduces an unacceptable loss of brightness with time and/or exposure to light or elevated temperatures. The residual lignin also interferes with the bonding and fiber conformability necessary for development of high strength in the paper product. These difficulties have prevented broader use of high yield pulps in premium grades requiring high strength and brightness. Each of these obstacles must be overcome before widespread use of high yield pulps in premium grades can become a reality.

Environmental Impact. The U.S. pulp and paper industry operates in an increasingly restrictive regulatory environment which offers significant incentives to reduce or eliminate environmentally questionable effluents. Although the industry has made great strides in recent years, through the efforts of the National Council for Air and Stream Improvement and others, new environmental issues continue to surface. In recent months, concerns over dioxin, chloroform, and other chlorinated organic compounds alleged to

originate in pulp bleaching operations have intensified. In the long term, the industry would be well-served by development and adoption of processes with a diminished environmental impact. Elimination of chlorine from bleaching processes and sulfur from pulping are appropriate long-term goals of the industry.

Although the NCASI has been chartered to assist the industry in resolution of pressing issues related to the environment, the Institute also has an important role in this regime. NCASI has an important role in measurement and characterization of effluents, risk assessment, participation in the regulatory process, and development of near-term solutions to environmental problems. The Institute is the premier cooperative research organization in the United States, whose mandate and expertise in the organic chemistry of pulping and bleaching are sound bases for identification of entirely new, cost-effective, environmentally sound, pulping and bleaching processes.

Development of alternative pulping and bleaching processes must be completed with the understanding that entire systems -- including alternative pulping and bleaching processes, chemical recovery, property development, as well as environmental control -- have to be developed before an alternative process can be implemented. The integrated research program of the Institute is well-equipped to address the broad spectrum of topics required for progress in this area.

Reduced Operating Costs. Low cost production is a central theme in an industry whose international competition includes countries whose growing seasons are long and whose wage rates are comparatively low. Low cost production remains an essential factor in profitability, particularly in the commodity grades such as newsprint, linerboard, and market pulp where competition is most likely to be based on price.

Short-term profitability is clearly the province of individual mills and companies. To prosper, they must insure that they must control costs and implement new technology to maintain productivity at competitive levels.

Suppliers of chemicals and equipment assist the companies in their quest for low cost production.

Lowering the cost of production in the long term -- through development and promulgation of new technology -- is the proper goal of the Institute, working through vendors and individual member companies to insure implementation of the new technology. Cooperative research is an effective tool for developing new technology that will reduce the operating costs of pulp and paper manufacture, make more efficient use of raw materials and labor, and stimulate the development of cost-effective manufacturing methods for the future.

IV. C Research Project Summaries.

(Note to the RAC: Projects in the Forest Biology Division (30) continue to be reviewed and updated. The most recent revised version of the plan is included here for completeness; however, updates to this plan are possible after the RAC meeting and after a special Forest Biology PAC meeting to be scheduled in January, 1988).

A total of twenty-four separate projects are proposed for study over the next five year period. Some of these projects represent an entirely new research initiative, whereas other projects will be terminated during the next five years. Some projects in the mainstream of the Institute research plan will continue with an expanded scope throughout the period. The proposed projects are listed in Table 1 and summarized in this Section.

Of the twenty-four proposed research projects, four are identified as exploratory projects where the goal is to conduct limited research investigations, either to justify expansion or elimination of the effort or to clarify the precise research objective to be pursued. In general, these are research topics where a strong RAC endorsement for an ongoing project was not forthcoming, but where the Institute staff believes additional exploratory study is warranted.

Many of the research projects currently in progress or proposed for future study address more than one area of industry need. For example, the original motivation for the pioneering work in impulse drying was the opportunity to effect energy savings in pressing and drying, and to reduce the capital cost of the dryer section of the typical paper machine. These goals fit neatly under areas of industry need involving capital effectiveness and reduced operating costs, respectively. However, it has become clear recently that impulse drying will also permit the use of less expensive fibers in furnishes without sacrificing strength or other measures of product performance. Impulse drying therefore offers significant advances in the end use performance and raw materials areas of industry need.

To capture the breadth of appeal of the Institute program, the research projects proposed for the five-year plan are presented in Table 2 as a matrix -- projects versus area of industry need. The indication "Hi" or "Med" indicate either a high or moderate justification for each project, based on the applicability of project goals to the indicated area of critical industry need.

TABLE 1
PROPOSED IPC RESEARCH PROJECTS FOR FY 89-93

DIVISION 10 PROJECTS

Fibrous Structure Fundamentals	Continuation with New Topics
Property Development and Characterization	Continuation with New Topics
Product Characterization	Continuation with New Topics
Automatic Process Control	Continuation with New Topics

DIVISION 20 PROJECTS

Ultrahigh Yield Pulp	Continuation
Environmentally Compatible Process for Bleached Chemical Pulp	Continuation with New Topics
Improved Kraft Recovery Furnace Technology	Continuation with New Topics
Biological Treatment of Chlorinated Bleach Plant Effluents	Exploratory -- Limited Scope
Non-Sulfur Pulping and Recovery	Exploratory -- Limited Scope

DIVISION 30 PROJECTS

Mass Propagation of Genetically Improved Softwoods	Continuation
Mass Propagation of Genetically Improved Hardwoods	New
Biochemical Bases of Clonal Propagation	Continuation
Molecular Basis of Commercially Important Traits	Exploratory -- Limited Scope

TABLE 1 CONTINUED

DIVISION 40 PROJECTS

Recovery Fireside Corrosion	New Project
Fundamentals of Flue Gas Corrosivity	New Project -- 1990 Start
Fundamentals of Corrosion Control in Paper Machines	Concluding Project -- 1990 Stop
MAPPS	Continuing Project
Kraft Black Liquor Delivery Systems	New Project
Medium Consistency Forming	Continuing Project
Fundamentals of Wet Pressing	Continuing Project
Displacement Dewatering	Continuing Project
Impulse Drying	Continuing Project
Sensor and Control Technology	Continuation with New Topics
Fundamentals of Coating Systems	Exploratory -- Limited Scope
Functional Polymers in Paper Products	Exploratory -- Limited Scope

TABLE 2
THRUST AREAS FOR PROPOSED PROJECTS
FY 89-93

	Capital Effectiveness	End Use Performance	Raw Materials	Environmental Impact	Reduced Operating Cost
<u>Division 10</u>					
Fibrous Structure Fundamentals		Hi	Med		Med
Property Development and Characterization		Hi	Med		Hi
Product Characterization and Manufacture		Hi	Med		Med
Automatic Process Control	Med	Hi	Med		Hi
<u>Division 20</u>					
Ultrahigh Yield Pulp	Med	Med	Hi	Hi	Hi
Environmentally Compatible Process for Bleached Chemical Pulp			Med	Hi	Med
Improved Kraft Recovery Technology	Hi			Med	Hi
Biological Treatment of Chlorinated Bleach Plant Effluents	Med		Med	Hi	Hi
Non-sulfur Pulping and Recovery Technology	Med			Hi	
<u>Division 30</u>					
Mass Clonal Propagation of Genetically Improved Softwoods	Hi	Med	Hi		Hi
Mass Clonal Propagation of Genetically Improved Hardwoods	Hi	Med	HI		Hi

TABLE 2 CONTD

	Capital Effectiveness	End Use Performance	Raw Materials	Environmental Impact	Reduced Operating Cost
Biochemical Bases of Clonal Propagation	Hi	Med	Hi		Hi
Molecular Basis of Commercially Important Traits	Hi	Med	Hi	Hi	Hi
<u>Division 40</u>					
Recovery Fireside Corrosion	Hi				Med
Fundamentals of Flue Gas Corrosivity	Hi			Med	Med
Fundamentals of Corrosion Control in Paper Machines	Hi				Med
MAPPS	Med	Med	Med	Med	Hi
Kraft Black Liquor Delivery Systems	Hi			Med	Hi
Medium Consistency Forming	Hi	Med			Med
Fundamentals of Wet Pressing	Hi	Hi			Med
Displacement Dewatering	Hi	Med			Med
Impulse Drying	Hi	Hi	Hi		Med
Sensor and Control Technology	Med	Hi	Med	Med	Hi
Fundamentals of Coating Systems	Med	Hi			Hi
Functional Polymers in Paper Products		Med	Hi		

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MASTERS

INDEPENDENT STUDY

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
Aloisi	Modification of the MAPPS simulation program to include dynamic systems.	Jones
Arnold	The effects of nonuniform z-direction density on paper properties.	Sprague
Bartz	Economics of a simulated linerboard mill incorporating the impulse drying process.	Lavery
Best	Kraft pulping.	Malcolm
Bogenschutz	Electroporation-mediated genetic transformation of Norway spruce cells.	Becwar
Breining	Paper sizing with polysoaps.	Stratton
Burkhead	Sheet bulk development during impulse drying.	Lindsay
Burrill	Determination of the mechanism of liquid-level corrosion in white liquor storage tanks.	Yeske
Bucknell	(Special Student)	Habeger
Cedergren	The effect of lignin and hemicellulose removal on the short span compressive strength potential of white spruce.	Waterhouse
Christensen	Evaluation of the circular internal reflection unit for the analysis of pulp and paper.	Easty
Curtis	Biochemistry of tissue culture.	Becwar
Dudek	Encapsulation of somatic embryos.	Nagmani
Exarhos	Pollen ultrastructure, EM.	Connors
Friese	Analysis of adsorbed polymer configuration using FTIR spectroscopy with a CIR sample cell.	Stratton
Fruhirth	A comparative study of tension wood and normal wood fibers in the papermaking process.	Connors

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
Fukushima	Two-dimensional wet pressing flows.	Lindsay
Gaudette	The effect of nozzle design on the performance of kraft liquor spray nozzles.	Grace
Ginnow	Modeling the flow in the headbox and forming zone.	Jones
Graf	The dissociation constant of hydrogen sulfite ion.	Malcolm
Hagen	Sample preparation techniques for determination of metals by inductively coupled plasma spectrometry.	Easty
Hamman	Comparison of somatic and zygotic embryos, EM.	Conners
Hamel	Freeness measurements in refiner control.	Sprague
Hille	Pulp fiber identification using FLOPS.	Halcomb
Horstmann	Use of synthetic polymer additives to enhance paper strength properties.	Stratton
Hull	Formaldehyde measurement.	Easty
Jolly	Dynamic modeling of evaporators using DYSCO.	Parker
Jokio, M.	(Special Student)	Waterhouse
Jokio, P.	(Special Student)	Stratton
LaFond	The effect of flowing kraft smelts on corrosion rate.	Yeske
Lang	Characterization of genetic differences, molecular level.	Dinus
Logsdon	Gene expression at various stages of development.	Dinus
Lundberg	Static and dynamic headspace analysis of volatiles in paper.	Easty
Lynde-Maas	Hormonal effects on embryo development, molecular level.	Johnson
Macdonald	Effect of the rush-drag ratio on the mechanical properties of paper.	Baum

<u>Student</u>	<u>Topic</u>	<u>Advisor(s)</u>
Mauie	Proposal to formulate a rate equation for the reaction between sulfur dioxide and sodium carbonate fume particles.	Cameron
McAdams	Expert systems development both as stand-alone packages and interfaced with MAPPS.	Jones
Merchant	Mycorrhizal associations with somatic embryos.	Nagmani
Myers	Ultrasonic tissue porosity testing.	Habeger
Park	Sludge treatment or utilization by biotechnology.	Johnson
Rivard	Designing and constructing an experimental process control system.	Jones
Rosik	Modeling end use performance characteristics.	Jones
Sachs	Dependence of charge density on the flexibility of a polyelectrolyte.	Stratton
Santkuyl	Impulse drying.	Sprague
Spielbauer	Method to determine object size and three dimensional position from flash x-ray images.	Grace
Tembreull	Fume Generation	Cameron
Thomas	User-friendly interface for MAPPS.	Parker
Thompson	Corrosion in recovery boiler flue gases.	Yeske
Tracey	The effects on pulp properties of changes in the pH profile of the kraft cook.	Malcolm
Wadsworth	Adding a second impulse dryer to prevent two-sidedness.	Sprague
Walker	Culture of somatic embryos in bioreactors.	Becwar
Weber	Expert systems shell development.	Malcolm
Willhelm	The evaluation of loss tangent as a means to predict mechanical properties of paper.	Habeger
Woitkovich	Raman studies of delignification of loblolly pine.	Atalla
Zavaglia	Flash x-ray investigation of the impulse drying process.	Lindsay

February 22, 1988

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
Pugliese	6/8/84	11/7/84	A kinetic analysis of kraft pulp chlorination.	McDonough, chr. Cameron	K211
Byers	9/4/84	10/4/84	An autoradiographic study of the hemicellulose distribu- tion in the cell walls of <u>Pinus Resinosa</u> tracheids.	Atalla, chr. Johnson (Thompson)	K221
Reed	9/4/84	12/11/84	The role of sulfur species in pulping reactions.	Dimmel, chr. Malcolm	K232
Molinarolo, S. (Not in residence Sept. 1984 thru Dec. 1984). (Also July & Aug. 1986).	9/4/84	3/14/85	Sorption of xyloglucan onto cellulose fibers.	Stratton, chr. Johnson (Thompson)	34
Molinarolo, W. (Not in residence Sept. 1984 thru Dec. 1984)	9/4/84	3/14/85	The high temperature alkaline degradation of phenyl- β -D- glucopyranoside.	Dimmel, chr. (Schroeder) Malcolm	K210
Berger, Brian	3/28/85	3/14/85	The effects of refining and yield on the z-direction elastic properties of paper.	Habeger, chr. (Baum) Waterhouse	66 K27
Berger, Bernard	9/10/85	11/14/85	Transient effects of moisture sorption at various tempera- tures on the ultrasonically measured elastic moduli of cellulosic materials.	Habeger, chr. Stratton Waterhouse (Baum, ex officio)	K66

<u>Student</u>	<u>Passed to Thesis Candidacy Approval</u>		<u>Subject</u>	<u>Committee</u>	<u>Room</u>
Bither	9/10/85	1/27/86	Strength development through internal fibrillation and wet pressing.	Waterhouse, chr. Habeger Stratton	203A
Barkhau	12/6/85	12/16/85	Anthraquinone inhibited lignin condensation.	Dimmel, chr. Malcolm	K206
Wozniak	4/7/86	3/12/86	Preparation and reactions of Diels-Alder adducts of lignin-derived quinones.	Dimmel, chr. Van Lente Malcolm (Pearl)	K205
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.) Cameron	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.	Lindsay, chr. (Farrington) Dr. Shands (Beloit)	203A
Kulas, K. (Not in residence summer 1986)	6/13/86	12/2/86	An overall model for the combustion of a single droplet of kraft black liquor.	Clay, chr. Grace Atalla	69
Harper (Not in residence summer 1986)	6/13/86	11/24/86	Sulfur release during black liquor burning.	Clay, chr. Grace McDonough	K115
Burns, B.	6/27/86	10/6/86	A kinetic study of medium consistency chlorination.	McDonough, chr. Cameron Lindsay	168 and 49
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
Jones	9/8/86	9/3/86	A kraft recovery furnace model.	Grace, chr. Cameron Clay	SR11
Walsh	9/8/86	9/11/86	Development of a computer model for black liquor combustion in a recovery furnace.	Grace, chr. Jones Clay	SR11

<u>Student</u>	<u>Passed to Candidacy</u>	<u>Thesis Approval</u>	<u>Subject</u>	<u>Committee</u>	<u>Room</u>
Burns, J.	9/23/86	1/7/87	Investigation of the constrained expansion phase of wet pressing.	Lindsay, chr. Sprague	251
Sumnicht	9/23/86	11/24/86	Computer model of a char bed.	Grace, chr. Clay (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.	Cameron, chr. Grace (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	7/16/87	12/8/87	A fundamental study of boiling heat transfer mechanisms in impulse drying.	Lindsay, chr. Sprague (Lavery)	143
McKibben (Not in residence summer 1987)	8/7/87	12/18/87	A numerical and experimental study of a splash-plate type black liquor spray nozzle.	Lindsay, chr. (Farrington)	
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.	Clay, chr. Atalla Lindsay	
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				
Luetngen (Not in residence summer 1987)	1/18/88				
Bunker (Not in residence summer 1987)	11/19/87				

STATUS REPORTS

TO THE

PULPING PROCESSES PROJECT ADVISORY COMMITTEE

March 22-23, 1988

The Institute of Paper Chemistry

Appleton, Wisconsin

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PROJECT SUMMARY FORM

DATE: February 16, 1988

PROJECT NO. 3283: 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 1987 TO JUNE 1988): \$75,000

SUMMARY OF RESULTS SINCE LAST REPORT:

We have continued to pursue the implications of our findings concerning the structure of native fibers for both pulping and papermaking processes. Our hypothesis concerning the development of fiber structure during pulping has led us to carry out Solid State ^{13}C NMR studies of pulp fibers, prepared from morphologically homogenous samples of wood, by two different pulping processes. We find that fibers prepared by the kraft process have a higher proportion of I_{β} type cellulose in their crystalline cores than do the fibers prepared by the chlorite process. These results are consistent with our view that the crystalline domains in cellulosic fibers are nucleated and formed during the isolation process. The results do not preclude a high degree of order in the native state; they indicate rather that it is a transient order and somewhat less coherent than that which is developed in the isolated pulp fibers. We believe that this finding has important implications for understanding the effects of pulping conditions on fiber structure and mechanical properties.

The results of our studies of cellulose formation in bacterial cultures also support our basic hypothesis concerning the structure of cellulose in woody tissue. It is clear now that when the biosynthesis of cellulose is carried out in the presence of oligosaccharides and lignin precursors, its crystallinity is modified. The oligosaccharides and lignin precursors are included to simulate the environment prevailing in the primary and secondary walls during the biosynthesis of wood. The cellulose generated under these conditions is less crystalline than control samples generated in the absence of the additives. The results indicate that the assembly of the cellulose is modified by the adsorption of oligosaccharides and lignin precursors.

We continue our effort to measure the effects of drying cycles on fiber structure. Though the evidence for development of internal stresses during drying is unequivocal, we have not yet succeeded in direct measurement of the structural changes which we believe to result from these stresses, and which we believe are directly related to the degradation of fiber properties during recycling.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Continue the work using Solid State ^{13}C NMR, X-ray diffraction, and Raman spectroscopy to define the structure of cellulose and hemicelluloses in native plant tissue. Relate the variations in structure to differences in mechanical properties, chemical reactivities and process response.

We will continue emphasis on characterizing structural properties that are related to handsheet mechanical properties, and to the effects of cyclic drying and rewetting.

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 relationship 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.

STUDENT RELATED RESEARCH:

Erin Byers, Ph. D.
Ingegard Uhlin, Ph.D. (Gunnar Nicholson Fellow)
Tan Zheng, special student from China

PROJECT SUMMARY FORM

DATE: February 16, 1988

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 (JULY 1987 TO JUNE 1988): \$45,000*

SUMMARY OF RESULTS SINCE LAST REPORT:

Our new microprobe system is now operational, and preliminary exploratory studies are underway to develop operating procedures. It has been established that we are indeed able to acquire spectra with far greater efficiency than was heretofore possible. Spectra on a variety of sample materials will be available for presentation at the committee meeting.

We have encountered evidence of photochemical transformation of the lignin in the laser beam at the power levels we have been using to acquire spectra. It is not clear to us whether we are indeed degrading the lignin or inducing chemical transformations which reduce the Raman scattering coefficient associated with the aromatic ring stretching band at 1595 cm^{-1} . We are actively pursuing answers to these questions, both because of their relevance to interpretation of the spectra, and because of their connection to our effort in the photophysics of lignin.

In addition to the microprobe system we now have the time resolved spectroscopy system operational. This is currently being used in the effort to develop an on-line lignin sensor, and to carry out preliminary characterization of the photophysical processes which follow the excitation of lignin by laser pulses. These studies will be directed at a fundamental understanding of the dynamics of transitions involving excitation of lignin fragments, and their relation to photochemical transformations. Advances in this area are clearly relevant to the problem of understanding processes involved in brightness reversion of high yield pulps.

*This work will also be supported by a DOE grant in fiscal year 88/89 (\$72,000).

In support of both the microprobe program and the parallel effort towards the on-line lignin sensor, we are assessing the correlations between the spectra we observe in lignins and the spectra of the model compounds studied by S.M. Ehrhardt for her doctoral dissertation. We are also extending the analyses to additional model compounds. Such correlations will enable us to derive the majority of the information in the spectra.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

We will continue exploration of the spectra of different woods and native fibers with the new microprobe system. The effects of chemical treatments on the architecture of the cell walls will also be investigated.

We will continue calculations using Ehrhardt's force constants, to help interpretation of the spectra of lignins. We also plan to correlate the changes in band intensities with the results of chemical analyses.

With respect to the system for time resolved studies, our primary emphasis will be on developing more precise procedures for controlling the gating of the detector relative to the excitation pulses from the laser. We also believe that we will be able to enhance the efficiency of the sampling optics. These are two areas for optimization which we have not attended to in the recent past because of our preoccupation with the problem of getting the system operational.

FUTURE ACTIVITY:

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

STUDENT RELATED RESEARCH:

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

PROJECT SUMMARY FORM

DATE: February 8, 1988

PROJECT NO. 3456-2: SMELT-WATER EXPLOSIONS

PROJECT LEADER: T. M. Grace

IPC GOAL:

Increase the capacity potential of processes

OBJECTIVE:

An increased understanding of the phenomena underlying recovery boiler explosions, and the application of that knowledge to reduce the hazards of operating recovery boilers.

CURRENT FISCAL YEAR BUDGET (JULY 1987 TO JUNE 1988): \$20,000

SUMMARY OF RESULTS SINCE LAST REPORT:

The experiences in the industry on explosions and recovery boiler safety continue to be monitored. In the past few years we have played a major role in identifying combustible gas explosions originating from black liquor pyrolysis as a distinct hazard and getting the industry to recognize this hazard by working with the API Recovery Boiler Committee and BLRBAC. Our analysis of past incidents also identified that over two-thirds of the recent recovery boiler explosions involved a failure to follow generally recognized safe practices to some extent. This has helped to focus attention on the role of management and operator training in this continuing problem.

We carried out on-site investigations of four major recovery boiler explosions in 1987, either under auspices of API Recovery Boiler Committee or consultation contracts. We have kept abreast of regulatory and insurability issues and are serving as a member of API's task force on recovery boiler safety which is developing a plan for dealing with these issues.

A separate project entitled "Energetics of Smelt-Water Explosions," which was funded by the U.S. Nuclear Regulatory Commission, has been completed and papers based on the work are in preparation. The first phase of the study determined the energy conversion efficiency (thermal to mechanical) for some 20 smelt-water explosions. The energy conversion efficiencies for all of the cases analyzed was very low, < 0.5%. Since these cases included most of the major recovery boiler explosions, it appears that energy conversion efficiencies in recovery boiler explosions are inherently very low. These results were reported in an official NRC report, NUREG/CR-4745. The second and final phase of the study attempted to gain insight into the reasons for the low conversion efficiencies in the smelt-water system, and to try to develop scaling criteria for comparing results between different hot-cold fluid pairs and different system sizes. A postdoctoral student, Dr. Niann Shiang, contributed extensively to this second phase of the project. A graduate student under Professor Corradini at UW-Madison was supported on a half-time basis to define the thermodynamic bounds for the smelt-water explosions and to derive scaling criteria based on an explosion model previously developed at Madison.

The analysis of scaling criteria provided a convincing rationale that smelt-water explosions in recovery boilers are inherently low efficiency events.

A salt bridge model, which takes into account mass transfer of components between the two fluids, was developed and proved successful in interpreting the effects of composition on explosiveness in the smelt-water system. The model is based on the fact that the main smelt constituent, sodium carbonate, is not soluble in water at temperatures approaching the critical point, while certain other constituents are soluble. The soluble substances allow a substantial increase in the critical temperature of the solution, which in turn shifts the range of contact interface temperatures (between the spontaneous nucleation temperature and the critical temperature of the coolant) at which spontaneous explosions can occur to higher values. The model was able to provide an explanation of why NaCl, NaOH and Na₂S act as smelt sensitizers and a semiquantative definition of the concentration ranges in smelt and in the quench solution where spontaneous explosions are likely.

We continue to keep abreast of the state of knowledge concerning the physical phenomena involved in smelt-water explosions as it is developed at other universities and laboratories.

A high speed motion picture of some test explosions carried out at Sandia National Laboratory using thermite and water, which we obtained from Professor Corradini, has been incorporated into a video tape along with some background information on smelt-water explosions. About 50 copies of this tape have been distributed to various mills. We are charging \$80 per copy to cover the costs of preparation.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Remain active in API Recovery Boiler Committee and BLRBAC.

Pursue opportunities defined by API Safety Task Force.

Pursue implications of the explosion energetics results from the NRC study.

FUTURE ACTIVITY:

Continue explosion monitoring and support activities.

Possibly greater involvement in safety education and audit activities.

STUDENT RELATED RESEARCH:

In view of the sensitivity of the issues involved, this is not normally a suitable topic for student research.

PROJECT SUMMARY FORM

DATE: February 8, 1988

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

PROJECT LEADERS: T. M. Grace, J. H. Cameron, and D. T. Clay

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 production, 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 (JULY 1986 TO JUNE 1987): \$250,000*

SUMMARY OF RESULTS SINCE LAST REPORT:

Char Burning

Greg Aiken completed his Ph.D. thesis on the burning of char in a pile with an air jet directed vertically down onto the surface. He established the factors that govern the ratio of CO to CO₂ in the product gases. His results are in general agreement with the expectations based on the sulfate-sulfide concept. At higher temperatures, the reactions tend to be mass transfer controlled and the sulfur is almost entirely present as sulfide. At lower temperatures, sulfate-carbon reaction rates can be limiting and reduction is not as good. An interesting find in his work was that the smelt did not penetrate the bed after it was formed but instead remained on the surface. Another student, Dan Sumnicht, has initiated char burning experiments in which the air passes horizontally over the surface of the bed. Experimental data on bed burning in the DOE reactor is now being obtained.

Fume Formation

This work is now being carried out entirely as student research. Chris Verrill has developed an apparatus for measuring the production of fume during single-particle burning and will pursue this subject for his Ph.D. research. Kristin Goerg is studying the deposition of fume particles on cooled surfaces for her Ph.D. thesis. An M.S. project on reactions of SO₂ with Na₂CO₃ fume particles has been completed by Greg Maule and a paper is being prepared.

Recent movies obtained from Mikko Hupa of Abo Akademi in Finland show intense fume generation during the sulfide reoxidation phase of a single-particle burn. These findings have been confirmed by recent tests at IPC. This means that oxidation-enhanced fume formation, a phenomenon first recognized as applying to fume formation in kraft furnaces by Cameron, may well be the primary mechanism responsible for fume formation in a recovery boiler.

* Additional support through DOE under Project 3473-6.

Single-Particle Burning

The single-particle reactor has been modified so that the particle can be subjected to radiant heat transfer from hot walls as well as to convection from hot gas. There are two separate studies underway. The funded portion of the study is aimed at relating burning behavior to liquor composition and properties. The experimental part of this latter study is complete and a comprehensive report is in preparation. The collaboration with Professor Mikko Hupa of Abo Akademi in Finland is continuing. In addition, a Ph.D. thesis by Kathy Kulas (Crane) will acquire detailed experimental burning data and develop a quantitative model of single-particle burning of black liquor.

Sulfur Release

A Ph.D. thesis by Frank Harper on sulfur release during pyrolysis and burning of black liquor has been initiated. This work is still in the early stages.

Smelt Reactions with Hydrogen

The main reactions studied were H_2 reduction of Na_2CO_3 to form NaOH and H_2 reduction of Na_2SO_4 to form Na_2S . Hydrogen reduction of Na_2SO_4 is an autocatalytic reaction with Na_2S serving as the autocatalytic agent. The reaction is nearly first order in hydrogen and has an activation energy of 23,000 cal/mol. Hydrogen reduction of Na_2CO_3 is slowed significantly once a few percent of NaOH is formed. This work is nearly complete.

Corrosion

Greg Kulas, a Ph.D. student, has developed an apparatus for studying the corrosion of mild steel in molten smelt under conditions where a frozen smelt layer adheres to the steel surface and is now obtaining corrosion rate data.

Drying

A Ph.D. thesis on drying of black liquor drops by Mark Robinson is complete. His results indicate that although the drying tends to be controlled by heat transfer external to the drop, the droplet expansion that accompanies drying causes an increase in the internal heat transfer resistance. The increased internal resistance counterbalances the increased surface area, which also accompanies the expansion. The net result is a complex drying behavior that is markedly influenced by the initial liquor solids content.

DOE Combustion Project

There is a close tie between the DOE-sponsored work on black liquor combustion and this funded research project. The in-flight reactor has been operational in both upflow and downflow modes. Extensive data on drying rates, pyrolysis, carbon fixation, and particle characteristics have been obtained and a comprehensive report written for publication by DOE. The char bed reactor is now operational and bed burning data is being acquired.

DOE Liquor Spray Project

A spray test facility has been constructed which allows testing of spray nozzles using real black liquor at temperatures, pressures and solids contents that are representative of commercial practice. A flash x-ray technique is used to "photograph" the spray patterns. Image analysis techniques can then be applied to determine spray size distributions and the angular distribution of the liquor coming off the nozzle. Further developments of the technique will allow determining the velocity distributions as well. A proposal to the DOE for support for this program has been approved and we expect this support to begin to be available in March 1988. With the resignation of Ted Farrington, responsibility for this project now lies with the Recovery Group.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Char Burning

The basic chemistry of char burning is now established. Continuing work will focus on quantification of the mass transfer resistance and the effect of geometry variables. A substantial amount of char burning data will be acquired on the DOE reactor. An industrial fellow, Craig Brown, will concentrate on understanding char burning in the DOE reactor. Pat Medvecz will begin a Ph.D. thesis on spectroscopic analysis of selected gases above the char bed in the DOE reactor.

Fume Formation and Deposition

Chris Verrill will begin his thesis on the quantification of fume formation during single-particle burning. Kris Goerg will continue her work on fume deposition. Greg Maule will complete his M.S. research on reactions between SO_2 and Na_2CO_3 fume. A postdoctoral fellow, Jay Hsu, will implement an in situ method of monitoring fume concentration and size distribution in the DOE reactor.

Single-Particle Burning

Kathy Kulas (Crane) will continue her Ph.D. thesis on single-particle burning in combined convective/radiative heat fields. The collaboration with Mikko Hupa will continue.

Sulfur Release

Frank Harper will continue his Ph.D. thesis on sulfur release in black liquor pyrolysis and burning.

Corrosion

Greg Kulas will continue his Ph.D. thesis on the corrosion of mild steel in smelt with a frozen smelt layer on the metal surface.

Smelt Chemistry

The focus of smelt chemistry studies will shift toward reactions of sodium and potassium chlorides. Particular attention will be paid to reactions which may affect deposits and/or create a corrosive environment within deposits.

DOE Project

Data will continue to be obtained from the DOE project. The char bed reactor will be used to obtain fundamental data on bed burning rates, structure and behavior. The industrial fellow, Craig Brown, will focus on char bed burning studies and in translating the results of experiments on the laboratory scale reactor to recovery boilers. The Phase-3 equipment to study fume deposition processes in simulated furnace environments will be installed.

Liquor Spray Project

The black liquor spray and nozzle characterization project will continue and be expanded as DOE funding becomes available. An image analyzer will be obtained at a very early stage to facilitate data analysis. A new chemical engineer will be hired to facilitate rapid progress on this project.

Synthesis

Much of the information on black liquor burning now exists as fragments in various stages of completion. We will be examining methods for synthesizing this into a comprehensive theory of black liquor burning. At this stage, we do not know the form that will be used to achieve this goal.

FUTURE ACTIVITY:

The work already underway to understand black liquor combustion and apply it to recovery boilers will be completed within the next two to three years.

We will be expanding burning and fundamental smelt chemistry research to include the behavior of chlorine compounds in the system.

Expanded corrosion studies will be carried out in cooperation with the Corrosion Group.

We will work with individual companies, trade associations, and manufacturers in applying results for improved recovery boiler operation.

STUDENT RELATED RESEARCH:

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

PROJECT SUMMARY FORM

DATE: February 15, 1988

PROJECT NO. 3474: IMPROVED PROCESS FOR BLEACHED PULP

PROJECT LEADER: T. J. McDonough

IPC GOAL:

Improved process for bleached chemical pulp

OBJECTIVE:

Define pulping and bleaching technology that will decrease the number and size of the required process stages, including reduced needs for effluent treatment.

CURRENT FISCAL YEAR BUDGET (JULY 1987 TO JUNE 1988): \$60,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Early work on this project was concerned with defining the lower limits on unbleached lignin content achievable with the kraft and kraft anthraquinone pulping processes. Suitable operating conditions and limits were determined for both processes under various constraint scenarios by empirical modeling. The models were also used for evaluation of the economics of pulping to low lignin contents; the economics were found to be sensitive to assumptions concerning chemical costs, mill bottlenecks and site-specific constraints. Low lignin pulps were bleached in conventional, low chlorine and nonchlorine sequences; the expected reductions in chlorine requirements were observed.

The sulfite-anthraquinone process was subsequently investigated as a selective route to low lignin pulps. Kinetic studies of this process were undertaken to better understand the reasons for the factors governing its selectivity in the latter stages of pulping. Conditions were found that gave extremely low lignin contents at acceptable viscosity and yield levels. Further improvements will require an understanding of the kinetics of delignification and carbohydrate degradation. This work is being continued as Ph.D. thesis research.

Research on nonchlorine bleaching was first aimed at identifying effective cellulose protectors by understanding the action of harmful radicals on pulp carbohydrates during oxygen bleaching. An improved understanding was achieved but it has not yet resulted in identification of effective control methods. Emphasis was subsequently shifted to improving selectivity by accelerating delignification instead of retarding carbohydrate degradation. Pretreatments with nitrogen oxides and peracetic acid have been investigated in considerable detail. The former was shown to play the dual role of delignification catalyst and carbohydrate protector, prompting efforts to learn more about the mechanism of its action. Pretreatment with halogens has also been investigated, mainly to provide mechanistic information but also to test the feasibility of sequences based on them. An initial treatment with bromine was shown to be more effective than the same amount of nitrogen dioxide. After a subsequent oxygen stage, the bromine pretreated pulp was more completely delignified at the same viscosity

level. Hydrogen peroxide delignification has been investigated as an alternative to oxygen by evaluating transition metal ions for their catalytic potential. Copper was shown to be catalytic for both delignification and carbohydrate degradation. Manganese, on the other hand, was found to be an efficient carbohydrate protector while only slightly inhibiting the delignification reaction.

More recently, we have continued to study nitrogen dioxide pretreatment for oxygen bleaching, the principal objective being to understand its mechanism of action. In experiments based on the work of Samuelson and his co-workers, pretreatment conditions were found that result in more pronounced effects; these differ from those used previously by employing higher temperature and higher consistency. In addition, impregnation with solutions of nitric acid, sodium nitrate or their mixtures, gave improved delignification, especially at higher NO_2 charges.

In work designed to provide information on structural changes incurred by NO_2 , we have determined the phenolic hydroxyl group content of both untreated and treated samples by aminolysis. Similar experiments were done with kraft lignin in place of kraft pulp. No significant change in phenolic hydroxyl content was observed, suggesting that the observed improvements in oxygen delignification are not due to an increased concentration of phenolic groups to serve as reaction initiators. Analysis of the filtrate from washing of NO_2 treated lignin samples has shown that oxalic acid is produced and that there is a good correlation between NO_2 charge and the amount of oxalic acid produced. Other organic acids were also produced, and their amount also correlated well with NO_2 charge.

Fourier transform infrared (FTIR) spectroscopy of untreated and treated lignins has indicated that aromatic character is lost and that nitro or nitroso groups are introduced. The carbonyl group absorption introduced into pulp spectra by NO_2 is not introduced into the lignin spectrum, showing that it originates with carbohydrate.

Experiments are in progress to isolate the protective effect of NO_2 -modified lignin on carbohydrates. In these experiments, lignin samples, both untreated and treated with varied amounts of NO_2 under varied conditions, are added to simulated oxygen bleaches of cotton linters and the viscosity of the linters is determined.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Experiments will be done to demonstrate the effects of known methods of limiting the amount of chlorine required to bleach kraft pulp, including improved brownstock washing, oxygen delignification preceded by a pretreatment, partial or complete substitution of chlorine dioxide for chlorine in the chlorination stage, and use of oxygen and hydrogen peroxide in the extraction stage. The effects of these changes on production of organic chlorine will also be measured.

The structural changes resulting from NO_2 treatment of pulp will be determined and used to formulate hypotheses concerning the mechanism of its effects on oxygen bleaching. Comparative experiments involving other pretreatments will be included, and experiments initiated to test the hypotheses arrived at.

FUTURE ACTIVITY:

Experiments will be done to test the hypotheses that result from current work. Subsequently, the information gained will be used to identify alternatives to currently known additives.

In a broader sense, we will continue to expand our understanding of the kinetics of pulping and bleaching reactions, with a view to achieving more selective delignification.

STUDENT RELATED RESEARCH:

S. Pugliese, Ph.D.-1986; B. Burns, M.S.-1986, Ph.D.-; M. Breining, M.S.-1986; J. Fisker, M.S.-1986; J. Rogers, M.S.-1986; K. Biasca (Sime) M.S.-1986, Ph.D.-; D. Boyle, M.S.-1987; T. Stroh, M.S.-1987; S. Graf, M.S.-; W. Tracy, M.S.-; M. Best, M.S.-.

PROJECT SUMMARY FORM

DATE: February 5, 1988

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.

A better understanding of the chemistry and structures will lead to the development of processes which require less energy, conserve resources, increase productivity, and lower air and water emission problems.

CURRENT FISCAL YEAR BUDGET (JULY 1987 TO JUNE 1988): \$150,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Lignin Reactions

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. After substantial design modifications, an electrochemical cell has been developed which can function at temperatures (165°C) in aqueous alkali. Cyclic voltammetry studies of mixtures with bleached kraft pulp and wood meal have allowed us to observe the catalytic action of AQ/AHQ during simulated pulping. A new version of our electrochemical is now being tested. We expect improved sensitivity, more accurate measure of the internal temperature, and the ability to sample directly from the solution.

Most studies directed at establishing the nature of lignin reaction pathways have involved soluble lignin models. Studying the chemistry of insoluble lignin models will help establish the validity of soluble model conclusions and help define the importance of physical effects during delignification reactions. Several types of insoluble lignin model compounds have been synthesized. The insoluble models having trityl model-to-polystyrene linkages were not stable to pulping conditions; the benzyl bound models appear suitable.

Carbohydrate Reactions

The main thrust of the research in this area concerns understanding the chemistry and factors associated with polymer carbohydrate chain cleavage reactions. 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; the latter can be determined by gel permeation chromatography (GPC). Earlier work in this project involved developing the GPC method.

Recent work has been directed at preparing a high viscosity, stabilized amorphous cellulose sample and comparing its reactions to those of a crystalline cellulose sample. We find that under the same high temperature alkaline conditions the amorphous sample exhibits a much more rapid loss of DP (as determined by viscosity measurements) than does the crystalline sample. This result implies that "physical" effects are important in chain cleavage reactions.

Because of its higher reactivity, amorphous cellulose should be an excellent substrate for studying chemically induced chain cleavage reactions. For example, numerous experiments with AQ and either crystalline or amorphous cellulose provide data which indicates that AQ does not cause DP losses.

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. The thesis work of M. Bovee has produced such an insoluble model. Additional amounts of this polymer bound cellulose model have been prepared by us. In a step which couples the carbohydrate unit to the polymer, we employed a DMF, rather than THF, as the solvent. This led to a different degree of loading and distribution of model onto the polymer than what Bovee observed. Some parts of the latest sample have carbohydrate units which are bound to regions of the polymer which are not accessible with certain solvents. Several new techniques have been developed to characterize these polymer supported carbohydrate models.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Our electrochemical studies will focus primarily on improving the cell sensitivity, correlating electrochemical behavior with delignification rates, and assessing the potential of these techniques. Selected mechanistic studies aimed at better understanding delignification chemistry will be used to fill in the time gaps during electrochemical cell development.

Emphasis will be placed on the reactions of bleaching chemicals with crystalline and amorphous cellulose. An investigation of the effects of oxygen will serve as a starting point. The amount of carbohydrate model that is "accessible" to reaction in water at 170°C will be determined for the polymer bound carbohydrate model. Proper model degradation conditions will be assessed and preliminary product characterization will commence.

FUTURE ACTIVITY:

The high temperature electrochemical studies will be expanded into evaluating methods to monitor pulping and promoting (probably indirectly) beneficial pulping reactions. As new information on SET reactions becomes available, we will examine novel ways to promote these reactions in an economical manner.

The thesis work of J. Wozniak, concerning generating pulping catalysts from lignin, will be pursued in a joint DOE sponsored project with the Solar Energy Research Institute. The research will be aimed at developing a sulfur-free selective pulping process.

Methods which have been developed for determining cellulose molecular weight distribution will be applied to assess the effect of carbohydrate physical structure (crystalline vs. amorphous) on the extent of chain cleavage reactions. A systematic study as to how changes in pulping and bleaching conditions affect carbohydrate chain cleavage reactions will be pursued. Such studies will involve the reactions of oxygen (with and without metals present), nitrogen dioxide, peroxide, ozone, etc., and the effects of "dead load" (increased ionic strength) on cellulose samples. The aim will be to develop a fundamental understanding of bleaching chemistry which may lead to better nonchlorine bleaching systems.

The reactions of appropriate insoluble lignin and carbohydrate model compounds will be investigated; a comparison of the chemistries of soluble and insoluble model reactions will (1) clarify the suitability of the former model studies and (2) provide data on "physical effects."

STUDENT RELATED RESEARCH:

W. Molinarolo, Ph.D.-1988; R. Barkhau, Ph.D.-1988; J. Wozniak, Ph.D.-1988; G. Reed, Ph.D.-1988; M. Van Lente, postdoctoral fellow.

PROJECT SUMMARY FORM

DATE: February 8, 1988

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 BUDGET: \$60,000.

SUMMARY OF RESULTS SINCE LAST REPORT:

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.

Studies were recently initiated to evaluate near-infrared spectrometry (NIR) for measuring lignin in pulp and paper. Pulps and paper handsheets with a range of lignin contents were prepared at the Institute and submitted to Pacific Scientific for NIR analysis. Second derivative NIR spectra clearly showed differences between samples with different lignin contents. The spectra have been interpreted as representing a carbohydrate band with its intensity reduced in proportion to the pulps' lignin content. A linear relation was obtained between measured kappa numbers of pulps and kappa numbers computed from the 1680 nm NIR band.

Wetting of the pulps changed the intensity of their second derivative NIR spectra. Improved precision in NIR measurements on wet pulps was obtained by use of the 2106 nm band.

The limited data obtained thus far show the considerable potential value of NIR for estimation of lignin in pulp and paper. It is evident that there is a spectrometric basis for lignin measurements via this technique.

Results from a small exploratory project on Identification of Paper Sizing Chemicals have indicated that rosin size and alkyl ketene dimer can be detected in paper by silation of the paper and GC/MS analysis of the products.

PLANNED ACTIVITY THROUGH FISCAL 1988:

The thrust of this work will continue to be development of improved techniques for analysis of pulp, paper, and relevant process streams.

Pacific Scientific is considering placement of a near-infrared spectrometer at the Institute on consignment. The instrument would be used to investigate the feasibility of NIR for lignin monitoring. If the instrument is made available to us, studies will be undertaken to reveal wood species effects, to look further at measurements on wet samples, and to determine what sample pretreatments are required to yield precise data.

Further work on identification of paper sizing chemicals will involve direct insertion MS as well as GC/MS analysis of saponification products.

An inductively coupled plasma (ICP) spectrometer has been purchased. An early use of this instrument will be the development of optimized procedures for determination of metals in pulping liquors. This work was prompted by discordant data obtained on samples submitted to instrument vendors.

Student research (M.S. degree) is nearing completion on quantitative determination of volatiles in paper by headspace analysis and on use of the CIRCLE cell for infrared analysis of aqueous solutions. Student projects are getting underway on sample preparation for ICP spectrometry and determination of formaldehyde in paper.

Project 3477

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FUTURE ACTIVITY:

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

STUDENT RELATED RESEARCH:

L. Christensen, M.S.-1988; M. Lundberg, M.S.-1988; B. Hagen, M.S.-1989;
K. Hull, M.S.-1989.

PROJECT SUMMARY FORM

DATE: February 5, 1988

PROJECT NO. 3524: FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT LEADERS: 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 (JULY 1987 TO JUNE 1988): \$140,000

SUMMARY OF RESULTS SINCE LAST REPORT:

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 has 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-quinoid 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}P NMR analysis was developed to aid in the quantification. While the o-quinoid 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.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Additional professional support to this project will enable more rapid progress to be made. This will include both theoretical and applied research. From the mechanistic point, we need to establish the isomeric nature of the ferulic acid and investigate its role as a chromophore in yellowing. Work aimed at understanding the elementary mechanistic steps in yellowing will be started. The applied work will center on ways to interrupt the yellowing sequence. Acetylation will be considered in the initial stage of this research.

FUTURE ACTIVITY:

Once mechanism of color reversion is known, efforts will be directed to modify and/or block the undesirable reaction pathways.

STUDENT RELATED RESEARCH:

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

PROJECT SUMMARY FORM

DATE: February 18, 1988

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 methods of wood fiber separation which will allow the production of separated fibers having the same physical strength and geometrical form possessed when bound in the original wood matrix.

CURRENT FISCAL YEAR BUDGET (JULY 1987 TO JUNE 1988): \$175,000

SUMMARY OF RESULTS SINCE LAST REPORT:

In earlier work, chemimechanical pulps were 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 were 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.

Batch laboratory fiberizations were used to obtain information on the fiber separation mechanism. 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.

More recently, 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 thermo-mechanical pulping sacrifices strength for surface development by separating fibers at less than the optimum temperature for fiber strength retention.

An unambiguous interpretation of the effect of temperature of separation on fiber strength requires that the effect of heating alone be known. Thus, fibers separated at high temperature may be stronger either because they have undergone less damage during separation or because heating to the higher temperature has strengthened them. To distinguish between these possibilities, the effect of heating fibers separated at low temperature is currently being determined.

The importance of improving high yield fiber tensile strength relative to that of improving interfiber bond strength is an important factor in choosing future research directions. A related issue concerns the relative strengths of high

yield and chemical (low yield) pulp fibers. Work is in progress to clarify this, in view of the earlier observations that pine mechanical pulp fibers are nearly as strong as the corresponding chemical pulp fibers while for spruce, the low yield fibers are stronger. A stronger mechanical pulp fiber would argue in favor of concentrating work on interfiber bonding.

Efforts to cause strong, intact chemimechanical pulp fibers to form a sheet with kraft-like 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 S₂ layer was observed under all treatment conditions. The distribution can be manipulated to a limited extent by varying liquor pH and Na₂SO₃ 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.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Work in progress on fiber strength and bonding of strong fibers will be completed. Experiments to determine the mode of bond failure in sheets of high strength, high yield fiber will be initiated. Effects of fiber wall component removal on fiber strength will be determined. The prehydrolysis pulping data will be reproduced on a larger scale.

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.

STUDENT RELATED RESEARCH:

T. Cornbower, M.S.-1987; T. Heazel, Ph.D.-1988; E. Byers, Ph.D.-1986.

PROJECT SUMMARY FORM

DATE: February 8, 1988

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 mathematical model of fireside processes in a recovery furnace. The model would be based on first principles and will incorporate and integrate the results of ongoing fundamental studies of black liquor combustion.

CURRENT FISCAL YEAR BUDGET (JULY 1987 TO JUNE 1988): \$40,000

SUMMARY OF RESULTS SINCE LAST REPORT:

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 has been found to be adequate. The source code has been obtained 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 Newton's 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. We are now in the process of integrating the particle and gas flow models together. The steps needed to do this are identified and estimated convergence times are now in hand.

The char bed model is not as far along as the other models because of the need to first acquire some bed burning data. Modeling is now proceeding, and the bed model will be available for incorporation into the rest of the model at the appropriate time.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1988:

Cold flow modeling with 50,000 nodes will be completed to demonstrate the adequacy of this number of nodes. Modifications to the source code to permit handling the desired number of species will be completed.

Between March and June we will interface the particle and gas models together (along with a simplified bed surface model) and obtain a converged solution to the base case.

We will also exercise the particle model in a fixed, prescribed flow-temperature-O₂ field to look at sensitivities.

We will begin documentation of the model.

FUTURE ACTIVITY:

The remainder of 1988 will be devoted to model refinement, documentation and the development of graphical display methods. Two of the students should complete their theses by the end of 1988. The bed model work should be completed by the first half of 1989. During 1989 we will exercise the model to study variable sensitivity and explore different firing methods. A postdoctoral student will be sought for this.

When the model is completed, it will be used for the following purposes:

1. sensitivity analyses of variables and variable combinations,
2. exploration of radically different methods for introducing liquor or air into the furnace, and
3. reduction and interpretation of field data from recovery boilers.

STUDENT RESEARCH:

A. Jones, Ph.D.-1988, A. Walsh, Ph.D.-1988, D. Sumnicht, Ph.D.-1989.

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