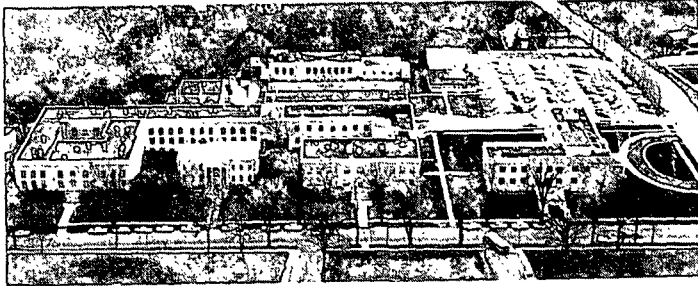


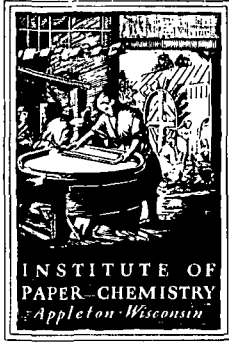
Institute of Paper Science and Technology  
Central Files



THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

PULPING PROCESSES  
PROJECT ADVISORY COMMITTEE MEETING

April 1-2, 1985  
The Institute of Paper Chemistry  
Appleton, WI 54912



THE INSTITUTE OF PAPER CHEMISTRY  
Post Office Box 1039  
Appleton, Wisconsin 54912  
Phone: 414/734-9251  
Telex: 469289

March 8, 1985

TO: Members of the Pulping Processes Project Advisory Committee

The next meeting of the Project Advisory Committee for the Pulping Processes area will be held in Appleton on April 1 and 2, 1985. The meeting will convene at 8:30 Monday morning, April 1, in the Seminar Room of the Continuing Education Center at The Institute of Paper Chemistry. Overnight accommodations have been arranged for Committee Members at the Continuing Education Center. For those of you staying at the CEC, you will find enclosed a pink "Security Card" which has instructions for entering the building in the event you arrive and find it locked. If you have not yet let us know your plans, including lodging, please do so.

The information enclosed with this letter is for your review prior to the upcoming meeting. The enclosures include:

- (1) List of Committee Members,
- (2) Agenda for the meeting,
- (3) Preliminary Project Summary Forms for the upcoming fiscal year, F85/86,
- (4) A brochure containing a listing of current M.S. and Ph.D. student research in progress, and
- (5) The summary Status Reports for individual projects.

The morning and evening sessions will permit full discussions on individual projects. Future directions for each project area are a major item for discussion in our spring meetings. The evening session will start with a summary of the upcoming research program and finish with selected presentations on relevant student research. The Tuesday morning session is primarily for Committee business. The Committee meeting will adjourn at approximately 10:30 in the morning, leaving enough time for those of you who wish to catch either the 10:50 a.m. or 1:00 p.m flight out of Appleton to Chicago.

TO: Members of the Pulping Processes  
Project Advisory Committee

March 8, 1985  
Page 2

I look forward to seeing you in Appleton on April Fools Day! If you have any questions on the enclosures or on the meeting itself, please give me a call.

Sincerely,



Earl W. Malcolm  
Director  
Chemical Sciences Division

EWM/gmk  
Enclosures

PULPING PROCESSES PROJECT ADVISORY COMMITTEE

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A G E N D A

PULPING PROCESSES PAC MEETING

THE INSTITUTE OF PAPER CHEMISTRY  
APPLETON, WISCONSIN

APRIL 1-2, 1985

MONDAY, APRIL 1, 1985  
CONTINUING EDUCATION CENTER SEMINAR ROOM

8:30	CONVENE		P. Wollwage
8:35	OVERVIEW OF CURRENT RESEARCH		E. Malcolm
8:45	PROJECT DISCUSSIONS		
	FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES (Project 3473-1)	-- Page 3	T. Grace J. Cameron D. Clay R. Kapheim
	INCREMENTAL CAPACITY IN RECOVERY BOILERS (Project 3558)	-- Page 14	T. Grace
	SMELT-WATER EXPLOSIONS (Project 3456-2)	-- Page 2	T. Grace
10:30	BREAK		
	FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING (Project 3475)	-- Page 8	D. Dimmel L. Schroeder
	DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES (Project 3477)	-- Page 10	D. Easty
NOON	LUNCH		

1:00 PROJECT DISCUSSIONS (CONTINUED)

FINE STRUCTURE OF WOOD PULP FIBERS -- Page 1 R. Atalla  
(Project 3288)

IMPROVED PROCESSES FOR BLEACHED PULP -- Page 6 T. McDonough  
(Project 3474) N. Thompson

3:00 BREAK

HIGH-YIELD PULPS -

FUNDAMENTALS OF BRIGHTNESS STABILITY -- Page 13 W. Lonsky  
(Project 3524)

SEPARATION OF STRONG, INTACT FIBERS -- Page 15 T. McDonough  
(Project 3566)

5:00 BREAK

6:00 DINNER

7:00 85/86 RESEARCH PLAN

E. Malcolm

STUDENT RESEARCH

Staff & Students

TUESDAY MORNING, APRIL 2, 1985

7:00 BREAKFAST

8:00 COMMITTEE MEETING

10:30 ADJOURN

FUNDED PROJECT BUDGETS (\$1000) - CHEMICAL SCIENCES DIVISION

	<u>F85/86</u>	<u>F84/85</u>	<u>Change (F86-F84)</u>
<u>Chemical Pulping</u>			
Fine Structure of Wood Pulp Fibers (3288)	45	48	
Fundamentals of Selectivity in Pulping and Bleaching (3475)	175	180	
Improved Processes for Bleached Pulp (3474)	130	145	
Development and Application of Analytical Techniques (3477)*	<u>22</u>	<u>20</u>	
	<u>372</u>	<u>393</u>	<u>-21</u>
<u>Recovery</u>			
Fundamental Processes in Alkali Recovery Furnaces (3473-1)	220	185	
Smelt-Water Explosions (3456-2)	20	25	
Incremental Capacity in Recovery Boilers (3558)	50	70	
Development and Application of Analytical Techniques (3477)*	<u>21</u>	<u>20</u>	
	<u>311</u>	<u>300</u>	<u>+11</u>
<u>High Yield Pulping</u>			
Separation of Strong, Intact Fibers (3566)	170	140	
Fundamentals of Brightness Stability (3524)	110	90	
Raman Microprobe Investigation of Molecular Structure (3521-2) and Organization in the Native State of Woody Tissue	40	45	
Development and Application of Analytical Techniques (3477)*	<u>22</u>	<u>20</u>	
	<u>342</u>	<u>295</u>	<u>+47</u>
<u>Exploratory</u>			
Exploratory Research (3534)	<u>70</u>	<u>50</u>	<u>+20</u>
TOTALS	1,095	1,038	+57 (5.5%)

\*1/3 assigned to this area.

E.W.M.  
3/85

PROJECT TITLE: Fine Structure of Wood Pulp Fibers

Date: February 1985

PROJECT STAFF: R. H. Atalla

Budget: \$ 45,000

PRIMARY AREA OF INDUSTRY NEED: Properties related to  
end use

Period Ends: 6/30/86

PROGRAM AREA: Performance and properties of paper and  
board

Project No.: 3288

Approved by VP-R:

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. Emphasis is on full chemical pulps.

## 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. The latter relationships are the subject of this project.

## RESULTS TO DATE:

SS  $^{13}\text{C}$ -NMR studies have shown native celluloses to be composites of two crystalline forms,  $I_{\alpha}$  and  $I_{\beta}$ . Their Raman spectra show them to have the same molecular conformation, but to have different hydrogen bonding patterns. The distribution between the two forms varies over a wide range among native celluloses. There are indications that their susceptibilities to swelling and chemical reaction differ. The relative amounts of the two forms in a native cellulose are, therefore, likely to be important determinants of properties.

We continue to refine our methods for detecting differences between celluloses by combined chemical and spectroscopic techniques.

## PLANNED ACTIVITY FOR THE PERIOD:

1. Use SS  $^{13}\text{C}$ -NMR and Raman spectra to characterize the differences between the responses of  $I_{\alpha}$  and  $I_{\beta}$  to chemical reactions and to pulping conditions.
2. Explore further the range of variation in wood-derived celluloses.
3. Study aggregation of cellulose with related cell-wall polysaccharides.

## POTENTIAL FUTURE ACTIVITIES:

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 and product properties. New information on cellulose and fine fiber structure will be useful in guiding activity. Future work will focus on the structure of native wood fibers and its modification in both conventional chemical and high yield pulping processes. Particular attention will be given to the factors (yet to be determined) which control fiber strength and conformability.



PROJECT TITLE: Smelt-Water Explosions

Date: February 1985

PROJECT STAFF: T. M. Grace

Budget: \$ 20,000

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

Period Ends: 6/30/86

Project No.: 3456-2

PROGRAM AREA: Recovery Systems

Approved by VP-R:

PROGRAM GOAL: Increase the capacity potential of processes

PROJECT OBJECTIVE:

An increased understanding of the phenomena of explosions associated with rapid phase transitions (explosive boiling), and the application of that knowledge to reduce the hazard of smelt-water contacts.

PROJECT RATIONALE:

Recovery boilers are subject to the additional hazard of smelt-water explosions, as well as the normal hazards of all combustion equipment. The costs of this problem tend to be borne through reduced unit availability due to greater downtime and through higher insurance premiums. A better understanding of the critical factors that determine whether or not a smelt-water explosion will occur and the level of violence, should permit the development of means for reducing smelt-water explosion hazards.

RESULTS TO DATE:

We continue to review the state of knowledge concerning the phenomena involved in smelt-water type explosions. Contacts have been established with key people in universities and in other industries experiencing similar problems.

The experiences in the industry on explosions and recovery boiler safety continue to be monitored. Implementation of ways to improve safety is done through working with the API Recovery Boiler Committee and BLRBAC.

A separate project (3575) has been initiated to determine the energetics of smelt-water explosions by relating explosive violence to the amounts and conditions of smelt and water involved. This work is supported by the Nuclear Regulatory Commission and is done in cooperation with IIT Research Institute.

PLANNED ACTIVITY FOR THE PERIOD:

Pursue implications of the explosion energetics results from NRC study.

Keep abreast of developments on the theory of these types of explosions and interpret same for the smelt-water system.

Remain active in API Recovery Boiler Committee and BLRBAC.

POTENTIAL FUTURE ACTIVITIES:

Formal collaboration with Professor Corradini at UW-Madison to apply theories of steam explosions to the smelt-water system.

PROJECT TITLE: Fundamental Processes in Alkali  
Recovery Furnaces

Date: February 1985
Budget: \$ 220,000
Period Ends: 6/30/86
Project No.: 3473-1
Approved by VP-R:

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

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 evolutionary optimization. A much better understanding of black liquor combustion fundamentals is needed to guide optimization strategies.

RESULTS TO DATE:

Char burning via the sulfate-sulfide cycle has been conclusively established. A comprehensive, technical report summarizing this work and discussing furnace implications has been published.

Progress is being made in understanding fume formation. Quantitative rate data are being obtained and an alternative explanation for oxidative fuming has surfaced. Further work is needed to determine the cause of fuming to allow translation of the results to the furnace.

A phenomenological study of black liquor burning behavior using the single-particle reactor has been initiated. This program uses a variety of mill liquors and will provide a data bank on burning behavior and its relation to measurable properties. Student thesis work on black liquor drying and pyrolysis/swelling is complementary to this effort.

PLANNED ACTIVITY FOR THE PERIOD:

Work on fundamentals of fume formation will continue. This work should reach a definite conclusion on the cause of oxidative fuming and a quantitative understanding of the variables that control it.

The phenomenological study of burning behavior will continue. The data base will be broadened by including more mill liquors. We especially want to include liquors that burn remarkably well or very poorly.

## Project 3473-1

We will initiate a study of the fundamentals of sulfur release and recapture in the furnace. This is the next key furnace process to be addressed. This information is essential to interpreting the data obtained on the DOE reactor (Cooperative Project 3473-6). Initial studies are underway as an M.S. thesis project.

We will extend our capability to measure physical properties of smelt and char and begin measurements on key eutectic mixtures. Equipment for measuring properties was developed in an M.S. research project.

## POTENTIAL FUTURE ACTIVITIES:

Simulation of new black liquor combustion process concepts on the DOE reactor (reactor now partially operational).

Develop a new mathematical model of a recovery boiler incorporating information gained in these studies (initiated as an M.S. project).

Write a book on the theory of black liquor combustion and its application to recovery boiler operation.

Expand recovery boiler corrosion studies in cooperation with corrosion groups.

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

## STUDENT RELATED RESEARCH:

P. Miller, Ph.D.-1986; M. Robinson, Ph.D.-1987; D. Hennessy, M.S.-1985; B. Moreland, M.S.-1985; J. Wozniak, M.S.-1985; E. Buehler, M.S.-1986; T. Coenen, M.S.-1986, K. Crane, M.S.-1986; K. Goerg, M.S.-1986; D. Sumnicht, M.S.-1986.

PROJECT TITLE: Improved Process for Bleached Pulp

PROJECT STAFF: T. J. McDonough, N. S. Thompson

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

PROGRAM AREA: Reduction of Process Complexity

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

Date: February 1985
Budget: \$ 130,000
Period Ends: 6/30/86
Project No.: 3474
Approved by VP-R:

#### PROJECT OBJECTIVE:

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

#### PROJECT RATIONALE:

Conventional bleaching of standard kraft pulps requires complex bleach plants of high capital cost and produces an effluent whose handling 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 allow a reduction in the amount of residual lignin and should change the structure of the lignin to render it more easily removable.

The bleaching process should produce an effluent which can be recycled to a standard recovery boiler. In practice, this means a nonchlorine bleaching process, likely based on oxygen. This would turn the effluent problem into an advantage, in the form of increased energy recovery. In addition, elimination of corrosive chlorine-containing bleaching agents would allow the use of cheaper materials in the construction of the bleach plant, thereby lowering its capital cost.

Combined improvements in pulping and bleaching technology may lead to fewer, smaller bleaching stages, with reduced needs for effluent treatment.

#### RESULTS TO DATE:

Experimental pulping, mathematical modeling, and computer simulation have shown that low lignin pulping can offer an attractive route to improved process economics. Alkaline sulfite-anthraquinone systems have been shown to be capable of reaching extremely low kappa numbers at acceptable viscosity and yield levels. Means of improving the economics of this process are being sought by means of a study of the kinetics of the system. Substantial quantities of kinetic data have been obtained on the rates of bulk and residual phase reactions in this system. They relate to the effects of pH and chemical concentration on the rates of delignification, and carbohydrate dissolution. More recently, additional data have been obtained on initial phase rates of the same processes. Rate laws derived from this data will constitute a theoretical model of the system that is expected to lead to significant insight into the chemical and transport mechanisms operative during pulping.

Earlier research on this project has suggested that cellulose degradation proceeds independently of lignin degradation during our oxygen bleaches. The pathways of fiber degradation are being explored, but the detailed mechanistic pathways of cellulose degradation are still poorly understood, and it is not possible to control them. The alternative path is to accelerate lignin reactions, if it can be done without increasing cellulosic degradation. Preliminary results at the Institute (circa 1972), and recent research by Samuelson in Sweden and Lachenal in France suggest this goal can be attained.

Project 3474

PLANNED ACTIVITY FOR THE PERIOD:

Investigation of the chemical and engineering fundamentals of ASAQ pulping will be continued until satisfactory rate laws for lignin and carbohydrate reactions during all three phases have been developed. Modified pulping sequences suggested by them will be investigated, and the bleachability of the pulps evaluated.

Emphasis of the research on reactions of oxygen-derived species with pulp will be shifted from controlling carbohydrate degradation to enhancing delignification. Initially, selected pretreatments will be investigated. The effects of these sequences and their methods of application on both lignin removal and cellulose modification will be examined. The relationship between changes in chemical properties of the lignin component and the response of lignin and cellulose to bleaching will be monitored.

POTENTIAL FUTURE ACTIVITIES:

Emphasis will continue on understanding the kinetics of both lignin and carbohydrate removal during pulping operations with a view to achieving more selective delignification and controlling the structure of the residual lignin to make it more amenable to removal in subsequent bleaching operations.

STUDENT RELATED RESEARCH:

M. Burazin, Ph.D.-1985; S. Pugliese, Ph.D.-1986; E. Arrington, M.S.-1985; R. Barkau, M.S.-1985; J. Bastian, M.S.-1985; S. Dibbs, M.S.-1985; R. Kirk, M.S.-1985; 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.

PROJECT TITLE: Fundamentals of Selectivity in Pulping and Bleaching

Date: February 1985

PROJECT STAFF: D. R. Dimmel, L. R. Schroeder

Budget: \$ 175,000

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

Period Ends: 6/30/86

PROGRAM AREA: Reduction of process complexity

Project No.: 3475

PROGRAM GOAL: Improved process for bleached chemical pulps

Approved by VP-R:

#### PROJECT OBJECTIVE:

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

- (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:

Modern chemical pulping technology generally employs alkaline conditions, coupled with various inorganic or organic additives, to delignify wood. Included are standard methods (kraft) and alternatives, such as soda-AQ and soda-O<sub>2</sub>. Lignin removal is the principal objective of chemical pulping; carbohydrate degradation is an undesirable side reaction. Control of cellulose and other carbohydrate loss is a necessity for successful pulping. Alkaline reactions are also important in several bleaching stages (extraction, hypochlorite, peroxide, oxygen). A thorough understanding of the basic reactions is needed to guide process innovation aimed at more selective and controllable pulping and bleaching. This should result in greater productivity of a higher quality product with improved economics.

#### RESULTS TO DATE:

The chemistry of anthraquinone pulping has been singled out for study because of the high selectivity of this process. Much information is now known about its overall mechanism of action. Recent studies into the detailed chemistry of anthraquinone-lignin interactions suggest a unique pulping mechanism, single electron transfer (SET). It is likely that SET reactions compete with the traditionally accepted ionic mechanism. The studies have employed both conventional and electrochemical approaches.

Studies of a cellulose model have indicated that anthraquinone has the potential to accelerate random chain reactions and thus cause pulp viscosity loss.

#### PLANNED ACTIVITY FOR THE PERIOD:

Efforts will continue toward developing conclusive proof for the existence of SET reactions in pulping systems. These studies include the application of high temperature electrochemistry to wood and wood model systems. One specific goal will be to develop an electrochemical cell that functions well under pulping conditions, providing information on SET reactions.

The study of the effect of anthraquinone on random chain cleavage will be directed toward determining what role stereochemistry and cellulose physical structure may play in the reaction.

Project 3475

POTENTIAL FUTURE ACTIVITIES:

The high temperature electrochemical studies will be expanded into evaluating methods to monitor pulping and, through indirect techniques, promoting beneficial pulping reactions. Should SET reactions be shown to be important to efficient pulping, we will examine novel ways to promote these reactions in an economical manner.

Mechanistic studies of cellulose chain cleavage in alkaline pulping indicate that increased ionic strength could accelerate the cleavage reaction. Thus, the effect of "dead load" (increased ionic strength) on cellulose chain cleavage during pulping will be examined.

STUDENT RELATED RESEARCH:

P. Apfeld, Ph.D.-1985; D. Smith, Ph.D.-1985; M. Henderson, Ph.D.-1986; D. Geddes, Ph.D.-1986; G. Reed, Ph.D.-1987; J. Fitzgerald, M.S.-1985.

PROJECT TITLE: Development and Application of Analytical Techniques

PROJECT STAFF: D. B. Easty, Analytical Department

PRIMARY AREA OF INDUSTRY NEED: Various

PROGRAM AREA: N/A

PROGRAM GOAL: N/A

PROJECT OBJECTIVE:

Date: February 1985
Budget: \$ 65,000
Period Ends: 6/30/86
Project No.: 3477
Approved by VP-R:

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:

A method has been developed for determining elemental and polysulfide sulfur in pulping liquors. The procedure was reported to the membership via IPC Technical Paper Series Number 143 and was published in Journal of Chromatography 299(2):471 (Sept. 21, 1984).

Ion chromatography (IC) was shown to be a valid and efficient technique for determining sulfoxy anions, chloride, carbonate, but not sulfide, in pulping liquors. These results were reported in IPC Technical Paper Series Number 142 and have also been accepted for publication in Paperi ja Puu.

In a study of bleach liquor analysis, IC has been shown capable of determining chlorine-containing anions, chlorine dioxide (as chlorite), and chlorine (as hypochlorite).

Diffuse reflectance Fourier transform infrared spectrometry (FTIR) has been found to provide an estimate of kappa number and Klason lignin in unbleached pulps.

PLANNED ACTIVITY FOR THE PERIOD:

The evaluation of ion chromatography for bleach liquor analysis should be completed by the end of fiscal 1985.

Studies of lignin determination by diffuse reflectance FTIR will involve analysis of more pulps and rigorous evaluation of the data obtained. Results will indicate how good FTIR is at estimating lignin in pulps.

POTENTIAL FUTURE ACTIVITIES:

Future work will involve continued studies of pulp and liquors by chromatographic and spectrometric techniques. Likely topics are: improved material balance in unbleached pulp analysis, pyrolysis gas chromatography, and determination of volatiles by headspace analysis.



PROJECT TITLE: Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue

Date: February 1985

Budget: \$ 40,000

PROJECT STAFF: R. H. Atalla

Period Ends: 6/30/86

PRIMARY AREA OF INDUSTRY NEED: Properties related to end use

Project No.: 3521-2

PROGRAM AREA: Performance and properties of paper and board

Approved by VP-R:

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:

In conjunction with work sponsored by the DOE, use the Raman microprobe to develop a better understanding of wood fiber structure. Establish, by Raman microprobe spectroscopy, the variability of molecular structure and organization in cell walls of native woody tissue. Also by the same methods explore the effects of mechanical and chemical treatments on structure and organization encountered in high yield pulp fibers. (This work is also supported by DOE under Project 3521-3 with a Fiscal 1985/86 budget of \$49,000.)

#### PROJECT RATIONALE:

The Raman microprobe permits one to obtain Raman spectra from very small areas. Many points on a given wood fiber cross section can be evaluated. This provides a method to obtain new information on fiber composition and molecular structure which is currently not obtainable by any other method. These data will be useful in relating changes in fiber structure caused by different process stages, (pulping, bleaching, refining) to properties of the final product.

#### RESULTS TO DATE:

Optimization of the Raman microprobe, together with the new techniques developed, have permitted acquisition of high quality spectra that clearly indicate a high level of organization of lignin in the cell walls. The spectra show lignin to be oriented with respect to the plane of the cell wall surface, and to vary in amount, relative to cellulose, from point to point within the secondary wall.

#### PLANNED ACTIVITY FOR THE PERIOD:

Exploration on the spectra of different woods and native fibers will be continued. The effects of mechanical and chemical treatments on the architecture of the cell walls will be investigated in conjunction with our high yield pulping program.

#### POTENTIAL FUTURE ACTIVITIES:

Continuation of the program in conjunction with the DOE supported effort is anticipated through Fiscal 1986/87.

#### STUDENT RELATED RESEARCH:

J. Wiley, Ph.D.-1985.

PROJECT TITLE: Fundamentals of Brightness Stability

Date: February 1985

PROJECT STAFF: W. F. W. Lonsky

Budget: \$ 110,000

PRIMARY AREA OF INDUSTRY NEED: Raw Materials

Period Ends: 6/30/86

PROGRAM AREA: Much Higher Yield Pulps for Conventional Product Lines

Project No.: 3524

Approved by VP-R:

PROGRAM GOAL: A significant increase in yield of useful fibers

PROJECT OBJECTIVE:

Elucidate mechanism for brightness loss in high yield pulps.

PROJECT RATIONALE:

One of the major drawbacks of high lignin 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 to evaluate both photobleaching and color development has been set up. The presence of oxygen is a necessity for both types of reactions. Results to date confirm our concept of yellowing being induced by singlet oxygen. We have support, but no proof yet, that photobleaching is a result of triplet oxygen interaction with the quinone triplet state. Photobleaching with visible light was shown to be possible, but not economically feasible. A computerized UV/visible spectrophotometer system has been set up and used for experiments on color development in high lignin pulps upon exposure to ultraviolet radiation. A UV monochromator has been set up to evaluate the photo-activity of narrow UV wavelength ranges on paper (290 to 400 nm in 4 to 10 nm intervals). The highest photo-activity was found in the wavelength range around 310 nm.

A brightness stabilization concept has been developed based on selective absorption of harmful UV radiation with subsequent fluorescence in a longer wavelength range that will serve to photobleach. It has been found that commercial optical brighteners do not absorb UV radiation in all the required wavelength ranges. Some basic structures of suitable fluorescing compounds have been elucidated. Problems remain with compound stability, color, and efficiency. Contacts with dye producers have been established, but interest and support is poor.

The kinetics of the yellowing reaction has been developed and permits a quantitative comparison of brightness stability of various bleached and unbleached, softwood and hardwood, sheets. Laboratory results have been verified by outdoor experiments. Alkali/peroxide bleached pulp yellows much faster than the unbleached pulp. The light-induced yellowing reaction is not affected by heavy metals remaining in the sheets of industrial grade pulps. Heavy metals appear to have some effect on thermal aging.

PLANNED ACTIVITY FOR THE PERIOD:

Verify the interactions of singlet or triplet oxygen in photobleaching and yellowing reactions. Demonstrate suppression of yellowing by quenching singlet oxygen and/or lignin modification, including clarification of the organic peroxide structures formed during alkali/peroxide bleaching and how they affect brightness stability. Factors limiting the brightness of high yield pulps will be defined.

Project 3524

POTENTIAL FUTURE ACTIVITIES:

Evaluate the effect of sizing and filler materials on brightness stability. Determine best light stability possible based on combination of such as light absorption, photobleaching, and lignin modification. Define the effect of treatments used to improve the physical strength of high yield pulp on brightness level and stability.

STUDENT RELATED RESEARCH:

G. Furman, Ph.D.-1985; S. Lebo, Ph.D.-1986; W. Welsh, M.S.-1985; D. Fox, M.S.-1986.

PROJECT TITLE: Exploratory Research (Chemical Sciences Division)

Date: February 1985

PROJECT STAFF: Division 20

Budget: \$ 70,000

PRIMARY AREA OF INDUSTRY NEED: Open

Period Ends: 6/30/86

PROGRAM AREA: N/A

Project No.: 3534

PROGRAM AREA: N/A

Approved by VP-R:

PROGRAM GOAL: N/A

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; some will not.

RESULTS TO DATE:

Exploratory work has been done in such areas as analytical test methodology, oxidative extraction (E/O), cellulose in fresh water algae, electrochemistry at high temperatures, supercritical fluid pulping, and use of NMR to define water in pulp fibers.

PLANNED ACTIVITY FOR THE PERIOD:

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

PROJECT TITLE: Incremental Capacity in Recovery Boilers  
 PROJECT STAFF: T. M. Grace, D. T. Clay  
 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: February 1985
Budget: \$ 50,000
Period Ends: 6/30/86
Project No.: 3558
Approved by VP-R:

PROJECT OBJECTIVE:

Develop procedures for assessing the degree to which capacity increases can be obtained by operating changes or retrofits. Evaluate approaches for achieving incremental capacity.

PROJECT RATIONALE:

Because of the large capital cost of new units, there is a compelling need for methods that will give incremental capacity increases for existing recovery units based on incremental investments.

RESULTS TO DATE:

Work on high intensity black liquor oxidation has been completed, with significant input from the Ph.D. program. It was concluded that this is not a feasible method for obtaining incremental recovery boiler capacity because the associated gelling of the liquor cannot be overcome by any economical method.

A review article on incremental capacity in recovery boilers has been published.

PLANNED ACTIVITY FOR THE PERIOD:

Prepare a detailed "checklist" of capacity limiting factors and methods for determining which factors govern a particular boiler.

Reach a decision regarding critical research needs for capacity improvement.

POTENTIAL FUTURE ACTIVITIES:

If an approach is found to be feasible, we will proceed toward commercial implementation.

STUDENT RELATED RESEARCH:

S. Francoeur, M.S.-1985; T. Cartwright, M.S.-1986.

PROJECT TITLE: Strong, Intact, High Yield Fibers

Date: February 1985

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

Budget: \$ 170,000

PRIMARY AREA OF INDUSTRY NEED: Raw Materials

Period Ends: 6/30/86

PROGRAM AREA: Much higher yields for conventional product lines

Project No.: 3566

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

Approved by VP-R:

#### 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.

#### PROJECT RATIONALE:

Most high strength, high brightness pulp is now made by the kraft process at yields of about 50%. 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, means can 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 may provide 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:

Preliminary experiments showed that high (80 to 85%) yield pulps can be prepared with sheet strength approaching that of kraft and fiber strength better than that of kraft. The strength of the fibers in spruce and pine wood has been determined and found to be significantly higher than that of pulp fibers. Work is in progress to determine the change in fiber strength that accompanies fiber separation under various conditions.

#### PLANNED ACTIVITY FOR THE PERIOD:

The short term goals are to identify the factors governing retention of fiber strength and integrity during fiber separation, to develop methods of controlling them and to determine the effects of selective chemical modification of fiber wall components and structural elements on fiber properties.

## Project 3566

The following activities are planned: (1) Completion of literature survey to collect and interpret results of previous work relevant to the short term goals; (2) determination of the effect of thermomechanical fiberization on the strength and size of southern pine and spruce fibers; (3) investigation of mathematical models of the cell wall to evaluate their usefulness in guiding experimental work on chemical modification of the fiber; (4) initial experimentation to determine the effects of wall component modification; (5) measurement of relevant wood properties before and after chemical treatment and correlation with fiberization behavior; and (6) identification of candidate alternative fiber separation methods, as well as preliminary experimentation and equipment design for subsequent work in this area.

## POTENTIAL FUTURE ACTIVITIES:

Determination of effects of chemical solvent and biological treatments on relevant wood properties to predict fiberization behavior and evaluation of alternative fiberization methods.

## STUDENT RELATED RESEARCH:

T. Heazel, Ph.D.-1986; E. Byers, Ph.D.-1986; C. Nordberg, Special Student-1985.

STATUS REPORT  
TO THE  
PULPING PROCESSES  
PROJECT ADVISORY COMMITTEE

APRIL 1-2, 1985  
THE INSTITUTE OF PAPER CHEMISTRY  
APPLETON, WI 54912



## TABLE OF CONTENTS

	Page
FINE STRUCTURE OF WOOD PULP FIBERS (Project 3288) .....	1
SMELT-WATER EXPLOSIONS (Project 3456-2) .....	2
FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES (Project 3473-1) ....	3
IMPROVED PROCESSES FOR BLEACHED PULP (Project 3474).....	6
FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING (Project 3475) ...	8
DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES (Project 3477) ...	10
FUNDAMENTALS OF BRIGHTNESS STABILITY (Project 3524) .....	13
INCREMENTAL CAPACITY IN RECOVERY BOILERS (Project 3558) .....	14
SEPARATION OF STRONG, INTACT FIBERS (Project 3566) .....	15

PROJECT SUMMARY FORM

DATE: February 22, 1985

PROJECT NO. 3288: Fine Structure Of Wood Pulp Fibers

PROJECT LEADER: R. H. Atalla ~~RAA~~

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

CURRENT FISCAL BUDGET: \$48,000

SUMMARY OF RESULTS SINCE LAST REPORT:

We have continued to investigate the implications of the composite nature of native celluloses. Earlier SS  $^{13}\text{C}$ -NMR studies showed native celluloses to be composites of two crystalline forms,  $I_\alpha$  and  $I_\beta$ . Their Raman spectra in the skeletal region show that they have the same molecular conformation. More recent measurements of spectra in the OH stretching region show that  $I_\alpha$  and  $I_\beta$  celluloses have different hydrogen bonding patterns. The distribution between the two forms varies over a wide range among native celluloses. We now have indications that their susceptibilities to swelling and chemical reaction may be different. The relative amounts of the two forms in a native cellulose are, therefore, likely to be important determinants of fiber and sheet properties.

We have continued to refine our methods for detecting subtle differences between celluloses by combined chemical and spectroscopic techniques.

PLANNED ACTIVITY THROUGH FISCAL 1986:

1. Use SS  $^{13}\text{C}$ -NMR and Raman spectra to characterize the differences between the responses of  $I_\alpha$  and  $I_\beta$  to chemical reactions and to pulping conditions.
2. Explore further the range of variation in wood derived cellulose fibers, and the degree to which this may be a factor in the response of fibers to process conditions.
3. Look further into the nature of the forces responsible for aggregation of cellulose with related cell wall polysaccharides and with lignin.

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 and product properties. New information on cellulose and fine fiber structure will be useful in guiding program activities. Future work will focus on the structures of native wood fibers and their modification in both conventional chemical and high yield pulping processes. Particular attention will be given to the factors (yet to be determined) which control fiber strength and conformability.

PROJECT SUMMARY FORM

DATE: February 25, 1985

PROJECT NO. 3456-2: Smelt-Water Explosions

PROJECT LEADER: T. M. Grace

IPC GOAL:



Fundamentally increase the potential capacity of processes.

OBJECTIVE:

An increased understanding of the phenomena of explosions associated with rapid phase transitions (explosive boiling), and the application of that knowledge to reduce the hazards of operating recovery boilers.

CURRENT FISCAL BUDGET: \$25,000

SUMMARY OF RESULTS SINCE LAST REPORT:

The main activity on this project is participation in BLRBAC and the API Recovery Boiler Committee. The experiences of the industry with recovery boiler explosions and emergencies are monitored for insight into ways to improve safety.

Preliminary results are in on Case I of the Energetics of Smelt/Water Explosion project sponsored by the Nuclear Regulatory Commission. Only a very small fraction of the energy potentially present in molten smelt within the furnace shows up as deformation energy in the furnace structure. The best estimate of energy conversion efficiency for the Case I explosion is 0.25%. Accountable deformation energy is only about 5000 Btu or about 2.5 lb TNT equivalent. This is despite the fact that all four walls and the floor had to be replaced. Additional analyses are in progress to determine pressure-time loadings consistent with the observed damage, and the suppressing effect the bed would have on a "below-bed" explosion. Analysis of Case II, a CE unit, has also been initiated.

Steps toward formal collaboration with Professor Michael Corradini of the Nuclear Engineering Department at the University of Wisconsin, Madison, have been taken. He is an expert in the theory of liquid-liquid explosions and has access to the experimental work going on at Sandia on these types of explosions in the nuclear industry. He has proposed to have a graduate student at Madison look at two subtopics:

1. Fundamentals of mixing of smelt and water during an explosion in a stratified geometry.
2. Use the vapor explosion models they have developed to perform sensitivity calculations on the mechanical energy released from the explosion.

We are looking into this proposal and into funding for it.

PLANNED ACTIVITY THROUGH FISCAL 1986:

Continuation of above.

FUTURE ACTIVITY:

Possible joint proposal with Professor Corradini for vapor explosion research in a stratified contact mode.

PROJECT SUMMARY FORM

DATE: February 25, 1985

PROJECT NO. 3473-1: Fundamental Processes in Alkali-Recovery Furnaces

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

IPC GOAL:

*MB*

Fundamentally increase the potential capacity of processes.

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.

CURRENT FISCAL BUDGET: \$185,000

SUMMARY OF RESULTS SINCE LAST REPORT:

The summary technical report on the char burning work has been issued. This comprehensive report provides the quantitative verification of the sulfate-sulfide cycle theory of char burning, and discusses the implications on recovery boiler operation. Publication of this report completes work on char burning per se.

Progress Report Three on carbon oxidation in molten salts has been issued. This provides detailed data on the rates of carbon oxidation in molten mixtures of carbonate, sulfate and sulfide. It is one report in a series describing the fundamental processes occurring in a recovery furnace. Portions of this data were used in support of the sulfate-sulfide cycle theory of char burning.

Work continues on fundamentals of fume formation. Previous work had shown that intense fuming occurred when sodium sulfide was oxidized to sodium sulfate in a sodium carbonate melt. This phenomenon, which we called "oxidative fuming," was unexpected and very difficult to interpret in terms of existing concepts of fume formation. The initial interpretation postulated a volatile sodium-oxygen intermediate formed during sulfide oxidation. Later studies suggested an alternate explanation; elimination of gas-side mass transfer resistance to sodium volatilization by reaction of oxygen and sodium vapor very close to the gas-melt interface. Work in this most recent period has focussed on trying to determine which, if either, of these two explanations is correct. Experiments conducted included examination of the effect of CO<sub>2</sub> concentration on the fuming rate, use of tagged oxygen, variations in the ratios of K/Na (and Li/K/Na) in the melt, and effects of using high sulfide and/or oxygen concentrations. Although very interesting data were obtained, the results are currently still inconclusive with respect to the fuming mechanism.

The phenomenological study of the black liquor burning behavior using the single-particle reactor has been initiated. Seventeen different mill liquors have been obtained so far. All of these liquors have been analyzed for heating value, active alkali, and sulfated ash. A subset of five liquors was taken through a statistically designed set of pyrolysis runs using nitrogen gas. The planned set of runs has been completed, but the data have yet to be analyzed.

## Project 3473-1

Subsequent combustion tests will then be done on these liquors. When the complete set of runs on the five liquor subset is complete, an experimental plan for the remaining liquors will be developed. We also will continue to expand the liquor data base by seeking further samples. Progress on this work has been delayed somewhat, because the people involved are also involved in the installation and start up of the Phase I Central Unit of the DOE Continuous Flow Reactor.

There is a good deal of related student work which contributes heavily to this project. Within the current reporting period:

P. Miller has completed the phenomenological portion of his Ph.D. thesis on swelling of black liquor during pyrolysis. Key variables governing swelling have been defined.

M. Robinson has initiated a Ph.D. thesis on the drying of black liquor droplets. J. Wozniak completed an M.S. project which resulted in an experimental system for measuring the density, viscosity and surface tension of molten salt mixtures.

B. Moreland completed an M.S. project on the effects of moisture content on the combustibility of high-solids black liquor.

D. Hennessy completed an M.S. project on the rate of sulfate reduction by hydrogen gas which shows very complex behavior.

J. Cantrell is working on an M.S. thesis on sulfur release during pyrolysis of black liquor.

In addition, four new M.S. projects were initiated:

K. Georg - Gasification of kraft char with  $CO_2$ .

T. Coenen - Effect of catalysts in sulfate reduction with CO.

K. Crane - Modeling the combustion of a spherical black liquor particle.

D. Sumnicht - Recovery furnace model: smelt bed through liquor guns.

### PLANNED ACTIVITY THROUGH FISCAL 1986:

Work on fundamentals of fume formation will continue. This work should reach a definite conclusion on the cause of oxidative fuming and a quantitative understanding of the variables that control it.

The phenomenological study of burning behavior will continue. The data base will be broadened by including more mill liquors. We especially want to include liquors that burn remarkably well or very poorly.

We will initiate a study of the fundamentals of sulfur release and recapture in black liquor burning. This is the next key furnace process to be addressed. This information will be essential to interpreting the data obtained on the DOE Continuous Flow Reactor (Cooperative Project 3473-6).

We will extend our capability to measure physical properties of smelt and char and begin measurements on key entectic mixtures. Equipment for measuring properties is in hand as a result of an M.S. research project.

During this period the Phase I DOE reactor will become fully operational. We will obtain extensive data on the in-flight processes of drying, pyrolysis, gasification and gaseous combustion under continuous flow conditions. Design of the Phase II reactor for continuous char combustion will be undertaken.

Project 3473-1

FUTURE ACTIVITY:

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

Development of a comprehensive mathematical model of a recovery boiler incorporating information gained in these studies. (This has been initiated as an M.S. project.)

Write a book on the theory of black liquor combustion and its application to recovery boiler operation.

Expand recovery boiler corrosion studies in cooperation with the IPC Corrosion Group.

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

PROJECT SUMMARY FORM

DATE: February 27, 1985

PROJECT NO. 3474: Improved Process for Bleached Chemical Pulp

PROJECT LEADERS: T. J. McDonough, N. S. Thompson

IPC GOAL: Improved bleach 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 BUDGET: \$145,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Fundamental chemical and engineering aspects of alkaline pulping and nonchlorine bleaching have continued to be the focus of our efforts on this project. The chemical kinetics and transport phenomena of the component processes of alkaline sulfite anthraquinone (ASAQ) pulping are being studied with the aim of achieving a better understanding of the factors governing selectivity in this and other alkaline pulping processes. The fundamentals of the reactions of oxygen-derived species with kraft pulp fibers are being investigated with a view to achieving highly selective bleaching without resorting to the use of chlorine.

Our work on the kinetics of delignification, carbohydrate degradation and cellulose chain cleavage has recently been directed at understanding these phenomena during the early stages of the pulping reaction. We have characterized this phase of the process with respect to rates of removal of individual wood components and rate of pulping chemical consumption. We have also done kinetic experiments to establish the dependence of the rates of component removal on the concentrations of sulfite and anthraquinone. Work is in progress to determine the corresponding activation energies. The data we are obtaining on the initial phase of ASAQ pulping is also relevant to our high yield pulping research.

The effect of several antioxidants, in addition to those already tested, on the degradation of kraft pulp during oxygen bleaching has been evaluated. These additives were not as effective as magnesium ion in preserving pulp viscosity at a given kappa number. They did result in pulps with greater viscosities than those produced in the absence of antioxidants. Nevertheless, no additive tested to date equals the effectiveness of magnesium ion in its ability to stabilize pulp against oxygen degradation and the likelihood of finding one is not good. This experimental approach has, therefore, been terminated.

Experiments to determine the mechanism of radical decomposition of pulp fibers during oxygen bleaching have led to the conclusion that the observable degradation proceeds through the amorphous regions of the fiber rather than the crystalline region as was postulated earlier. These regions include both the interface between cell wall layers and fibrillar structures and the amorphous regions within the crystalline cellulosic fibrils. The degradation is hindered by the presence of lignin, perhaps because of both accessibility and chemical considerations. The degradations are not thought to be initiated by the superoxide radical but by a decomposition product derived from it.

## Project 3474

The mechanism by which the degradation proceeds through the amorphous regions of fibers is not known but is thought to proceed by way of a chain mechanism. The degradation probably involves radicals and will be investigated further.

Attempts were made using controlled amounts of superoxide to modify the surface of unbleached kraft tracheids in a manner similar to that achieved using cotton fibers. Initial analysis suggests that the presence of lignin hindered the reaction by acting as a physical barrier and as a radical quencher.

### PLANNED ACTIVITY THROUGH FISCAL 1986:

Investigation of the chemical and engineering fundamentals of ASAQ pulping will be continued until satisfactory rate laws for lignin and carbohydrate reactions during all three phases have been developed. Modified pulping sequences suggested by then will be investigated, and the bleachability of the pulps evaluated.

Emphasis of the research on reactions of oxygen-derived species with pulp will be shifted from controlling carbohydrate degradation to enhancing delignification. Initially, selected pretreatments will be investigated. The effects of these sequences and their methods of application on both lignin removal and cellulose modification will be examined. The relationship between changes in chemical properties of the lignin component and the response of lignin and cellulose to bleaching will be monitored.

### FUTURE ACTIVITY:

Emphasis will continue on understanding the kinetics of both lignin and carbohydrate removal during pulping operations with a view to achieving more selective delignification and controlling the structure of the residual lignin to make it more amenable to removal in subsequent bleaching operations.



PROJECT SUMMARY FORM

DATE: February 27, 1985

PROJECT NO. 3475: Fundamentals of Selectivity in Pulping and Bleaching

PROJECT LEADERS: D. R. Dimmel, L. R. Schroeder

IPC GOAL:

*D.R.D. L.R.S.*

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 composition and location of lignin, hemicelluloses, and cellulose that remain in the pulp during pulping and bleaching.

CURRENT FISCAL BUDGET: \$180,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Electrochemical techniques have been applied to the study of the interaction of anthrahydroquinone (AHQ) species with lignin model quinonemethide (QM) species at room temperature in organic solvents. We have been able to show that AHQ ions participate in single electron transfer (SET) reactions with QMs to cause the latter to initially polymerize and finally to fragment to phenol products. Fragmentation reactions of lignin model compounds at 150° in aqueous alkali in the presence of AHQ ions have also been a focus of recent work. These studies have been plagued by problems in accurately analyzing the phenol product yields. Even so, we have completed our study of a set of models which show that steric hindrance to reaction is insignificant, lending support for a SET mechanism operating under pulping conditions. Work continues on demonstrating that fragmentation of QMs under pulping conditions initially produces phenoxy radicals. Several new models were synthesized, along with a sample of allyl anthrone. Resorcinol, but not other simple phenols, has been shown to efficiently fragment lignin models; however, resorcinol has a relatively low effectiveness as a pulping additive in wood delignification.

Previous studies have shown that soda-anthraquinone causes DP losses in amylose, but the effect on cellulose (cotton linters) was, at most, very small. A program to determine whether the difference in the reactivity of anthraquinone toward these two carbohydrate polymers is due to stereochemical factors and/or intermolecular association (crystallinity and solubility) has been initiated. Two disaccharide model compounds are being used to address the role of stereochemistry in the anthraquinone reaction. Studies of the cellulose model, 1,5-anhydrocellobiitol, are now complete. These have shown that anthraquinone, but not its reduced analog, anthrahydroquinone, does have the potential to accelerate cleavage of the glycosidic bonds in cellulose. Similar studies of the amylose model, 1,5-anhydromaltitol, are still in progress. Thus far, the studies indicate that alkaline cleavage of both  $\beta$ -1,4, and  $\alpha$ -1,4 glycosidic bonds can be accelerated by anthraquinone. Thus, stereochemical factors do not account for the different responses of amylose and cellulose to soda-anthraquinone.

Project 3475

PLANNED ACTIVITY THROUGH FISCAL 1986:

Studies will continue to be directed at showing that unique SET reactions promote delignification kinds of reactions. The work will swing away from convention approaches, and shift toward exploring the high temperature electrochemistry of aqueous alkaline solutions of lignin models, lignin, and wood. Our initial goals will be to fabricate an electrochemical cell which will function under modest pulping-like conditions and to test the value of electrochemistry for studying pulping reactions. Partial support of this work from the Department of Energy is being sought; an electrochemical group at the Solar Energy Research Institute will be cooperating with us in this research.

The study of the effect of anthraquinone on random cleavage of polysaccharides will be continued. Specifically, the studies of 1,5-anhydromaltitol will be completed and then the effect of soda-anthraquinone on decrystallized cellulose will be examined.

FUTURE ACTIVITY:

Studies involving high temperature electrochemistry will be expanded into evaluating methods to monitor and promote (desirable) pulping reactions. Should SET reactions be shown to be important to efficient pulping, we will examine novel ways to promote these reactions in an economical manner.

Mechanistic studies of cellulose chain cleavage in alkaline pulping indicate that increased ionic strength could accelerate the cleavage reaction. Thus, the effect of "dead load" (increased ionic strength) on cellulose chain cleavage during pulping will be examined.

PROJECT SUMMARY FORM

DATE: February 27, 1985

PROJECT NO. 3477: Development and Application of Analytical Techniques

PROJECT LEADER: D. B. Easty *DE*

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:

Analysis of Pulping and Bleaching Liquors by Ion Chromatography

A method for determining chlorine dioxide in bleach liquors by ion chromatography (IC) has been developed and tested. It is based upon a chlorite response in the IC conductivity detector found to be proportional to the  $\text{ClO}_2$  injected. Chlorine dioxide contents of liquors determined by IC were in close agreement with values obtained by the tyrosine and iodometric procedures. A ten-fold excess of chlorine was found not to interfere with the  $\text{ClO}_2$  determination.

Chlorite -  $\text{ClO}_2$  mixtures are analyzed by IC in two steps. The first result represents chlorite plus  $\text{ClO}_2$ . In the second step, chlorite alone is determined following removal of  $\text{ClO}_2$  with nitrogen sparging. This technique was demonstrated by successful analysis of mixtures of known concentration.

In pH 10.8 eluent, chlorine is converted to hypochlorite and determined by IC using the electrochemical (amperometric) detector. Ion chromatographic results agreed with those from iodometric titration. Chlorine dioxide did not interfere with the IC determination of chlorine.

Quantitative spike recovery values documented the validity of IC for determining oxalate in bleaching effluents. This concludes the planned investigation of IC for bleach liquor analysis.

Determination of Lignin in Wood Pulp by Diffuse Reflectance  
Fourier Transform Infrared Spectrometry

The past several months have been devoted to the training of a new infrared specialist. Consequently, no further work has been done on this project.

PLANNED ACTIVITY THROUGH FISCAL 1986:

Results of the study of IC analysis of bleach liquors will be reported to the membership and submitted for publication, perhaps by the end of fiscal 1985.

Studies of lignin determination by diffuse reflectance FTIR will involve analysis of more pulps and rigorous evaluation of the data obtained. Results will indicate how good FTIR is at estimating lignin in pulps.

FUTURE ACTIVITY:

Future work will involve continued studies of pulp and liquors by chromatographic and spectrometric techniques. Likely topics are: improved material balance in unbleached pulp analysis, pyrolysis gas chromatography, and determination of volatiles by headspace analysis.

PROJECT SUMMARY FORM

DATE: February 25, 1985

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:

In conjunction with outside sponsors, use the Raman Microprobe to develop a better understanding of wood fiber structure.

OBJECTIVE:

- (1) Establish by Raman microprobe spectroscopy, the variability of molecular structure and organization in cell walls of native woody tissue. Also by the same methods explore the effects of chemical treatments on structure and organization. (This work is also supported by the DOE under Project 3521-3 with a Fiscal-1984/85 budget of \$47,200.)

CURRENT FISCAL BUDGET: \$45,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Optimization of the Raman microprobe, together with the new techniques developed, have permitted acquisition of high quality spectra that clearly indicate a higher level of organization of lignin in the cell walls than heretofore recognized. The spectra show lignin to be oriented with respect to the plane of the cell wall surface, and to vary in amount, relative to cellulose, from point to point within the secondary wall.

We have continued to refine our procedures to improve space resolution achieved with the microprobe. Current limits are 1.5 to 10 micrometers, depending on the objective lens in use. We have also used the microprobe in studies of the polarization sensitivity of the spectra of fibrillar aggregates of celluloses derived from valonia and ramie. We believe these will provide us with a basis for the most definitive assignment of the spectrum of cellulose to date, and may lead us to a new procedure for determining fibrillar angles in cell walls. We have also acquired spectra from substantially deuterated celluloses derived from *Cladophora glomerata* cultured in deuterium oxide; these too will contribute to the definitive assignment of the spectrum.

PLANNED ACTIVITY THROUGH FISCAL 1986:

Exploration of the spectra of different woods and native fibers will be continued. The effects of chemical and mechanical treatment on the architecture of the cell walls will also be investigated. This work is part of the IPC program on high yield pulps.

FUTURE ACTIVITY:

Continuation of the program in conjunction with the DOE supported effort is anticipated through Fiscal 1986/87.

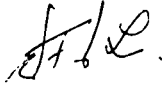
PROJECT SUMMARY FORM

DATE: February 27, 1985

PROJECT NO. 3524: Fundamentals of Brightness Stability

PROJECT LEADER: W. F. W. Lonsky

IPC GOAL:



Significant increase in yield of useful fibers

OBJECTIVE:

Define mechanism for brightness loss in high lignin pulps.

CURRENT FISCAL BUDGET: \$90,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Heavy metals at concentration levels found in commercial spruce TMP do not significantly effect the brightness stability upon light exposure. Heavy metals appear to have some effect on thermal aging.

A UV monochromator has been set up to evaluate the photoactivity of narrow UV wavelength ranges on paper (290 to 400 nm in 4 to 10 nm intervals). The highest photoactivity was found in the wavelength range around 310 nm. Lignin structures absorbing light at 350 nm are converted to p-quinones. The newly formed absorption band has an absorption maximum at 405 nm as obtained from s and k calculations for spruce TMP sheets.

Oxygen plays a dominant role as reaction partner in the photoyellowing and photobleaching reaction. It has been shown that oxygen is enriched on the fibers vs. air. Experiments on  $^{16}O_2$  and  $^{32}O_2$  participation in the reactions gave ambiguous results.

PLANNED ACTIVITY THROUGH FISCAL 1986:

Lignin modification reactions will be performed to suppress the yellowing reactions. The detailed yellowing mechanism will be elucidated. It will be clarified whether organic peroxide structures are formed during alkali/peroxide bleaching and how they affect brightness stability.

Factors limiting the brightness of high yield pulps will be defined.

FUTURE ACTIVITY:

Evaluate the effect of sizing and filler materials on brightness stability. Determine best light stability possible based on combination of such as light absorption, photobleaching, and lignin modification. Define the effect of treatments used to improve the physical strength of high yield pulp on brightness level and stability.

PROJECT SUMMARY FORM

DATE: February 25, 1985

PROJECT NO. 3558: Incremental Capacity in Recovery Boilers

PROJECT LEADERS: T. M. Grace, D. T. Clay, R. J. Kapheim

IPC GOAL:



Increase the capacity potential of processes.

OBJECTIVE:

Develop a methodology for determining recovery boiler capacity limiting factors and evaluate techniques for gaining incremental capacity.

CURRENT FISCAL BUDGET: \$70,000

SUMMARY OF RESULTS SINCE LAST REPORT:

The review article on incremental capacity in recovery boilers was published in the November issue of Tappi Journal.

No other work on the specific objectives of this project was undertaken in this period because of the press of other activities.

Student related research in this period is as follows.

S. Francoeur completed an M.S. project on the conceptual design of a cyclone system for dried solids firing.

T. Cartwright has initiated an M.S. project on the fluidized bed drying of black liquor.

E. Buehler has initiated an M.S. project on intensified black liquor combustion.

PLANNED ACTIVITY THROUGH FISCAL 1986:

Prepared a detailed "checklist" of capacity limiting factors and methods for determining which factors govern a particular boiler.

Reach a decision regarding critical research needs for capacity improvement.

FUTURE ACTIVITY:

If an approach is found to be feasible, we will proceed toward commercial implementation.

PROJECT SUMMARY FORM

DATE: February 25, 1985

PROJECT NO. 3566: Separation of Strong, Intact Fibers

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

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

OBJECTIVE:

Develop wood fiber separation and treatment methods that will allow good control of the strength and physical form of the resulting fibers. The mechanical properties should be as good as or better than those possessed by the fiber as it existed in the original wood, and the geometrical form of the original fibers should either be preserved or altered in controlled directions.

CURRENT FISCAL BUDGET: \$170,000

SUMMARY OF RESULTS SINCE LAST REPORT:

The in-situ tensile strength of earlywood and latewood spruce and pine fibers has been determined by the methods developed earlier. In addition, variation between and within trees has been determined for each species. Sulfonation was shown to increase the strength of wood fibers in situ, but only in proportion to the accompanying yield reduction. Currently, effort is being directed toward pulping of the wood in simulated thermomechanical and chemimechanical processes, determining the strength of the resulting fibers, and measuring the effects of pulping variables on fiber strength retention.

PLANNED ACTIVITY THROUGH FISCAL 1986:

The short term goals are to identify the factors governing retention of fiber strength and integrity during fiber separation, to develop methods of controlling them and to determine the effects of selective chemical modification of fiber wall components and structural elements on fiber properties.

The following activities are planned: (1) Completion of literature survey to collect and interpret results of previous work relevant to the short term goals; (2) determination of the effect of thermomechanical fiberization on the strength and size of southern pine and spruce fibers; (3) investigation of mathematical models of the cell wall to evaluate their usefulness in guiding experimental work on chemical modification of the fiber; (4) initial experimentation to determine the effects of wall component modification; (5) measurement of relevant wood properties before and after chemical treatment and correlation with fiberization behavior; and (6) identification of candidate alternative fiber separation methods, as well as preliminary experimentation and equipment design for subsequent work in this area.

FUTURE ACTIVITY:

Determination of effect of chemical solvent and biological treatments on relevant wood properties to predict fiberization behavior and evaluation of alternative fiberization methods.