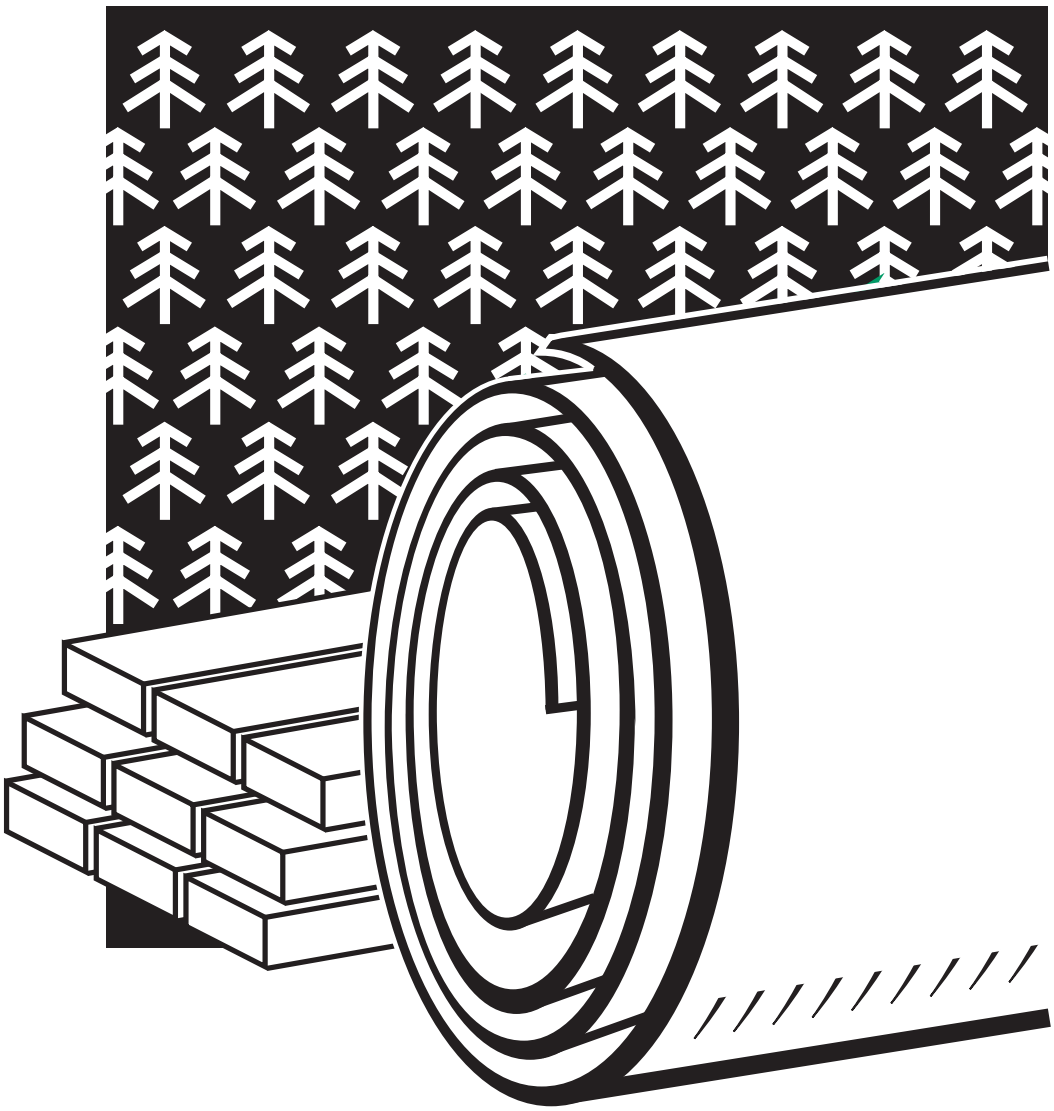
Forest Products Industry of the Future

Quarterly Status Reports

As of June 30, 2004



U.S. DEPARTMENT OF ENERGY

02-GA50113-09

Forest Products

Industry of the Future

Quarterly Status Reports

As of June 30, 2004

Contacts

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Special Projects

Enhanced Raw Materials

Mill Processes: Pulping

Mill Processes: Papermaking

Mill Processes: Process Control

Mill Processes: Recovery / Environmental

Improved Fiber Recycling

Wood Processing

Energy Challenge

Whitaker: Institute of Paper Science and Technology

GO10220, CPS#00257

DOE QUARTERLY REPORT

For: Energy Challenge 2004: A Paper Snow Board Competition

Covering Period: April 1, 2004 – June 30, 2004

Date of Report: July 30, 2004

Recipient: Institute of Paper Science and Technology at Georgia Tech

Award Number: DE-FC36-97GO10220

Contact: Timothy Patterson, PhD
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Project Team: Doug Hooker, Project Officer, 303-275-4780, Doug.Hooker@go.doe.gov

Project Objective:

1. Promote energy efficiency concepts in undergraduate and graduate education.
2. Stimulate and interest in pulp and paper industrial processes, which promote and encourage activities in the area of manufacturing design efficiency.
3. Attract both industrial and media attention.

Background:

In 1997, the Institute of Paper Science and Technology in conjunction with the U.S. Department of Energy developed a university design competition with an orientation to the Forest Products Industry. This university design competition is in direct alignment with DOE's interests in instilling in undergraduate education the concepts of developing energy efficient processes, minimizing waste, and providing environmental benefits and in maintaining and enhancing the economic competitiveness of the U.S. forest products industry in a global environment. The primary focus of the competition is projects, which are aligned with the existing DOE Agenda 2020 program for the industry and the lines of research being established with the colleges comprising the Pulp and Paper Education and Research Alliance (PPERA).

Budget Data:

Fourth Quarter: April 1, 2004 – June 30, 2004

Quarterly Financial Status Report
Project Numbers 1146A4179 and 1146658
For Period: 4/01/04 - 6/30/04

Phase / Budget Period			*Approved Spending Plan*			*Actual Spent to Date*		
			DOE Amount	*Cost Share*	*Total*	*DOE Amount*	*Cost Share*	*Total*
	From	*To*						
Year 1	*04/23/97*	*10/20/98*	*100,000*	*100,000*	*200,000*	*147,220*	*177,757*	*324,977*
Year 2	*10/21/98*	*10/20/99*	*100,000*	*103,081*	*203,081*	*52,780*	*83,372*	*136,152*
Year 3&4	*10/21/99*	*06/30/01*	*226,120*	*230,689*	*456,809*	*166,358*	*111,554*	*277,912*
Year 5-9	*07/01/01*	*06/30/06*	*584,313*	*584,313*	*1,168,626*	*387,750*	*378,568*	*766,318*
Totals			*1,010,433*	*1,018,083*	*2,028,516*	*754,108*	*751,251*	*1,505,359*

Status:

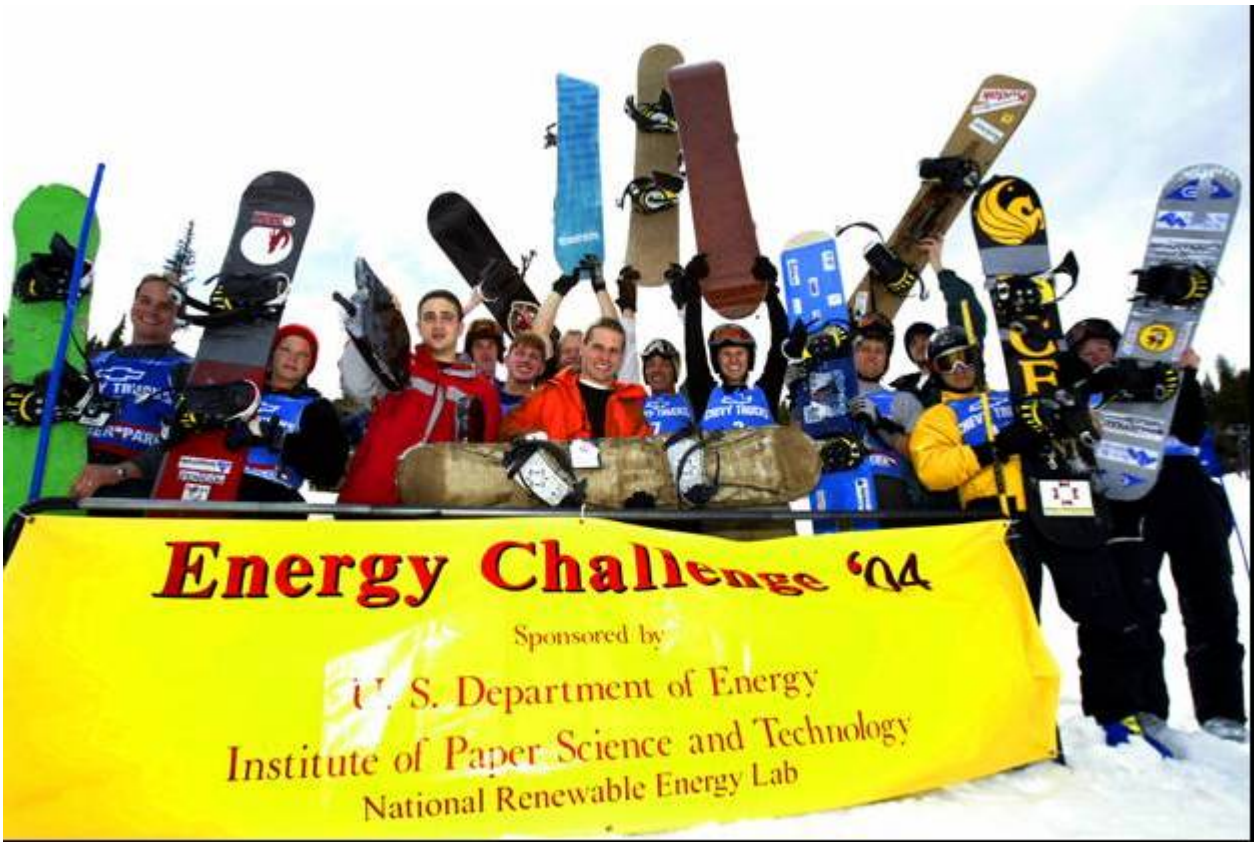
During the fourth quarter the most successful Energy Challenge competition to date was concluded. Of the 16 teams that submitted proposals, 13 teams were selected and competed in the Energy Challenge 2004 Paper Snowboard competition. Ten teams were sponsored directly through the joint IPST and DOE design competition. Two teams were sponsored by the National Renewable Energy Laboratory (NREL) and one team competed at its own expense. Previously, a maximum of ten teams competed in the Energy Challenge college design competition.

In addition to sponsoring 2 teams, NREL provided a tour of their facilities in Golden, Colorado. Energy Challenge themes of energy conservation, resource conservation, and biomass (fiber) utilization align well with the mission of the national laboratory. NREL also hosted the opening reception which included keynote addresses by Buddy Garland, DOE Program Manager - Industrial Technology, John Kerston, DOE Manager - Golden Field Office, and Jessie Harris, NREL Associate Director.

This was the seventh year and sixth competition in the ten year Energy Challenge program. The Energy Challenge program has afforded college and university students a unique opportunity to participate in a hands-on engineering project. They gained a myriad of experience interacting with industry representatives, as sponsors and mentors, along with DOE personnel, while converting technical theory to practical application. Energy Challenge is a vigorous and challenging engineering design and construction project. Many of the competing colleges and universities use the program as their senior design project. Energy Challenge is a multi-disciplinary design contest. A high value is placed on design innovation, novelty, and originality, leveraged resources, effective use of prior art, and cost effectiveness. An additional unique aspect of the contest is the emphasis placed on interaction with related industries by the competing teams.

The competition is not a single event but rather a complete process and the teams' efforts over the course of the competition are evaluated in a quantitative manner. The specific elements are mid project report, final project report, physical testing of construction, project documentary video, oral project presentation, and competition race results. Prior to the fourth quarter, the mid project reports and final project reports were evaluated. These comprehensive and detailed reports cover competition themes involving energy efficiency, waste minimization, and fiber content; design, construction and innovation; cost accounting including fundraising, sponsorship, and team support; and safety. The mid project report was worth 10% and the final report worth 20% of the overall competition score.

13 Colleges Compete in Energy Challenge 2004 at Winter Park, Colorado



The competition required the construction of two identical snowboards. One was to be used for the downhill race and the other was submitted to IPST for physical testing. Physical evaluation included non-destructive and destructive tests. To ascertain the strength and physical soundness of the construction, five physical properties were evaluated. These were density, flexural stiffness, compression strength, puncture resistance, and abrasion resistance. A major goal of the design project was to maximize fiber content. The percent fiber content of the snowboard was

used as a multiplier of the physical properties score. Testing protocols were based on TAPPI Test Methods T-220, T-836, T-825, T-803, and T-476, respectively. For each test, ten points were awarded to the team's board with the highest performance. Pro-rated points were awarded to the remaining teams based on their board's performance as related to the range of performance values. Thirty percent of the teams score was based on physical performance. Testing was completed at IPST by Robert Hall, Michael Schaepe and Tim Patterson.

On the day prior to the snowboard race, the competition judges gathered to review and evaluate the project documentary videos. These videos were to introduce the project teams; document the design and construction methods; showcase the novelty of design, material engineering, and aesthetics; address competition themes of energy efficiency, waste minimization, and fiber content maximization; and outline safety in design, construction, and racing. Production of a video would provide an avenue for the teams to express their creativity – also an evaluation factor. Ten percent of the overall competition score was based on the video.

Competition day started with team oral presentations. Using various visual aids including the competition snowboard, the presentations required that the teams describe the design and construction methods used, highlight the novelty of design, material engineering, and aesthetics, address competition themes of energy efficiency, waste minimization, and fiber content maximization, describe sponsor involvement, and discuss safety. The seven competition judges evaluated the presentation for content and professionalism. The scores for the presentation accounted for 10% of the overall competition score.

Seven judges evaluated the mid project reports, final reports, team documentary videos, and oral presentations. The judges were: Dr. Timothy Patterson, IPST; Michael Schaepe, IPST; Doug Hooker, DOE; Dr. Bonnie Hames, NREL; Robert Jeyseelan, Tyco Healthcare; Dr. Michael Shaffer, UCF-retired; and Dr. Stan Kozalak, UC-Berkeley-retired. The judges donated their time to evaluate the reports and attend the competition where they judged the oral presentations and videos. Additionally, they contributed to the efficient operation of the competition by answering team member questions and providing the odd hand at the competition starting line, awards ceremony, and reception. Without their contributions the competition could not have been executed with such success. Also contributing to the success of the program were MG Whitaker, IPST Project Manager, Anna Martinez-Barnish and John Horst, DOE, as well as other NREL, DOE, and IPST staff.

The competition was held in Winter Park, Colorado – a perfect venue for the snowboard competition and conveniently located near the Golden, Colorado offices of DOE and NREL. The venue host was Winter Park Resort. Winter Park Resort and its staff donated time and facilities to make this competition safe, comfortable, efficient, effective, and fun. Patty McCarthy was especially remarkable in coordinating functions and facilities at the competition venue. Without Winter Park Resort's contributions the competition would not have been possible.

A detailed media coverage plan was initiated by John Horst of the DOE. Additionally, David Bell of IPST contributed to execute a broad and extensive media coverage campaign. This resulted in 22 radio interviews with competitors, coverage in more than 100 publications and web sites, PR Newswire coverage seen by 118 journalist and 2,494 public viewers, and 35 television stories including Fox News with an estimated 777,000 viewers.

Two Competitors Navigating the Course

The Energy Challenge race, which requires a team member to compete on the product their team constructed, is the culminating event of this ambitious student engineering design and construction project. The race accounts for 20% of a team's total score and is the final activity of Energy Challenge. As usual, scoring at this point in the competition was close and the race finale served as exciting event conclusion. It is also a real world test for the product's performance as well as for the team's resilience. The race course was a moderately sloped slalom with rollers at the top and a jump at the base of the hill. These course features tested the board's robustness in a way unlike the testing in the controlled environment of the laboratory could. Here, the excitement of the competition and the desire to win caused the racer to push the board to its limit. The race, aside from being very exciting, was a visually and physically validating conclusion to the year long Energy Challenge project.

Energy Challenge 2004: Final Results

	TEAM	SCORES						TOTAL
		Mid-Term Report (max. 10)	Final Report (max. 20)	Performance & Engineering (max. 30)	Video (max. 10)	Presentation (max. 10)	Race Results (max. 20)	
1	Miami University	7.5	16.0	24.2	8.8	8.8	18.3	83.8
2	SCAD	8.7	17.9	17.0	9.0	9.3	16.7	78.5
3	Pasadena City College	7.7	15.9	13.8	8.3	8.2	20.0	73.9
4	University of Maine	8.2	16.2	16.3	8.3	8.7	15.0	72.5
5	NC State University	8.2	17.0	17.6	8.8	9.7	6.7	67.8
6	Lamar University	7.3	14.4	14.9	6.8	7.7	11.7	62.7
7	SUNY/Syracuse	7.6	15.6	8.8	7.9	8.4	13.3	61.6
8	Mississippi State University	3.7	12.8	14.6	7.9	7.3	10.0	56.2
9	Spartan School Aero.	7.1	13.6	14.4	6.3	8.3	5.0	54.6
10	Georgia Tech	7.4	15.7	12.8	7.6	8.3	0.0	51.8
11	Univ. Central Florida	6.2	13.6	9.6	6.3	7.7	8.3	51.7
12	Temple	7.5	14.3	7.3	6.3	6.9	1.7	44.0
13	Univ. of Colorado	7.0	10.2	0.0	0.0	6.3	3.3	26.7

Energy Challenge 2004: Snowboard Race Results

	TIME (seconds)			Best Time	PLACE
	Heat 1	Heat 2	Heat 3		
Pasadena	18.97	17.99	20.00	17.99	1
Miami-Ohio	19.02	18.44	22.77	18.44	2
SCAD	18.46	23.58	20.32	18.46	3
U Maine	19.45	19.43	18.99	18.99	4
SUNY	19.24	19.02	19.90	19.02	5
Lamar	38.89	24.71	22.11	22.11	6
Miss St	30.44	26.83	25.26	25.26	7
U C F	49.65	30.04	25.63	25.63	8
NCSU	33.88	138.36	31.41	31.41	9
Spartan	55.95		53.96	53.96	10
U Colorado	99.23			99.23	11
Temple		137.86		137.86	12
GT					13

Remaining activities include the issuance of the final newsletter and year end report, and updating the Energy Challenge web page. Although DOE has withdrawn funding for next year's program, IPST is investigating options to continue Energy Challenge. Possible funding sources include corporate sponsors and NREL. The plan for next year is to hold a competition to design and build a mountain bike frame or a whitewater kayak. A major change in the scope of the program is in expanding the competition beyond papermaking fibers to biomass. This change will open the competition to more broadly address energy issues and expand the engineering materials that can be used in the competition. IPST is looking forward to another successful and educationally valuable Energy Challenge in 2005

Summary Table: Energy Challenge Competition Results 1999 Through 2004

		1998-99 Thermal Insulated Impact Resistant Liquid Package	**2000** Paper Kayak	**2001** Sailboat Sail	**2002** Sailboard	**2003** Hang Glider Sail	**2004** Snowboard
1	Clarkson	x					
2	Georgia Tech Paper Sci	3	x		1	x	o
3	Georgia Tech ME						x
4	Lamar						x
5	Miami University of Ohio	x	3	3	2	x	1
6	Mississippi State	x	x		x		x
7	NC State #1	x		x	x	1	x
8	NC State #2				x		
9	NCAT					x	
10	Pasadena City College						3
11	SCAD					x	2
12	Spartan School of Aeronautics					2	x
13	SUNY-Syracuse		x	1			x
14	Temple					3	x
15	University New Mexico						o
16	University of Central Florida			x	x	x	x
17	University of Colorado	1	2				x
18	University of Maine	2	1	2	3	x	x
19	University of Minnesota		x				
20	Western Michigan University	x				x	o
	TOTAL	8	7	5	7	10	16

Note: number = place in competition, x = competing team, o = submitted proposal

Business Development Executive Program

Rice: Institute of Paper Science and Technology

GO10588, CPS#01250

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

QUARTERLY PROGRESS REPORT

Project Title: Business Development Executive Program

Covering Period: January 1 – March 31, 2004

Date of Report: June 9, 2004

Recipient: Institute of Paper Science and Technology (IPST)

Award Number: DE-FC36-00GO10588

Subcontractors: N/A

Other Partners: N/A

Contact: E.J. "Woody" Rice
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Atlanta, GA 30332-0620
Tel: 404-894-6702
Fax: 404-894-5301
woody.rice@ipst.edu

Project Team: Peter Salmon-Cox

Project Objective: Using the existing BDE pool of industry knowledge and expertise, they will efficiently and effectively communicate and demonstrate energy efficiency technology to the U.S. paper industry. In the global industry, economics are playing an ever-increasing role as low-cost, Southeast Asia paper producers begin to compete with U.S. mills. Lowering costs by making mills energy efficient keeps the U.S. paper industry more competitive and better able to survive.

Background: The Institute of Paper Science and Technology (IPST) currently employs, as consultants, retirees from the Forest Products Industry to act as technical liaisons between the paper mills, corporate offices, R&D facilities, etc., and IPST. Their mission is to communicate the technological needs of the mills to IPST, the capabilities of IPST to fill those needs and, if indicated, facilitate programs to do so. The Business Development Executives (BDEs):

1. have all been senior industry managers (vice president, operations, manufacturing, research, etc.),
2. are well known to and by the current management of their client companies,
3. are technically competent,

4. are willing to travel to their mill sites at least five or six days per month,
5. have a strong desire to stay active in the industry, and
6. have good communication skills.

Under this project, the BDE Program scope of work will be expanded to include dissemination of information to the industry about DOE/OIT programs.

Status:

Active BDEs this quarter

- Tom Bridges
- Doug Caulkins
- Dick Detrick
- Pete Howard
- Lynn Jonakin
- Ted Owens

Mills visited/called and/or meetings this quarter

- American Processes meeting at IPST, Atlanta, GA
- Creative Packaging International, West Monroe, LA
- Deerfield Paper, Augusta, GA
- DOE, Atlanta, GA
- Georgia-Pacific, Atlanta, GA
- Inland Containerboard and Packaging, Orange, TX
- IPST
- Smurfit-Stone, Brewton, AL
- Smurfit-Stone, Jacksonville, FL
- Steam Audit course March 3-4, 2004 at IPST, Atlanta, GA
- TAPPI / DOE re: upcoming Energy Fair and TAPPI Summit
- Weyerhaeuser, Henderson, KY
- Weyerhaeuser, Pine Hill, AL

Plans for Next Quarter: Continue to call on member and non-member mills with OIT presentations.

Budget Data:

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	03/01/00	09/30/00	150,000.00	14,128.00	164,128.00	(0.00)	0.00	(0.00)
Year 2	10/01/00	09/30/01	200,000.00	117,012.00	317,012.00	206,463.00	75,831.22	282,294.22
Year 3	10/01/01	09/30/02	400,000.00	33,800.00	433,800.00	134,206.61	23,290.10	157,496.71
Year 4	10/01/02	09/30/03	200,000.00	72,880.00	272,880.00	87,777.14	0.00	87,777.14
Year 5	10/01/03	09/30/04				57,385.21	0.00	57,385.21
		Totals	950,000.00	237,820.00	1,187,820.00	485,831.96	99,121.32	584,953.28

Environmental Influences on Wood Chemistry and Density of Populus and Loblolly Pine

Tuskan: ORNL, NREL

CPS#00681

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

QUARTERLY PROGRESS REPORT

Project Title: Environmental Influences on Wood Chemistry and Density of *Populus* and Loblolly Pine

Covering Period: October 31, 2003 through January 1, 2004

Date of Report: February 19, 2004

Recipient: Oak Ridge National Laboratory
Bethel Valley Rd., Oak Ridge, TN 37831

Award Number: FWP # CEED062

Subcontractors: Kurt Johnsen
U.S. Forest Service
Raleigh, NC

Other Partners: International Paper Co., North Carolina Tree Improvement Cooperative

Contact: Gerald A. Tuskan
Phone: (865) 576-8141, Fax: (865) 576-8143
E-mail: gtk@ornl.gov

Project Team: David Boron
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Washington, DC 20585

Project Objective: The objectives of the study are to: 1) determine the degree to which physical and chemical wood properties vary in association with environmental and silvicultural practices in *Populus* and loblolly pine and 2) develop and verify species-specific empirical models in an effort to create a framework for understanding environmental influences on wood quality.

Background: This project began in August 2001 and is a renewal effort for a previous Agenda 2020 project entitled: “Development and validation of marker-aided selection methods for wood property traits in loblolly pine and hybrid poplar.” Because environmental factors confound our estimates of genetic parameters, complicate gene discovery, and impact product quality this project was initiated in an effort to quantify these effects on wood properties.

Status: All data from this year has been collected up to 1/30/04. At the beginning of September the data loggers we use for recording the data ran out of memory. All data was downloaded and William Gensler was able to

recover about 2 weeks of data that could not be accessed. This data is currently being error checked. Data transformation is currently completed through 12/31/03 and is ongoing. During August all bands were inspected for reduction in clearance due to diameter growth. In all, 70% of the bands were moved back away from the stem. Because of this a program is being written to correct for diameter band changes due to moving the sensors. When this is completed graphs for 2003 growth will be prepared.

Work has been progressing to acquire absolute wood density values for the three *Populus* clones (72 total increment cores). Microcat scans of 17 species of known density were acquired for software calibration. The species were scanned under the same conditions and scanner parameters as the increment cores. The scanner's x-ray voltage was set at 60 kVp, the anode current was 500 *u*A. The source and detector's total rotation was 360 degrees accomplished in 600 steps. The resulting scanner data was reconstructed into 512 x 512 x 768 pixel dimension images and analyzed with ImageJ software. The species ranged in density from Balsa at 0.104 g/cc to Hickory at 0.939 g/cc (Figure 1).

Work continued this quarter on improving and testing the experimental apparatus. We have begun to collect spectra on the poplar cores and to develop protocols for assessing the changes in wood chemistry along the cores related to growth conditions. These experiments are being performed to begin to identify methods to relate wood chemistry determined by traditional analytical chemistry methods with NIR spectra collected on solid wood cores. Our initial experiments have been directed at determining whether regressions models developed on ground wood samples can be applied to solid samples. These experiments involve determining lignin and syringyl/guaiacyl (S/G) ratios along a core using NIR spectroscopy and then verifying the results using analytical pyrolysis.

These experiments were carried out on samples excised from a wood disk taken from a 7-year-old poplar tree. Figure 2 shows a wedge cut from the wood disk and the numbers indicate the position along the core where the NIR and pyMBMS were collected. Positions along the core were selected to ensure that spectra were collected from both springwood and summerwood. PyMBMS spectra were acquired on small samples that were carefully cut from a neighboring matched wedge cut from the same disk. Figure 3 shows the result of a principal component analysis (PCA) of the mass spectra collected from samples taken along the wedge. The analysis indicated that the lignin content was higher earlier in the tree growth and began to level off after year 3. A comparison of the pyMBMS spectra for springwood and summerwood selected from the same year did not detect a consistent change in wood chemistry. However, this

experiment is being repeated using a larger diameter disk wood selected from a different tree collected from the same area in which it is easier to identify spring and summer wood. NIR spectra are also being collected for the areas selected for pyMBMS analysis.

Plans for Next Quarter:

During the next quarter point dendrometers for the second year will be continue to be analyzed on all sampled loblolly pine. Environmental data collection will continue including detailed daily climatic data. At each of the CO_2 treatment rings, we will be summarize light level, stem sap flow, stem respiration and soil and air temperatures summed and evaluated for the first year data set. In addition, wood cell wall chemistry measures will be collected for all sample *Populus* increment cores using the near IR and wood density measurements will be completed.

Patents: None.

Publications/Presentations: None

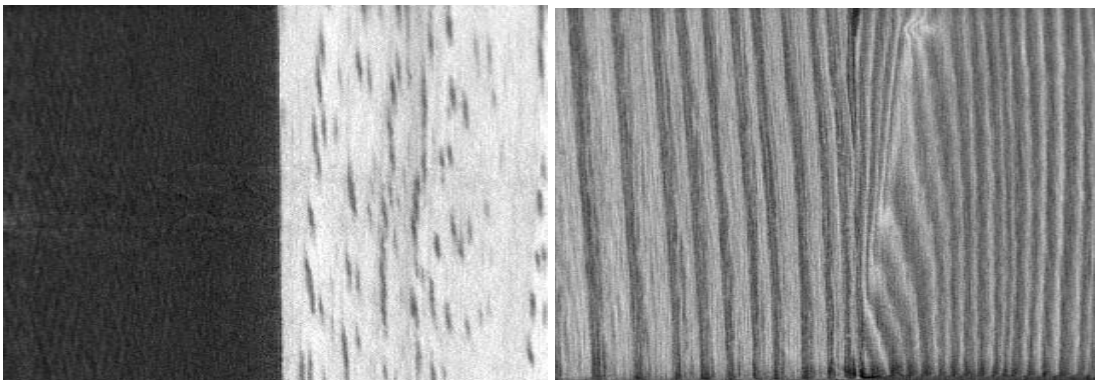
Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	*Populus* Wood Properties			
1.1.1	Physical Properties Determination	7/1/02		80% completed
1.1.2	Chemical Properties Determination	9/30/02		50% completed
2	*Populus* Modeling			
2.1.1	PLS Model Development	5/30/03		100% completed
2.2.1	PLS Model Verification	5/30/04		50% completed
3	Loblolly Pine Wood Properties			
3.1.1	Physical Properties Determination	1/30/04		
3.2.1	Chemical Properties Determination	6/30/04		
4	Loblolly Pine Modeling			
4.1.1	PLS Model Development	12/31/04		
4.2.1	PLS Model Verification	5/30/05		
5	Final Report	7/30/05		

Budget Data (10/01/02):

ORNL			Approved Spending Plan ($1000)			Actual Spent to Date ($1000)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	10/01	09/02	105	55	160	105	55	160
Year 2	10/02	09/03	135	55	190	135	55	190
Year 3	10/03	09/04	120	55	175			
Year 4	10/04	09/05	120	55	175			
Totals	10/01	09/05	480	220	700			

NREL			Approved Spending Plan ($1000)			Actual Spent to Date ($1000)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	10/01	09/02	75	0	75	75	0	75
Year 2	10/02	09/03	75	0	75	75	0	75
Year 3	10/03	09/04	70	0	70			
Year 4	10/04	09/05	70	0	70			
Totals	10/01	09/05	290	0	290			



Balsa Hickory W. Hemlock Red Mulberry

Species	Area	Mean Grayscale	Min Grayscale	Max Grayscale	Ab. Density
Balsa	16524	48.453	5	85	0.104
W. Hemlock	27600	142.285	50	215	0.465
Red Mulberry	18624	130.288	67	217	0.524
Hickory	17296	208.587	83	255	0.939

Figure 1. Density gradients among various wood samples of known density. These values, along which 14 additional samples, are used to determine the absolute density values for the MicroCAT estimates.

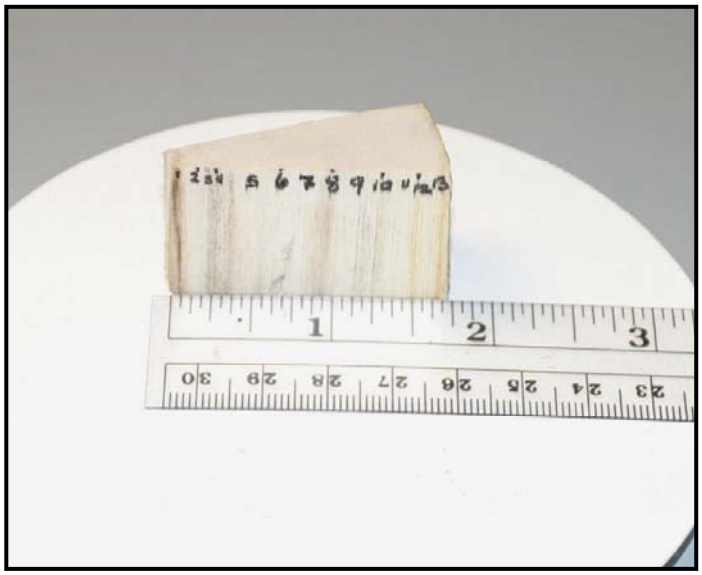


Figure 2. Poplar test wedge cut form a 7-year-old poplar tree. The numbers indicate areas selected for analysis using pyMBMS and NIR spectroscopy (see below).

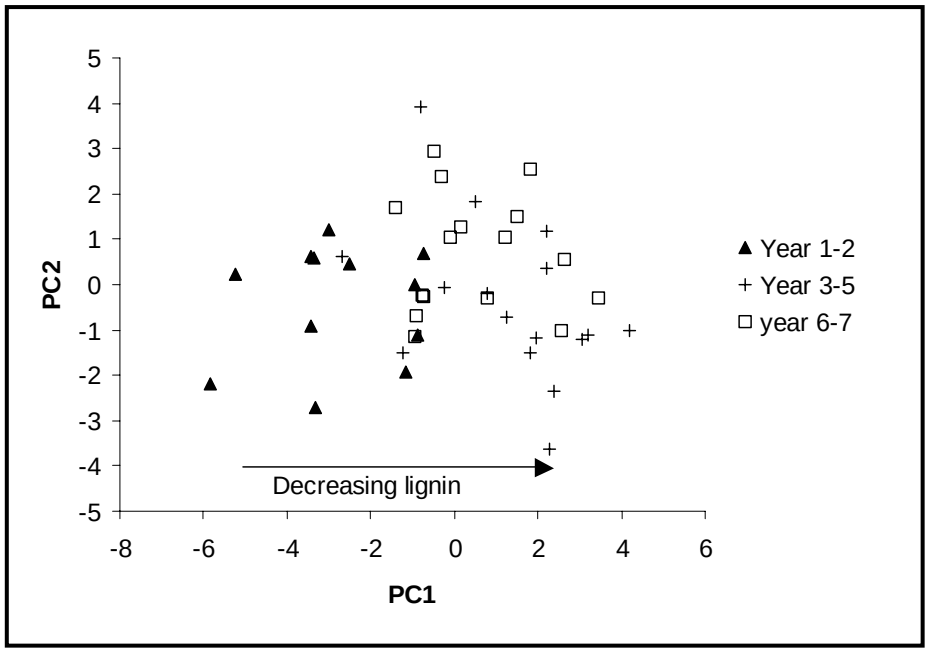


Figure 3. Scatter plot of principal component 1 vs principal component 2 of pyMBMS data obtained from wood sections taken as a function of growth.

Genetic Augmentation of Syringyl Lignin in Low-Lignin Aspen Trees

Tsai: Michigan Technological University, NREL

GO10617, CPS#01493

Quarterly Progress Report

For: Genetic Augmentation of Syringyl Lignin in Low-lignin Aspen Trees

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: June 30, 2004

Recipient: Michigan Technological University (MTU)
National Renewable Energy Laboratory (NREL)

Award Number: DE-FC36-01GO10617

Other Partners: International Paper Co.

Contact: Chung-Jui Tsai (906-487-2914), chtsai@mtu.edu

Project Team: Boron (OIT), Hooker (GFO), Gorin (GFOCont), Farrell (AF&PA), Lucier (NCASI), Kellison (Ind)

Project Objectives: Proposed research aims (1) to genetically augment the syringyl/guaiacyl (S/G) lignin ratio in 4CL1 transgenic aspen in order to produce aspen trees with reduced lignin content, more reactive lignin structures, increased cellulose content, and enhanced growth; and (2) to develop reliable and cost-effective methods, such as pyrolysis Molecular Beam Mass Spectrometry (pyMBMS) and NMR, for rapid evaluation of cell wall chemical components of transgenic wood samples.

Background: The removal of lignin from wood for papermaking is a costly, time-consuming procedure hindering pulping efficiency. The focus of this project is to improve pulping efficiency by genetically modifying lignin quantity and quality in wood. Previous research at MTU has shown that transgenic aspen trees deficient in a lignin-specific 4-coumarate:coenzyme A ligase (4CL1) accumulated structurally normal lignin, but at substantially reduced levels, and that the reduced lignin was compensated for by a concomitant increase in cellulose.

In addition to lignin quantity, lignin quality also controls wood pulping efficiency. The reaction rate of degrading lignin during chemical pulping of hardwood species is directly proportional to the S/G ratio in lignin. 4CL1, which appears to be a regulator for total lignin monomer accumulation, cannot modulate the S/G ratio in lignin. Thus, genetic augmentation of S lignin in the 4CL1 transgenic aspen trees could provide an opportunity to further enhance the value of these trees with a more reactive lignin.

We have recently cloned a novel S lignin-specific coniferaldehyde 5-hydroxylase (CAld5H) gene from developing xylem of both sweetgum and aspen. We propose to over-express the aspen and sweetgum CAld5H genes in 4CL1 down-regulated transgenic aspen, under the control of an aspen xylem-specific promoter.

The National Renewable Energy Laboratory will also be participating in this project by measuring the amount and structure of the respective monolignol constituents using solid state ^{13}C NMR or the pyrolysis Molecular Beam Mass Spectrometer (pyMBMS) technique (Tuskan *et al*. 1999). These methodologies require only milligrams of sample and can analyze more than 50 samples per day. These attributes make pyMBMS and NMR ideally suited for screening growing shoots.

Status:

Task 1 – Construct Preparation
Preparation of both constructs, *XP::LsCAld5H* and *XP::PtCAld5H* was completed.

Task 2 – Aspen Transformation
All proposed transformation tasks was completed.

Task 3 – Wet Chemical Analysis of Aspen Wood Samples
Completed as previously described

Task 4 – Development of calibration models for rapid analysis of aspen wood chemical properties
Completed as previously described

Task 5 – Greenhouse acclimation of transgenic aspen
Tissue harvest for molecular and chemical analyses was completed.

Task 6a – PCR and Southern analysis of 35S::CAld5H transgenic aspen
Completed as reported previously.

Task 6b – PCR and Southern analysis of XP::CAld5H transgenic aspen
PCR analysis was completed.

Task 7a – Tissue harvest, molecular and biochemical characterization of 35S::CAld5H transgenic aspen
Completed as reported previously.

Task 7b – Tissue harvest, molecular and biochemical characterization of XP::CAld5H transgenic aspen
Completed as reported previously.

Task 8a – Wet Chemical Analysis of Aspen Wood Samples
Completed as reported previously.

Task 8b – Wet Chemical Analysis of Aspen Wood Samples
Completed as reported previously

Task 9 – NMR and PyMBMS analysis in transgenic aspen
PyMBMS analysis for ~100 transgenic wood samples was completed. The results indicated augmented S lignin biosynthesis in many transgenic lines, harboring either the homologous or the heterologous gene construct.

Plans for Next Quarter: The project tasks have been successfully completed, and results presented in the DOE annual review meeting in conjunction with the 2004 TAPPI Paper Summit. Our results confirmed that the CAld5H gene is key to syringyl lignin biosynthesis. The outcomes of this research should be readily applicable to other pulpwood species, and promise to bring direct economic and environmental benefits to the pulp and paper industry.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
10617	Genetic Augmentation of Syringyl Lignin in Low-lignin Aspen Trees (1493) MTU, Tsai, PI	2/12/01 to 6/30/04		As of 6/30/04
Task 1	Construct preparation (MTU)	6/30/01	6/30/01	Completed
Task 2	Aspen transformation (MTU)	2/28/03	2/28/03	Completed
2a	Initiation of transformation	10/30/01	11/30/01	Completed
2b	Callus induction	2/28/02	2/28/02	Completed
2c	Shoot regeneration	4/30/02	4/30/02	Completed
2d	Shoot elongation	6/30/02	8/31/02	Completed
2e	Root induction	8/30/02	12/31/02	Completed
Task 3	Wet chemical analysis of aspen wood samples (MTU)	2/28/02	9/30/01	Completed
Task 4	Development of calibrations for aspen wood samples (NREL)	2/28/02	4/30/02	Completed
4a	NMR calibration	8/31/01	6/30/01	Completed
4b	pyMBMS calibration	2/28/02	4/30/02	Completed
Task 5	Greenhouse acclimation of transgenic aspen (MTU)	8/31/03	4/30/03	Completed
Task 6	PCR and Southern analysis of transgenic aspen (MTU)	6/30/03	--	--
6a	*35S::CAld5H* plants	8/30/01	9/30/01	Completed
6b	*XP::CAld5H* plants	6/30/03	9/30/03	Completed
Task 7	Tissue harvest, molecular & biochemical characterization (MTU)	10/31/03	--	--
7a	*35S::CAld5H* plants	2/28/02	5/31/02	Completed
7b	*XP::CAld5H* plants	10/31/03	3/31/04	Completed
Task 8	Wet chemical analysis of CAld5H transgenic aspen (MTU)	2/11/04	--	--
8a	*35S::CAld5H* plants	9/30/02	3/31/02	Completed
8b	*XP::CAld5H* plants	2/11/04	3/31/04	Completed
Task 9	NMR and PyMBMS analysis of transgenic aspen (NREL)	2/11/04	5/30/04	Completed

Budget Data:

MTU portion			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	2/12/01	2/28/02	93,172	35,329	128,501	96,172	28,834	125,006
Year 2	3/1/02	2/28/03	108,036	27,383	135,419	103,512	34,946	138,458
Year 3	3/1/03	2/28/04	102,185	38,798	140,983	103,709	37,839	141,548
		Totals	303,393	101,510	404,903	303,393	101,619	405,012

(Budget data was incomplete, due to delay in the amendment funds)

NREL portion			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	2/12/01	2/11/02	49,500	0	49,500	49,500	0	49,500
Year 2	2/12/02	2/11/03	0	0	0	0	0	0
Year 3	2/12/03	2/28/04	52,500	0	52,500	52,500	0	52,500
		Totals	102,000	0	102,000	102,000	0	102,000

Total project			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	2/12/01	2/11/02	142,672	35,329	178,001	145,672	28,834	174,506
Year 2	2/12/02	2/11/03	108,036	27,383	135,419	103,512	34,946	138,458
Year 3	2/12/03	2/11/04	154,685	38,798	193,483	156,209	37,839	194,048
		Totals	405,393	101,510	506,904	405,393	101,619	507,012

Quantifying and Predicting Wood Quality of Loblolly and Slash Pine Under Intensive Forest Management

Daniels: University of Georgia

GO10619, CPS#01494

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

Quantifying and predicting wood quality of loblolly and slash pine under intensive forest management

Recipient: University of Georgia

Award Number: DE-FC36-01GO10619

Subcontractors: USDA Forest Service
Silviscan, CSIRO

Other Partners: NC State University
University of Florida
Virginia Tech

Contact: Richard F. Daniels (706) 542-7298 ddaniels@uga.edu
Alexander Clark III (706) 559-4323 aclark@fs.fed.us

Report Date: July 31, 2003

Project Objective:
1) Quantify effects of intensive forest management on basic wood properties, including specific gravity, tracheid length, coarseness, microfibril angle, juvenile wood formation, and interactions with soils and geographic location; 2) correlate basic properties with strength, stiffness and yield properties and energy requirements for pulp, paper, and solid products; and 3) develop models that, given tree size and stand history, predict wood quality within the tree, from stump to tip and pith to bark.

Background:
The forest industry will increasingly rely on fast-growing intensively managed southern pine plantations to furnish wood and fiber. Intensive competition control and fertilization promise tremendous gains in wood production. How these technologies affect wood properties, product mix, energy efficiency, and profitability is unknown. For example, intensively managed trees grow rapidly during the early years of the rotation, reach merchantability at a younger age and may produce significantly higher proportions of juvenile wood, raising concern for the use of the new wood supply in traditional products. Juvenile wood is characterized as having lower specific gravity, shorter tracheids with thinner walls, larger microfibril angles and less alpha cellulose than mature wood. The number of annual rings of juvenile wood a tree produces varies geographically and increases from 5-6 years in the lower Coastal Plain to 10-12 years in the Piedmont. The stiffness and strength of structural lumber containing juvenile wood is significantly lower than that of lumber form mature wood and may not meet design specifications. Juvenile wood has significantly higher moisture content than mature wood and is more prone to warp during drying. Pulp chips containing large volumes of juvenile wood have significantly lower packed bulk density resulting in fewer chips per digester cook and yield less pulp per ton of green chips, thus requiring more energy to produce the same volume of pulp as traditional chips. Paper from juvenile wood pulp has good tensile, burst, fold and sheet

smoothness but significantly lower tear strength and opacity. The forest industry needs to understand the impact of intensive management on wood properties to facilitate production of quality products and minimize energy requirements.

There is a lack of information on the effects of silvicultural and genetic treatments on cell anatomical structure, specific gravity, wood strength and stiffness and length of juvenility and their interactions with soils and geographic location. Well-designed, long-term field studies are required to quantify and model the effects of intensive management on these wood properties. Fortunately, a wealth of such experiments exists through ongoing research cooperatives. Overlaying wood quality sampling on this existing experimental base is the most efficient way to meet industry's wood properties research and modeling needs. The approach of this project is to partner with the institutions responsible for these experiments to facilitate field sampling of their locations and support graduate student research. Standardized data collection and lab protocols will be implemented by a common team. Sample plots from each study will be measured by the UGA/Forest Service/Collaborator field crews. The studies to be sampled are described in the status section. One graduate student will be assigned to each of these intensive management studies.

General Data Collection Protocol:
As a target, 20-30 trees are sampled per treatment/location. Trees are cored with a 12mm increment borer at dbh and, where possible, 3 trees per treatment are felled for stem analysis and wood sample collection from stump to tip. Two 12mm increment cores are collected from each tree at the same vertical plane 3 inches apart to provide four radii. Radius 1 is used to determine specific gravity, and radial growth of earlywood and latewood (UGA and Forest Service x-ray densitometers). Radius 2 for selected trees is used to determine microfibril angle, ring-by-ring using Silviscan (subcontract) and will be available for further Near Infrared analysis. Radius 3 is used to determine whole core specific gravity by displacement (USDA Forest Service lab). The fourth radius will he held for future needs.

From each felled tree two 1-inch cross-sectional disks are cut at stump, dbh and 5 feet intervals to a 2-inch top. Two-foot bolts are cut from each tree at 8, 24 and 40 feet. One disk will be used to determine weight per cubic foot; the second cut into radial strips for x-ray densitometer analysis. The 2 foot bolts will be sawn into small clears and used to determine MOE, MOR, toughness, and dimensional stability of juvenile and mature wood using ASTM D143 for small clears (UGA, USDA Forest Service labs). Data will be analyzed to determine the effect of intensive management, soils and geographic location on the properties measured.

Modeling Approach:
Predictive models are being developed to describe the changes in wood properties within a tree. The goal will be to define how these tree wood properties change with intensive management treatments, geography, site quality, age, and environmental conditions. Mathematical models of tree volume and weight are used routinely to estimate timber stand volumes in forest inventories and in yield projection systems. Wood properties will be modeled in a similar fashion to wood content along the stem, using models analogous to taper functions. By incorporating these models for predicting wood quality into such applications, forest managers and planners will be able to incorporate wood quality considerations into forest management decisions.

Status:
The project has completed nearly two years of work. A scientist, Joseph Sanders, was hired in February 2002 on University of Georgia matching funds to support the project in the areas of data management and analysis. A Research Coordinator, Scott Howell, was hired on project funds to lead the field data acquisition and supervise the laboratory wood testing. Four graduate students are now working on the project. The project is at full staffing. Equipment purchases include three P-4 workstations for project staff. The final year subcontract to the USDA Forest Service has been submitted for payment. The second subcontract with Silviscan (CSIRO) in Australia will provide fiber property measurements, including microfibril angle (MFA), on increment cores collected from study sample trees.

Auburn University – COMP STUDY (Vegetation control with no fertilization).
A 15-year-old competition control study established at 13 locations from Virginia to Louisiana provided a unique opportunity to examine the effects of intensive vegetation control on wood properties across the South. This study, called the Competition Omission Monitoring Project (COMP), was a cooperative study established by industrial members of the Auburn University Silvicultural Herbicide Cooperative, the USDA Forest Service Southern Research Station, and Virginia Tech and Louisiana Tech Universities. In 1984-1985 genetically improved loblolly pines were planted in experimental plots in seven states. Treatments were: 1) no competition control after chopping and burning; 2) complete woody control for the first 3-5 years; 3) complete herbaceous control for the first 4 years; and 4) complete competition control for 3-5 years. Soil types have been described. The no competition control and complete control treatments were sampled at all 13 locations; all four treatments were measured on a subset of seven locations across the South. Sampling has been completed for all 13 Auburn/USDA Forest Service COMP study locations. To ensure continued integrity of this important study, trees were not felled and only increment cores were collected. Increment cores collected from this study were prepared in the laboratory for in-house x-ray densitometry and contracted MFA analysis. X-ray densitometry results are complete for the all locations.

Results: Early weed control has become a common practice in loblolly pine plantation establishment, providing seedlings with greater allocation of growth resources due to reduced competition from non-crop vegetation. The effects of weed control were evident in increasing early growth in these plots. Trees with weed control attained larger diameters (and heights) than untreated plots in the same time period (Figure 1). This effect led to a larger core of juvenile wood (with low specific gravity) at a given age for weed control treated trees. However, the weed control treatment did not affect the length of time in the juvenile stage of growth, which varied by physiographic location. That is, at any given location, the stands made the transition from juvenile wood to mature wood at about the same age regardless of weed control treatment. While juvenile rings were larger for weed control treatments there appear to be no effects on specific gravity by ring (Figure 2). Overall disk specific gravity is reduced slightly by weed control treatment due to the early increase in size of the juvenile core. Further analyses will be conducted with microfibril angle and other properties.

Figure 1. Average Ring Basal Area Over Rings From Pith By Competition Control Treatment

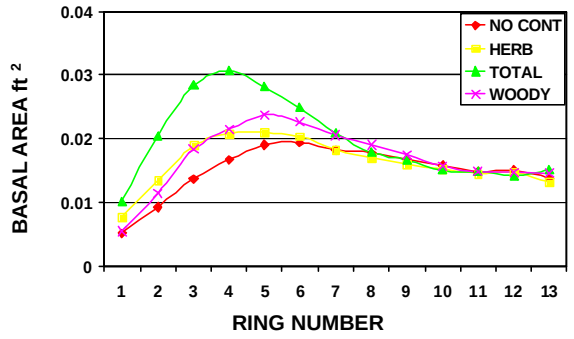
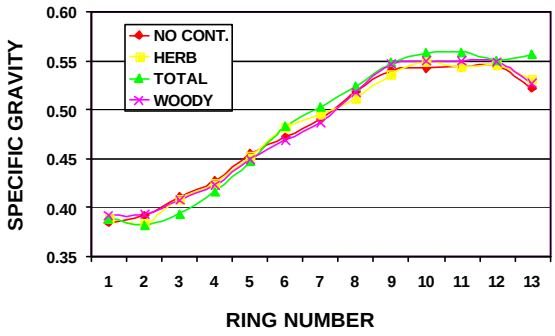


Figure 2. Average Ring Specific Gravity Over Rings From Pith By Competition Control Treatment



Virginia Tech Loblolly Pine Growth and Yield Research Cooperative

Southwide intensive culture studies.

The Virginia Tech Loblolly Pine Growth and Yield Research Cooperative established a series of 150 sets of plots, with improved stock, under intensive stand establishment regimes, from Virginia to East Texas. These stands represent the modern crop of fast growing plantations. Treatment plots are scheduled for thinning (at 45 feet tall, 6.5 inches dbh) over the next several years, providing an excellent opportunity to capture wood quality information. A limited number of these stands have been sampled. Logistics of sample collection and transport combined with the young age of these trees has limited the utility of these samples. Efforts have redirected to the older thinning study.

Southwide thinning study.

The older region wide loblolly pine thinning study provides a unique one time opportunity to destructively sample 30 to 40 year old loblolly plantations with known history to determine the effect of thinning, climate (physiographic region) and rotation age on wood strength and stiffness. The thinning study was established in 1980-1982 in 186 plantations throughout the native rage of loblolly pine, and consisted of two thinning treatment and a control. Thinning treatments were a light thin (approximately 30% of BA removed) and a heavy thin (50 % of BA removed). This study has been terminated for its original purpose and remaining plots are available for an extremely limited time for destructive sampling. Four trees will be destructively sampled in each of three treatment plots (control, light thin, and heavy thin) at four thinning study installations in each of the Atlantic Coastal Plain, Piedmont and Hilly Gulf Coastal Plain physiographic provinces. Cross-sectional disks will be cut at 5-foot intervals up the stem for annual ring growth and specific gravity analysis and weight per volume determination. Bolts 2-feet long will be cut at 8-, 24-, and 40- feet for strength, stiffness and toughness determination following ASTM D-143. The data collected will be analyzed to develop forest management guide lines for growing plantation loblolly pine with strength and stiffness needed to meet lumber standards.

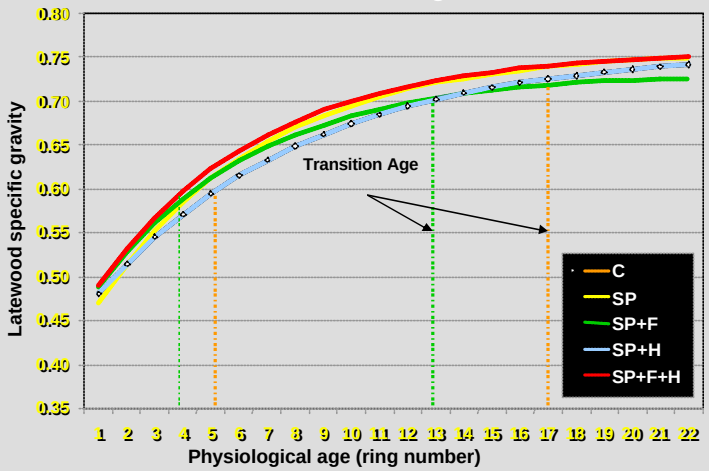
Forest Nutrition Effects on Wood Quality

Among intensive treatments, fertilization has the greatest potential to affect wood properties. Designed field experiments were identified early to examine the effects of 1) fertilization and site preparation alternatives at planting, 2) mid rotation treatments, and 3) multiple fertilization regimes on wood properties.

North Carolina State University – Regionwide 7 fertilization and site preparation alternatives at planting. The NC State Forest Nutrition Cooperative (NCSFNC) installed the Regionwide 7 studies from 1978 to 1981 to include 4-replications 2x2x2 factorial study of site preparation, weed control, and fertilization at planting. These studies have demonstrated the role of initial nutrition and site preparation on growth and they provide a unique opportunity to examine the effects of these treatments on wood properties near rotation age. Five treatments were sampled on 4 installations that have remained in-tact. A 5th installation had been harvested by the landowner and is no longer available for sampling. Sampling in the RW-7 was completed in June, 2002. Christian Mora, a joint student with NC State University has relocated to Athens from June through December, 2002 and completed all sample core preparation and x-ray densitometry in the UGA lab. He will complete his thesis in summer 2003.

Results: Analyses have been completed on the effects of initial fertilization on earlywood, latewood, and ring specific gravity on breast height cores. The fertilization effect is very similar to the results found in the COMP study: increasing early growth due to fertilization increases the size (proportion) of the juvenile core, decreasing overall wood density. Transition from juvenile to mature wood is also being examined by treatment and location. A nonlinear model was used to describe the transition of from juvenile wood to mature wood, using latewood specific gravity criteria (Figure 3). Differences in the transition age can be attributed to treatment and study location.

Figure 3. Asymptotic regression models for latewood specific gravity and estimated transition zone and transition age



Effects of early treatments on wood properties appears to be limited to 1) changes in the diameter of the juvenile core and, to a lesser extent, 2) changes in transition ages to mature wood properties. Both effects combine to affect the proportion of juvenile wood at harvest. However, early site preparation, weed control, and fertilization treatments do not seem to have an influence on the wood properties of mature wood *per se*.

A decision was made in November 2002 to concentrate sampling effort on mid rotation fertilization treatments and studies with multiple fertilization treatments. The following studies have been selected for sampling. All will be sampled during Summer 2003.

University of Florida – Understory competition control plus fertilization studies (G-series). A competition control plus fertilization study provides the opportunity to examine the effects of under story competition control plus fertilization at stand establishment and mid rotation on wood properties at age 15. Six sites are being sampled (3 loblolly and 3 slash) in Georgia and Florida. The 4 treatments to be sampled all include early weed control and mid-rotation brush control. The nutrition treatments include no fertilization; P at planting plus N+P at mid-rotation; N+ P at planting and N+P at mid-rotation; and N+P +K at planting and N+P+K at mid-rotation. 36 trees will be bored per treatment location (9 per rep) in each of the four treatments at each of the 6 locations. No trees will be felled due to young age of the study.

North Carolina State University – Regionwide midrotation fertilization studies. The NC State Forest Nutrition Cooperative (NCSFNC) has installed a series of regionwide studies (RW-13, 15) to determine the effects of mid-rotation fertilizations and multiple fertilizations. These studies were treated at age 12-15 and are now over 25 years old. They have been terminated for their original purpose and are available for destructive sampling. Two RW-13 studies (Virginia and NC) are being sampled. This study has the greatest range of nitrogen fertilization. Treatments include 4 mid- rotation fertilization treatments: 25 P, 100N+25P, 200N+25P, and 300N+25P. Three RW-15 studies are being sampled (SC and AL). In each, 36 trees will be bored per treatment and 8 trees per treatment will be destructively sampled for strength, stiffness, toughness, dimensional stability, and wood property profiles (SG, MFA) from stump to tip, by ring.

MeadWestvaco N + K study. MeadWestvaco established a study of mid-rotation N and K fertilization in loblolly pine. The site is 33 years old and available for destructive sampling. Treatments at age 20 include: 0N0K, 100N+0K, 200N+0K, 200N+100K. All plots had adequate P. The sampling protocol will match that in the NC State RW-13,15.

SETRES – USDA Forest Service and NC State University. A tremendous opportunity opened to look at wood properties in the continuously fertilized, irrigated SETRES study. Trees will be bored only in this 19 year-old landmark study including treatments: control, irrigation only, fertilization only, and irrigation+fertilization. Treatments have been applied annually since 1992.

University of Georgia – Planting stock X vegetation control studies.
The UGA Plantation Management Research Cooperative Loblolly Pine Improved Planting Stock X Vegetation Control Study has shed light on the effects and interaction of weed control and

genetics on stand development. Thirty-one installations were installed in 1986-7 in the Coastal Pain and Piedmont in AL, FL, GA, and SC. At each installation six common treatments (3x2 factorial) include planting stock (unimproved stock versus bulk lot improved versus single family) crossed with vegetation control (complete versus no competition control). Sampling these plots for wood properties at age 15 will add an important component to the understanding of these intensive treatment effects.

Four treatments were selected for sampling: unimproved stock with competition control, bulk-lot improved with and without competition control, and family block with competition control. Three loblolly pine families and two slash pine families were selected for the family block plantings. Ten loblolly sites and five slash sites were selected for sampling. Sampling began in December 2002 and will be complete in July 2003.

Modeling wood properties.

Significant progress has been made in developing and fitting mathematical models to describe the 3-dimensional changes in wood properties within the tree. Patterns of wood density were described ring-by-ring from the pith to bark and vertically from stump to tip using mathematical models derived from wood sheath increment. A three parameter Logistic function was used to describe the sigmoid curve of latewood specific gravity from pith to bark (Figure 4). These models have been refined further to describe mean ring density, latewood density, and latewood proportion. In addition, models have been developed to describe the baseline changes in wood stiffness (MOE), strength (MOR), and microfibril angle (MFA) within trees and identifying differences in these properties by Physiographic region across the South. These baseline models provide the basis for examining the effects of intensive treatments. As data come available from the studies being sampled in 2003, these models will be refit to determine how intensive silviculture changes these properties.

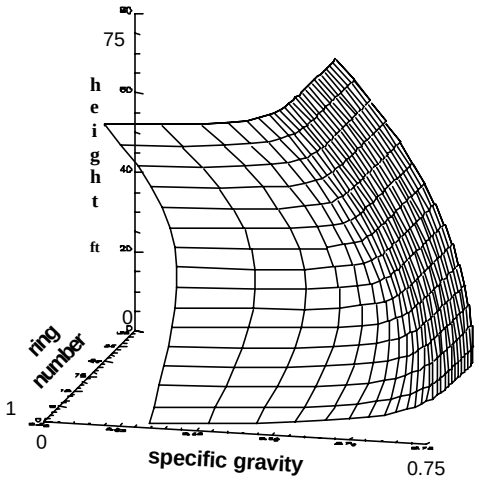


Figure 4. Three-dimensional prediction of latewood specific gravity from Logistic Model

Future Plans:

Field work will be completed in 2003 and early 2004 for these additional studies.

Milestone Status Table

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Quantifying and Predicting Wood Quality			
1.1.1	Commence Project/Receive funding	1/01/01	5/01/01	
1.1.2	Hire Post-doc	4/30/01	1/31/02	
1.1.3	Complete field plans	4/30/01	4/30/01	
1.1.4	Collect VA Tech samples	4/30/01	4/30/04	ongoing
1.2.1	Select Graduate Students	6/30/01	6/30/01	
1.2.2	Intensive Field Work – COMP study	8/01/01	9/01/01	First 12 locations
1.2.2a	Intensive Field Work – COMP study	8/01/02	8/01/02	13th location
1.2.3	Intensive Field Work – NC State RW 7 plots	7/31/02	7/31/02	
1.2.4	Intensive Field Work – Florida G-study	9/15/02	9/15/03	
1.2.5	Intensive Field Work – PMRC GxV Study	7/01/03		On schedule
1.3.1	Prepare and analyze COMP samples	12/31/01	4/01/02	
1.3.2	Prepare and analyze NC State samples	10/31/02	12/31/02	ongoing
1.3.3	Prepare and analyze VA Tech samples	12/31/01	ongoing	Prepared and being analyzed
1.3.4	Preliminary model relationships	12/31/01	10/31/02	
1.3.5	Select contractor for fiber analysis	12/31/01	12/31/01	Silviscan selected – samples sent
1.3.5	Analyze Silviscan Data	12/31/01	ongoing	
1.4	Model effects of treatments	4/04/04		

Budget Information

			Approved Spending Plan			Estimated Spent to Date (as of 3/31/03)		
Phase / Budget Period			DOE * Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	2/12/01	2/11/02	198,992	128,224	327,216	117,000	18,000	135,000
Year 2	2/12/02	2/11/03	223,230	132,677	355,907	200,000	200,000	400,000
Year 3	2/12/03	2/11/04	196,365	140,817	337,182			
Totals			618,587	401,718	1,020,305	317,000	218,000	533,000

*Partial first year award of $137,000 was received May 1, 2001. Second award, $123,230 received January 15, 2002 covers remainder of first year budget, $61,992, plus first partial budget for year 2, $61,238. Third partial award, $100,000 received January 15, 2003. This award will back pay committed funds for salaries and cover some contract costs committed for 2003. A fourth award of 97, 136 was received in May, 2003.

Exploiting Genetic Variation of Fiber Components and Morphology in Juvenile Pine

Chang: North Carolina State University

GO10624, CPS#01495

Progress Report

For: Exploiting Genetic Variation of Fiber Components and Morphology in Juvenile Loblolly Pine.

Covering Period: Apri1 1 to June30, 2004
Date of Report: July 29, 2004

Recipient: North Carolina State University

Award Number: DE-FC36-01GO10624

Other Partners: Robert C. Eckert Weyerhaeuser Company, in-kind support
Robert C. Kellison, International Paper, in-kind support
Richard B. Phillips, International Paper, in-kind support

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Project Team: James Alkire(james_alkire@nrel.gov)
Elmer Fleischman (fleisceh@inel.gov)

Project Objective:

- *Long Term Overall Objective:* Ensure Global Competitiveness through Enhanced Forest Productivity in the U. S. South – more efficiently produces more industrial wood on limited land with targeted characteristics.
- *Short Term Objectives:* The objective of the proposed research project is to provide a molecular genetic basis for tree breeding of desirable traits in juvenile loblolly pine. This area of research represents an interface among forest science, molecular biology and material science.
  - Wood and Paper Science Group: Develop micro analytical techniques that allow rapid characterization of fiber components and morphology in a large number of samples.
  - Forest Biotechnology Group: Detect allelic variation in candidate wood property genes, develop a pilot-scale mapping microarray, and assay candidate gene single-nucleotide polymorphisms (SNPs) that segregate in the families chosen for wood property analysis.
  - Tree Improvement Group: Identify parents or families that carry one or more major genes that control wood/fiber quality and develop new breeding strategies based accordingly.

Background:

In order to ensure the global competitiveness of the Pulp and Paper Industry in the Southeastern U.S., more wood with targeted characteristics have to be produced more efficiently on less land. Using a multidisciplinary research approach we will look to improve the productivity and quality of juvenile loblolly pine through a molecular genetic basis for tree breeding of desirable traits. The project consists of 4 tasks involving three distinct research groups; the Tree Improvement Group,

the Forestry Biotechnology Group, and the Wood and Pulping Chemistry Group, with each group having a specific assignment. This research team has recently been awarded two peer reviewed competitive research grants; NCBC #2000-MRG-1102, and NCSU #3-50557. The NCBC award is for equipment and supply money totaling $329,000. The NCSU Administrative award is a $15,000 seed grant. Both grants provide the necessary equipment and seed money to develop this current proposed research. Consequently, some of the tasks such as method development and sample collection have been initiated and have progressed to varying degrees.

Tree Improvement Group

Genetic variation and genotype by environment interaction (GxE) were studied in several juvenile wood traits of loblolly pine (*Pinus taeda* L.). Wood samples of 12 mm increment cores were collected from 11-year-old trees in two progeny tests. Earlywood and latewood of ring 3 (juvenile wood) and ring 8 (transition wood) for each increment core were analyzed for α-cellulose content (ACY), average fiber length (FLW), coarseness (COA) and lignin content (LIG). Transition wood (ring 8) had higher ACY, FLW, COA but lower LIG than juvenile wood (ring 3). Families differed significantly for all the chemical and morphological wood properties on both sites. Genetic variation due to general combining ability and specific combining ability was greater in transition wood than juvenile wood. Loblolly pine full-sib families differed significantly for all traits except for LIG on both sites. There were noticeable family rank changes between two sites for these traits, and there was a large site by specific combining ability interaction effect, which was due to non-additive genetic effect by environment interaction. While weak individual-tree and family heritabilities were found for ACY, FLW, and COA for the juvenile wood, the heritability estimates for the transition wood were moderately high. Favorable genetic correlations of volume and stem straightness were found with ACY, FLW, COA. Detail of these results was presented at the peer review session at the TAPPI Paper Summit in May.

We have prepared a manuscript entitled "Rapid Prediction of Wood Properties of Loblolly Pine using Transmittance Near Infrared Spectroscopy" for publication.

Wood and Pulping Chemistry Group

We continued analyzing the wood core samples for chemical components and fiber morphology. These analyses for fiber chemical composition and fiber morphology will continue over the next year. To date, we have completed analyses of sites 2 and 3. All of these core samples have been extracted to remove extractives. Each sample has been split into 4 sub-samples: earlywood and latewood from the 3rd and 8th rings. All these sub-samples were analyzed for their chemical composition and fiber morphology. The results from the completed Site 2 and Site 3 have been analyzed by the Tree Improvement Group.

In last quarter, we continue analyses of wood chemical and morphological traits of samples from both sites 1 and 4 simultaneously. We have now completed the analysis of samples from 7 and 6 families from sites 1 and 4, respectively. We have also worked to improve on NIR calibration lines for α-cellulose and lignin contents.

Forest Biotechnology Group

We have used the data from microarrays and metabolite profiles to look for correlated effects of gene specific transcripts and abundant metabolites. Data is obtained from differentiating xylem, cambial scrapings collected in 2003 and analyzed as described previously for metabolites and for transcript levels for 2109 genes expressed during wood formation. The results in Table 1 show correlations for 12 abundant metabolites and 728 specific gene effects.

Table 1. Genes identified by correlation with specific metabolites. Normalized levels of gene expression determined on an individual tree basis are correlated with the levels of specific metabolites using a q test criteria. The p value for the significance of the correlation is equal to or less than 0.05.

Metabolite significant genes ($p < 0.05$).

Metabolite	Up regulated	Down regulated
Coniferin	70	58
B-D-pyranose	11	12
Citrate	11	12
D-fructose	56	68
D-glucose	63	68
Inositol	29	41
Malate	16	20
Ononitol	56	23
Pinitol	21	26
Quinate	12	4
Shikimate	19	10
Sucrose	14	8

As an example, the significant genes identified are for sucrose level are shown below a t a *p value* of less than or equal to 0.05 after correction for multiple tests. The first column is the slope of the correlated effect and the second column is the individual p value. Of interest are two putative genes, one implicated in sucrose metabolism (sucrose synthase) and a lignin biosynthetic gene (cinnamyl alcohol dehydrogenase)

Up regulated for sucrose:

Clone ID	Annotation	Slope	individual p value
ST13F05	no hit	0.448	2.8E-008
ST12G02	unknown protein	0.337	3.27E-007
NXCI155E06	transketolase - like protein	0.282	4.7E-007
NXSI103A01	predicted GPI-anchored protein	0.28	5.63E-007
NXSI117C08	no hit	0.262	1.837E-005
NXSI103B01	no hit	0.258	3.14E-007
NXCI106C10	putative sucrose synthetase	0.254	1.045E-006
ST14B10	heat shock protein 18	0.241	1.493E-006
NXSI112B07	delta tonoplast integ. prot.	0.234	6.82E-007
ST04B07	unknown protein	0.223	1.6574E-005
NXCI118F05	SAR DNA-binding protein - like	0.206	1.1246E-005

ST15C08	unknown protein	0.184	2.0959E-005
NXSI131E09	unknown protein	0.183	2.4843E-005
ST02B03	cinnamyl alcohol dehydrog. -like	0.131	6.256E-006

Down-regulated with sucrose:

Gene ID	Annotation	Slope	p-value
NXSI109B06	60S ribosomal protein L37A like	-0.117	6.4616E-005
NXSI037F05	Ca-dependent memb-bind. annexin	-0.128	2.1135E-005
ST02E09	cytoplasmic aconitate hydratase	-0.138	4.9E-008
NXSI104E11	ornithine aminotransferase	-0.146	9.682E-006
NXRV132G06	putative glucosyltransferase	-0.146	6.8526E-005
NXLV022H09	cytoplasmic aconitate hydratase	-0.154	6.1226E-005
NXSI105A06	no hit	-0.157	3.828E-006
NXRV128C10	PRL1 protein	-0.166	1.5449E-005
NXSI113E06	xyloglucan endo-1	-0.223	7.2188E-005
NXNV096C09	glutamine-dep. asparagine synth.	-0.241	1.3754E-005
NXCI018F10	putative NADPH oxidoreductase	-0.267	2.2061E-005
NXNV096C08	unknown protein	-0.578	9.74E-007

Plans for Next Quarter:

We will continue analyses of chemical and morphological properties of increment core samples obtained from sites 1 and 4. We will start using NIR to determine lignin content instead of the Acid bromide method, since NIR give a better prediction and is less tedious. A correlation between NIR lignin content and acid bromide lignin content will be established.

We will carry out a technical replicate of the 52 tree analysis of high and low cellulose content. Using amplified RNA from the same samples tested in this past year, we will carry out a series of microarray hybridizations to verify results and reduce variation and increase the significance of our detection of candidate genes..

Our application for a no-cost extension of the project for one year beyond the original termination date of Feb. 11, 2004 has been approved. The extension will allow us to complete the project as planned. Completion dates for some tasks in the Milestone Table have been modified accordingly.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Method Development			
1.1	Resistograph	3/31/01	12/31/00	Completed
1.2	Extractive Removal	6/30/03		Completed
1.3	Holocellulose & α-cellulose	3/31/01	3/31/01	Completed
1.4	Fiber Analysis	3/31/01	3/31/01	Completed
1.5	Lignin Analysis, acetyl bromide method	3/31/01	3/31/01	Completed
1.6	Lignin Analysis, FTIR method	6/30/01	9/30/01	Completed
1.7	Modified DFRC	12/31/01	12/31/01	Completed
1.8	Molecular markers	12/31/02		On-going
2	Sample Collection			
2.1	For Tree Improvement Group	2/11/03		Completed
2.2	For Wood and Pulping Chemistry Group	2/11/03		Completed
2.2.1	Site 1	6/30/02	3/31/02	Completed
2.2.2	Site 2	12/31/01	12/31/01	Completed
2.2.3	Site 3	12/31/02	3/31/02	Completed
2.2.4	Site 4	6/30/03	3/31/02	Completed
2.3	For Forest Biotechnology Group	2/11/05		On-going
3	Sample Analysis and Sequencing			
3.1	Wood density	2/11/04	9/30/03	Completed
3.2	Fiber Morphology and Chemistry	2/11/05		On-going
3.2.1	Site 1	12/31/04		On-going
3.2.2	Site 2	6/30/02	12/31/02	Completed
3.2.3	Site 3	6/30/03	7/31/03	Completed
3.2.4	Site 4	12/31/04		On-going
3.3	Relationship of Gene Expression in Differentiating Xylem and Specific Wood Properties	2/11/05		
3.3.1	Verify Effects of Candidate Genes Using RT PCR	2/11/05		On-going
3.3.2	Correlate Gene Expression with Wood Properties	2/11/05		On-going
3.3.3	Examine the Effects of Alternative Sites on Gene Expression	2/11/05		On-going
3.3.4	Analyze Gene Expression Effects for within Family and between Family Variations	2/11/05		On-going
3.4	Selective Lignin Characterization	2/11/05		On-going
4	Field Trial and Strategic Development	2/11/05		
5	Final Report	2/11/05		

Budget Data (as of date): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods. A table such as the following could be used.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	2/12/01	2/11/02	195,142	175,848	370,990	143,845.75	171,818.00	315,663.75
Year 2	2/12/02	2/11/03	195,142	25,848	220,990	88,296.25	25532.24	113,828.49
Year 3	2/12/03	2/11/04	195,142	25,848	220,990	147,540.18	30598.26	178138.44
Year 4	2/12/02	2/11/05	0	0	0	78,846.95	13,199.55	92,046.50
		Totals	585,426.	227,544	812970	458,529.13	241,148.05	699,677.18

Molecular Physiology of Nitrogen Allocation in Poplar

Davis: University of Florida

ID13529, CPS#00758

QUARTERLY PROGRESS REPORT

Project Title: Molecular Physiology of Nitrogen Allocation in Poplar

Covering Period: April 1 through June 30, 2004

Date of Report: July 30, 2004

Recipient: University of Florida / IFAS
G022 McCarty Hall, P.O. Box 110110
Gainesville, FL 32611-0110

Award Number: DE-FC07-97ID13529

Other Partners: Daniel Carraway, International Paper Company

Contact: John M. Davis
(352) 846-0879
jmdavis@ufl.edu

Project Team: David Boron (HQ program manager)
David Robertson, Beth Dwyer (project mentors)
Joe Springer (contract specialist)

Project Objectives: The objectives of this research are to identify the early biochemical events that occur when poplars are fertilized, and to manipulate genes that are likely to play key roles in allocating nitrogen and thus maintaining C:N balance within the tree. Early biochemical events are identified by cloning genetic "sentinels" (as cDNAs) whose mRNA transcripts accumulate specifically in response to high or low nitrogen regimes. C:N balance is manipulated physiologically by imposing treatments that alter C or N availability to specific organs. C:N balance is manipulated genetically by producing transgenic poplars with altered ability to sequester C or N. The sentinel cDNAs are sensitive probes to monitor the global shifts in poplar gene expression that accompany the expected perturbation in nitrogen allocation.

Background: Despite the fundamental importance of nitrogen use efficiency (NUE) as a productivity determinant in plants, the molecular genetic basis for NUE is poorly understood. Poplar trees are ideal subjects for studies of NUE because they sequester enormous quantities of nitrogen when it becomes available. Perhaps this characteristic reflects an adaptation of poplar to the episodic influxes of nutrients that would occur in the riparian ecosystems in which poplars evolved. By identifying genes that are differentially expressed in poplar tissues after an acute dose of fertilization, we aim to elucidate the biochemical roadmap by which nitrogen fertilization conditions growth in this important woody biomass species. We have identified and used a large number of gene probes to

assess the tissues in which key “decisions” are made in poplar trees after anacute dose of nitrogen is delivered. Our current interest is to assess the relative timing and the magnitude of various processes so that we can identify cause-and-effect relationships among those processes.

Status: Progress continues on what we now envision as two manuscripts, one on architectural changes induced by N availability (sylleptic branching) and another on allocation and wood quality changes induced by N availability (lignin partitioning). Dr. Janice Cooke visited UF to coordinate the completion of these papers with PI John Davis and Dr. Tim Martin.

One objective of this project was to develop transgenic poplar lines with altered expression of genes known to act as sink strength determinants. We chose invertase to manipulate in transgenic poplars. Ongoing efforts to characterize phenotypes in the transgenic lines have been difficult, either due to subtle effects of the transgene on partioning and allocation, or silencing of the transgene, or absence of the transgene. Recently we began to suspect that our previous assays of transgene presence – which were based on protein (invertase) abundance assays, and high kanamycin resistance of the plant materials – may have been misleading. We initiated a series of experiments to distinguish among the various possibilities, and results from both PCR analysis and Southern blot analysis indicate that the invertase portion of the binary vector is not present in the lines. A new series of transgenic lines are in production, using a series of constructs that express the yeast invertase construct in distinct subcellular locations – specifically the apoplast, the cytosol and in the vacuole. The promoeter is a double 35S promoter, which is much more effective than the single 35S promoter in poplar. These plants are currently on shoot regeneration medium.

In order to gain insight on the expression of individual poplar invertase isoforms under a variety of treatments, full length probes have been designed based on poplar genomic sequence data. Four out of the final seven probes have been made and are ready for use.

Plans for Next Quarter: Full length mRNA expression probes will be made and then checked for isoform specific homology. If they are not isoform specific, then real-time RT-PCR will be employed as a means to gather isoform specific expression data. The overall goal is to determine which invertase genes play roles in specific tissues and under various environmental conditions. Transgenic poplars overexpressing yeast invertase are expected in the next quarter and will be hardened off for growth in the greenhouse.

Publications/Presentations:
The following manuscript is being **revised** for resubmission to another journal:
Booth JG, Casella G, Cooke JEK, Davis JM. Sorting periodically-expressed genes using microarray data. Being modified for Biometrics

The following manuscripts are **in preparation** for submission to a journal:
Cooke JEK, Dervinis C, Martin TA, Cline M, Davis JM. Architecture shifts dramatically and quickly in poplar trees provided with exogenous N. In preparation for Tree Physiology.
Cooke JEK, Martin TA, Davis M, Davis JM. Lignin is regulated in association with shifts in C:N balance. In preparation for Tree Physiology.
Bocock P, Cooke JEK, Martin TA, Pijut P, Davis JM. Nitrogen partitioning shifts in leaves detected by gene expression analysis. In preparation for Canadian Journal of Forest Research.
Lawrence SD, Dervinis C, Davis JM. Hormone treatments alter wound responsiveness and nitrogen partitioning in poplar leaves. In preparation for Tree Physiology.

Dominant Negative Mutations of Floral Homeotic Genes for Genetic Engineering of Sterility in Forest Trees

Brunner: Oregon State University

ID13552, CPS#00794

Project Title: **Development and Validation of Sterility Systems for Trees**
Covering Period: April 1, 2004 through June 30, 2004
Date of Report: July 30, 2004
Recipient: Oregon State University, Department of Forest Science, 350 Richardson Hall, Corvallis, OR 97331-5752
Award Number: DE-FC07-97ID13552
Contacts:

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Amy.Brunner@orst.edu	Steve.Strauss@orst.edu

PROJECT OBJECTIVE

The overall goal of this project is to develop and validate sterility systems in poplar and eucalyptus that fulfill the basic requirements for commercial use. For this, sterility must be complete and stable over multiple growing seasons, cause no detrimental effects on vegetative growth, and successful transformation events must be identifiable via molecular tests when trees are still juvenile. Because of the inherent difficulties in achieving and demonstrating complete sterility in trees, our approach is to study alternate sterility systems that are mechanistically redundant in Arabidopsis and/or early-flowering tree systems. We will complete evaluation of dominant negative mutant (DNM) sterility constructs initiated under our previous grant and also test sterility constructs that are designed to engineer sterility via two additional molecular mechanisms: floral cell ablation and high frequency gene-silencing. Constructs selected from lab and greenhouse evaluations, as well as constructs previously developed, will be tested in field trials of transgenic trees.

BACKGROUND

We have isolated and characterized six poplar gene homologs of well-studied Arabidopsis genes that control the early stages of flower development (2). All but *LFY*/*PTLF* belong to a family of

Arabidopsis Gene	Function in Arabidopsis	Poplar Homolog(s)
AGAMOUS (AG)	Stamen & carpel identity	*PTAG1, PTAG2*
APETALA3 (AP3)	Petal & stamen identity	*PTD*
APETALA1 (AP1)	Flower initiation; sepal & petal identity	*PTAP1-1, PTAP1-2*
LEAFY (LFY)	Flower initiation	*PTLF*

transcription factors named after its highly conserved DNA binding and dimerization region, the MADS domain (3). We will also isolate a poplar homolog of the recently identified single-copy gene from Arabidopsis *NOZZEL (NZZ*), which is necessary for both female and male fertility. It differs from the genes listed above in that it acts at very late stages of flower development (4, 5). It may allow sterility to be imparted while maintaining floral structures intact where that is ecologically desirable, and by targeting early and late development in redundant constructs it may provide a more robust system than constructs that target only a single developmental stage.

If studies in Arabidopsis identify a strong DNM transgene, we will produce the corresponding poplar DNM transgene and test it in early-flowering poplar. Additional studies focus on the development of floral ablation and dsRNA-induced gene silencing (RNAi) sterility systems. For this work, the poplar *PTAP1* and *NZZ* promoter ablation transgenes, and poplar and eucalypts NZZ RNAi transgenes will be tested in early-flowering poplar and eucalypts. Because overlapping gene function and the potential instability of transgene expression or silencing make it difficult to be confident that sterility will be absolute throughout a tree's life span, redundant sterility constructs will be generated to overcome these difficulties. We will combine the best sterility transgenes that act by distinct mechanisms and/or target different genes.

STATUS

Four DNM constructs that frequently induced loss-of-function floral phenotypes and sterility in Arabidopsis are being transformed into early-flowering female poplar clone 6K10, as well as female poplar clone 717 and male clone 353. For poplar clone 717, 52 transgenic poplar plants (PCR-verified) have been regenerated. For poplar clones 6K10 and 353, transformation is progressing and is either at the subculture stage or shoots are undergoing selection.

For evaluation of the PTAP1 promoter for use in floral ablation sterility constructs, we produced a transgene with the PTAP1 promoter driving expressing of the reporter gene GUS. Moreover, we created two versions of this transgene, one with flanking MAR elements and one without MARS. We have produced 18 PTAP1::GUS transgenics in poplar clone 6K10 and 52 transgenic trees in poplar clone 717. Transformation of poplar clone 353 is in progress. Our floral ablation constructs use either the PTLF, PTAP1 or PTD promoter to drive expression of the cytotoxin BARNASE, and a weak constitutive promoter to drive expression of the BARNASE inhibitor, BARSTAR, in order to mitigate detrimental vegetative effects due to low levels of BARNASE. For poplar clone 717, PTLF ablation transgenics were planted in the field in 2003. Transformation of poplar clones, 6K10, 717 and 353 is ongoing for the three ablation constructs, and 11 PCR-verified transgenic lines have been regenerated for clone 6K10.

Although we are evaluating the promoter of PNZZ for ablating gametes, the low sequence conservation among the Arabidopsis and poplar genes is a concern (i.e., the poplar gene might not have a function similar to the Arabidopsis gene). Thus, we are producing a transgene with the PNZZ promoter directing expression of the reporter gene GUS. This reporter construct will be transformed into early-flowering clone 6K10. If the expression is as expected for a NZZ homolog, we will proceed with production and testing of PNZZ sterility constructs. Recent studies in Arabidopsis and other annuals have identified additional genes that act during meiosis or at late stages of gamete formation. Once the assembled and annotated poplar genome is released (expected 9/22/04), we will identify poplar homologs and evaluate one to two of these genes for use in sterility constructs that would act late in reproductive development (i.e., flowers would appear normal, but be infertile)

We have regenerated a total of 258 transgenic poplars in clones 6K10, 717, and 353 with *PTAG*, *PTAP1*, *PTLF* and *PTD* RNAi transgenes. We are currently transforming the three poplar clones with four different redundant RNAi constructs that target different pairs of genes (e.g., *PTAG* and *PTLF*) for suppression.

PLANS FOR NEXT QUARTER

Transformation, selection, propagation, and evaluation of transgenics with floral ablation, DNM and other sterility constructs will continue. We will initiate transformation of a redundant RNAi sterility construct that targets 3 genes for suppression and co-transformation of this RNAi sterility construct with the PTLF promoter ablation construct.

MILESTONES

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
13552	Development and Validation of Sterility Systems for Trees Oregon State University, Brunner, PI	12/31/05		
Task 1	DNM sterility system evaluation in Arabidopsis	12/31/02	9/30/03	Four DNM transgenes selected for testing in poplar
Task 2	DNM sterility system evaluation in poplar and eucalypts	2/28/05		Beginning evaluation of select transgenes in poplar
Task 3	Evaluation of *PTAP1* promoter for floral ablation	11/30/04		Transgenic analysis ongoing
Task 4	Isolation of poplar and eucalypts *NZZ*	4/1/03	10/30/03	Putative poplar NZZ homolog identified
Task 5	Evaluation of *NZZ* poplar promoter for floral ablation	3/30/05		Ongoing
Task 6	Evaluation of RNAi sterility systems	3/30/05		Ongoing
Task 7	Redundant sterility system testing	11/30/05		Transforming constructs
Task 8	Establishment of transgenic poplar field tests	12/31/05		Field-tests will extend beyond the grant period

SPENDING PLAN

Project Spending and Estimate of Future Spending							
Quarter	**From**	**To**	**Estimated Federal Share of Outlays***	**Actual Federal Share of Outlays**	**Estimated Recipient Share of Outlays***	**Actual Recipient Share of Outlays**	**Cumulative**
	Start*	6/30/04		615,947		195,297	811,244
3Q04	7/1/04	9/30/04	42,000		17,150		
4Q04	10/1/04	12/31/04	40,778		17,100		
1Q05	1/1/05	3/31/05	35,000		14,500		
2Q05	4/1/05	6/30/05	35,000		14,500		
3Q05	7/31/05	9/30/05	40,000		15,800		
4Q05	10/1/05	12/31/05	40,000		15,800		
1Q06	1/1/06	3/31/06					
Etc.							
Totals			**232,778**	**615,947**	**94,850**	**195,297**	**811,244**

***Start is 9/01/97**

Accelerated Stem Growth Rates and Improved Fiber Properties of Loblolly Pine

Cairney: Institute of Paper Science and Technology

ID13876, CPS#01168

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

Progress Report

Project Title: Accelerated Stem Growth Rates and Improved Fiber Properties of Loblolly Pine

Covering Period: (July 01, 2003 to September 30, 2003)

Date of Report: (October 30, 2003)

Recipient: Institute of Paper Science and Technology (IPST)

Award Number: DE-FC07-00ID13876

Subcontractors: None

Other Partners: State of Georgia – Cash

Contact: John Cairney; Tel: 404 894-1079; email address john.cairney@ipst.edu

Project Team: (DOE-HQ David Boron)

Project Objective: We plan to isolate and characterize the structure and regulation of cambial meristem cyclins from loblolly pine. In addition, we propose to create transgenic loblolly pine trees that ectopically overexpress cambial cyclins specifically in cambial cells. We will investigate whether this ectopic overexpression stimulates stem growth rates and leads to more xylem cells with thinner secondary cell walls.

Background: A sustained supply of low-cost, high quality raw materials is essential for the future success of the U. S. forest products industry. Enhancing stem growth rates, by concentrating the photosynthetically fixed carbon in the stem, is one of the most desirable goals. To maximize stem growth, a fundamental understanding of the molecular mechanisms that regulate cell divisions within the cambial meristem is essential. It is well accepted that auxin is an essential regulator of cambial meristem activity. We hypothesize that auxin levels within the cambial meristem regulate cyclin expression and this in turn controls cell cycle progression as occurs in all eucaryotic cells studied.

Our plan is to isolate and characterize the cambial meristem cyclins from loblolly pine to gain a more fundamental understanding of the regulation of cell divisions within the cambial meristem. Additionally, work with model plant species has shown that ectopic overexpression of cyclins promotes cell division thereby increasing root growth > five times. We intend to test whether ectopic overexpression of cambial cyclins in the cambial zone of loblolly pine also promotes cell division rates that enhance stem growth rates.

Status:

Personnel: One full-time postdoc is working on this project.
Tasks (1-4) -***Tissue Collections for RNA Isolation & In situ Hybridizations***:

Year 1 collections June-August (Q2 & Q3)

We have focused much of our efforts on collecting material since this was our first season of growth during this award. We obtained tissues from *six* 17-year-old trees. For each tree, three stem sections were collected starting in the live crown and progressing downward (Table 1). For larger scale RNA isolations to prepare cDNA libraries and RNA gel blots (task 1 & 4) cambial regions were obtained by scraping the log and bark surfaces from isolated stem sections.

Table 1. Tree Collections Year 1

Tree #	Date	Log 1		Log 2		Log 3	
		S*	V^	S	V	S	V
1	6-15-00	+	+	+	+	+	+
2	6-16-00	+	+	+		+	
3	6-26-00	+	+	+	+	+	
4	6-27-00	+	+	+	+		
5	7-20-00	+	+	+	+		
6	7-24-00	+	+	+		+	

* scrapings; ^ tangential vibratome sections.

For more detailed expression studies (task 2 & 3), we collected with the vibratome a large number of individual 150uM thick tangential sections of phloem-cambium-xylem regions from disks obtained from the same five trees that scrapings were obtained. For future *in situ* hybridizations (tasks 2 & 3), small blocks of wood from log #1 were dissected, quick frozen in liquid N2 and freeze substituted in methanol/glutaraldehyde at –80^{o}C (Regan et al. 1999, Plant J. 19 (3) 363).

Year 2 collections April-September (Q6 & Q7)

Table 2. Summary of Samples Collected in 2001

DS = destructive scrapings, DP = destructive planeings, NS = nondestructive scrapings, NP= nondestructive planeings

Time	Day no.	Tree (D)	DS	DP	Cookie	Blocks (ht/ft)	Tree (N)	NS	NP
May 16	1						1-4	X	X
May 23	2	A	X	X	X	5			
May 30	3	B	X	X	X	5	5-8	X	X
June 6	4	C	X	X	X	5			
June 6	4	D				5,17,33			
June 8	5						9-24	X	X
June 20	6	E	X	X	X		1-4	X	X
June 20	6	F				5,17,33			
June 26	7	G	X	X	X				
June 26	7	H				5,17,33			
July 3	8	I	X	X	X		5-8	X	X
July 3	8	J				5,17,33			
July 16	9	K	X	X	X		9-15	X	X
July 20	10	L				5,17,33			
July 20	10	M	X	X	X				
July 20	10	N				5,17,33			
July 27	11	O				5,17,33	16-18	X	X
July 27	11	P	X	X	X	5,17,33			
Aug 3	12	Q	X	X	X	5	1-4, 19-21	X	X
Aug 15	13	R	X	X	X	5,17,33	22-24	X	X

Task 1 - Cyclin cDNA isolation

We have also constructed, amplified and characterized cDNA libraries from the xylem and phloem side scrapings in lambda Triplex. Full-length cyclin D has been obtained. Sequence analysis with BlastX shows that this cyclin D is most closely related to other plant cyclin D's obtained from tobacco and clustal analysis to the *Arabidopsis* cyclin D gene family indicates that it is more closely related to cyclin D2 than D1 or D3 (Figure 1).

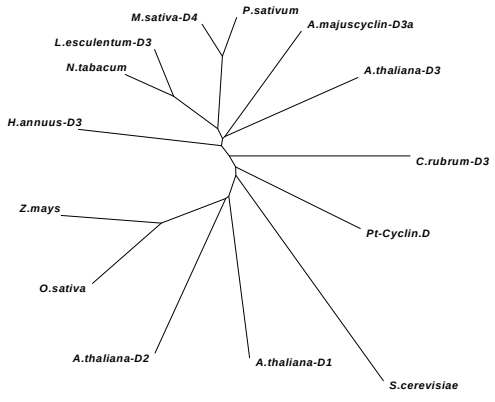

Figure 1. Unrooted, phylogenetic tree showing PtcycD1 similarity to other cyclin Ds

Task 2- Study the expression patterns of cyclins within cambial meristem cells

8 trees were felled between early May and the end of June. Scraping and planning the 2 ft. log sections at 5 ft., 17ft. and 35 ft. up the trees was done to collect cambial and xylem tissue samples. Disks were also taken from the base of these logs at each height to determine the # of cells in the cambial zone, which includes the cambial meristem & xylem mother cells, tracheid expanding and nonlignifying zone. The data on # of cells in the cambial zone indicates that trees collected in the last week of May had 1/2—1/3 the number of cells when compared to June (Figure 1). In addition, the number of cells in the zone also increased with height on the tree as expected (Figure 2). These collections represent an excellent sample set for determining whether quantitative differences in mRNA and protein levels of the cyclin D relative correlate with cell division rates. Additional samples for each tree at all heights have been collected for dissection of the differentiating zone by tangential sectioning and in situ hybridization. Table II summarizes all of the samples collected during the summer of 2001.

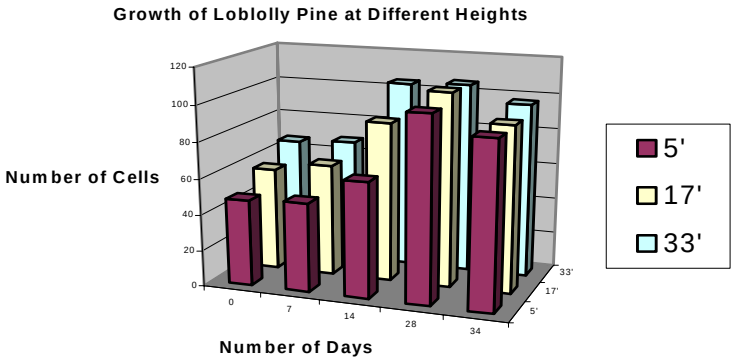

Figure 2. Number of cells in the cambial zone from 5 trees collected on successive weeks in May and June. The # of cells in the cambial zone was determined 5, 17, & 33 ft.

To relate changes in mRNA level of this cyclin to cell division rates we quantified the level of PtcyclinD1 in the nonlignified xylem from the trees characterized for cambial growth

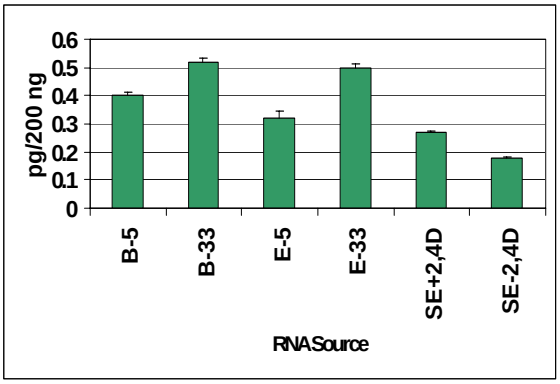

Figure 3. PtcyclinD1 mRNA levels detected by quantitative PCR in trees and somatic embryos. The results are of 3 replicate samples. Nonlignified xylem from tree B and tree E respectively at 5 ft and 35 ft. Early stage somatic embryo cultures with and without exogenous Auxin.

by quantitative RT-PCR. The hypothesis is that trees with more cells in the vascular cambial and expansion zones will have higher cyclin mRNA levels. At 5 ft tree E had twice the number of cells in the cambial and expansion zone as tree B. Figure 3 shows little difference in the amount of PtcyclinD1 mRNA between trees B and E at 5 ft. In addition a slight positive relationship between the height of the tree and the mRNA was detected. In contrast, we did observe in the same experiment that the level of PtcyclinD1 mRNA is slightly decreased in rapidly dividing early stage after withdrawal of exogenous auxin from somatic embryo cultures for 4 weeks.

An additional test to correlate PtcyclinD1 mRNA levels with secondary growth in stems was carried out with compression wood. One of the features of trees under compressive stress is that the rates of cambial divisions are increased on the underside of the stem relative to the top or opposite side. The advantage of this approach is that it provides a test within the same tree and tree to tree variation is minimized. In our experiment we had one naturally bent tree that had been under compression for at least 4 years and one manually bent tree that had been under compression for only 5 days were used. The nonlignified xylem from both the compression side and the opposite side were harvested and quantitative PCR was used to measure the mRNA levels of PtcyclinD1 and COMT as a control. Figure 4 shows the ratio of mRNA these genes. The data show a 20 fold increase in the level of PtcyclinD1 mRNA on the compressed side of the stem relative to the opposite. This suggests that higher secondary growth rates correlate with PtcyclinD1 expression. Similarly for the tree bent for only 5 days showed a slight increase in PtcyclinD1 expression. The results for COMT were as expected, a strong increase in mRNA level on the compressed side of the stem.

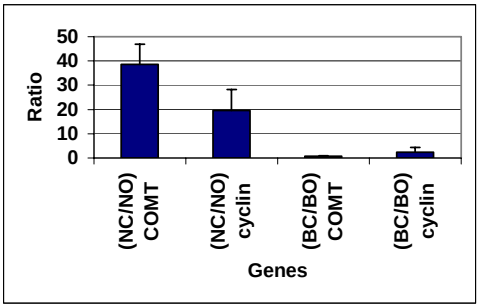

Figure 4. The ratio of PtcyclinD1 and COMT mRNA levels in nonlignified xylem from compressed and opposite sides of the stem from a naturally bent tree (NC/NO) and from a manually bent tree (BC/BO)

New trees have been identified for testing the hypothesis that increase cell divisions within the cambial meristem correlate with increased levels of PtcycD1. Figure 5 shows that the average ring width of 4 clonal replicates of 7 year old loblolly pine trees. Trees were selected based on stem diameter at year 4. Larger diameter trees show more growth during each year. Figure 5 shows that the increased growth in loblolly pine trees correlates with more cell divisions in the cambial meristem as expected. We are in the process of determining the levels of PtcycD1 mRNA levels in these fast and slow growing trees (Figure 6).

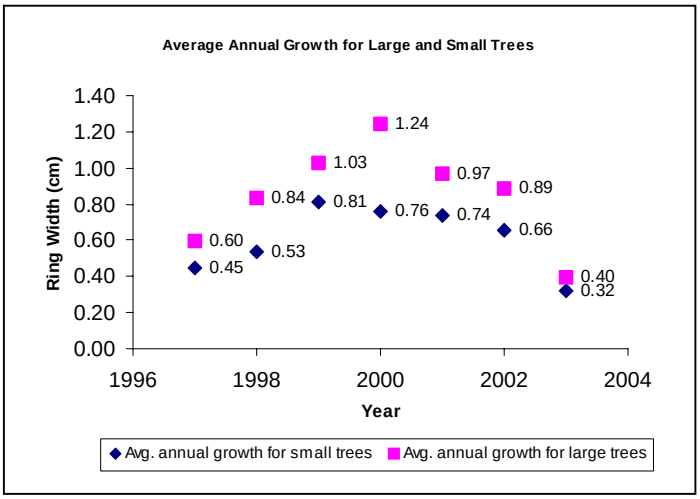

Figure 5. Seven year old loblolly pine clones that are larger in diameter grow faster in every season

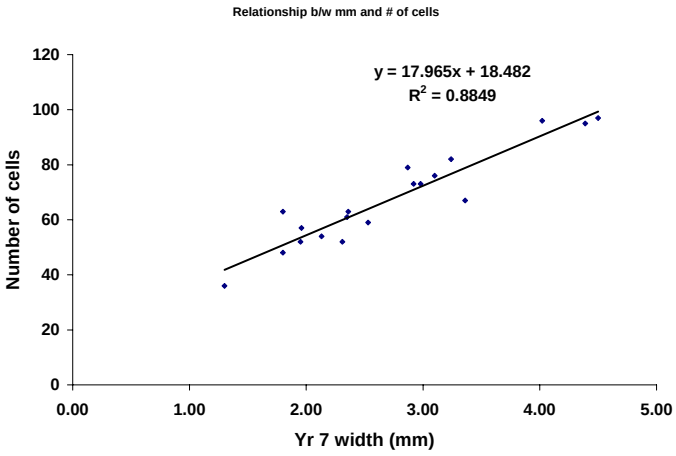

Figure 6. Faster loblolly pine stem growth rates are due to more xylem cells and higher rates of cell division in the cambial meristerm

To localize the cyclin mRNAs we are trying to develop tissue printing/in situ hybridization methods. In this method 15-30 um radial, tangential and cross-sections are cut using the cryomicrotome. For the tissue printing method, we have followed (Conley & Hanson 1997, Biotechniques 488: 491-496). Briefly, the

sections are thawed unto nylon membranes impregnated with gel mount and the RNA UV fixed to the membrane. Hybridizations have used digoxigenin labeled DNA probes and alkaline phosphatase/chemiluminescence detection. To standardize this method in our lab we are using AGP as a probe since it is a very abundant message. Preliminary data with an AGP probe looks promising in terms of signal to noise and specificity (Figure 7).

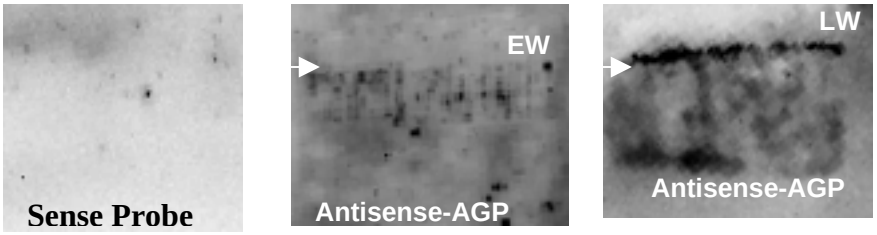

Figure 7. Cryotissue printing, cross sections from earlywood (EW) and latewood (LW) of 18 yr old trees were probed with sense and antisense AGP probes. Dark spots by arrows indicate AGP mRNA expression in cambial and expanding xylem zones.

With tissue printing approach described above it was difficult to localize the messages relative to cell types. Hence, we are now standardizing another approach using cryosectioning and in situ hybridization. In this method a CryoJane tape transfer system is used. With this system the soft cambial meristem and the cells in the expanding zone are maintained intact much better than with traditional cryosectioning. We are currently testing methods for improved freezing and fixation.

Sequential 30 uM tangential sections from earlywood (2 trees) and latewood (1 tree) have been collected. The RNA from these sections will be isolated and used for analysis of the zone that cyclins are expressed in. Preliminary tests show that using SMART-PCR we are able to amplify the mRNA from one section. Tests of SMART-PCR show that they tend to compress the differences in expression level between the abundant and not so abundant mRNAs. In contrast, aRNA amplification methods, which are linear and not exponential since they do not use PCR, do not compress the expression levels. aRNA amplification is suitable for amplifying RNA from one 30 uM tangential section.

Task 3- Isolate promoter(s) for cambial cell specific expression

We have isolated a promoter region whose mRNA is most abundantly expressed in secondary xylem. This mRNA is not detected in needles or early stage somatic embryo cultures (Figure 8). Our clone contains ~ 1 kb of the 5' promoter region of this fragment.

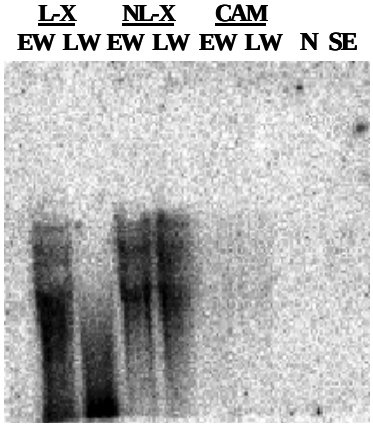

Figure 8. RNA gel blot with 10 ug of total RNA L-X is lignifying xylem, NL-X is nonlignifying xylem, EW is earlywood, LW is latewood, CAM is barkside scrapings, N is needles, SE is early stage somatic embryos

Task 4 – Construct plant vector for expressing cyclin(s) in cambial cells

We have cloned our full-length PtcycD1 into a 2X35SCaMV-TEVL- for preliminary overexpression experiments in pine.

Task 5 - Generate 5-10 independent transgenic lines of *P. taeda* with these gene constructs

Transformation efforts are on going with State of Georgia funds. We are optimizing selection procedures and DNA transfers with *Agrobacterium tumefacians*. Initial constructs for transformation procedure development include 2X-35S CaMV-TEVL-NPT II & 35S GFP-ER. We have made a T-DNA vector construct in pBIN19 that contains the maize ubi 1 promoter and intron regulating expression of the NPTII gene.

We now have putatively transformed early stage somatic embryo cultures growing on geneticin selection with the ubi1 promoter. These lines are growing whereas control untransformed lines are not growing on geneticin. Putatively transformed lines have been confirmed by PCR analysis. Sufficient tissue is being grown for seedling regeneration experiments. Unfortunately this tissue did not produce embryos.

We have found that growth of our best seedling producing lines was slow relative to other lines. Consequently we have gone back to optimize the tissue culture media to support faster growth of this line. Figure 9 shows media that improve the growth rate of early stage embryos from loblolly pine.

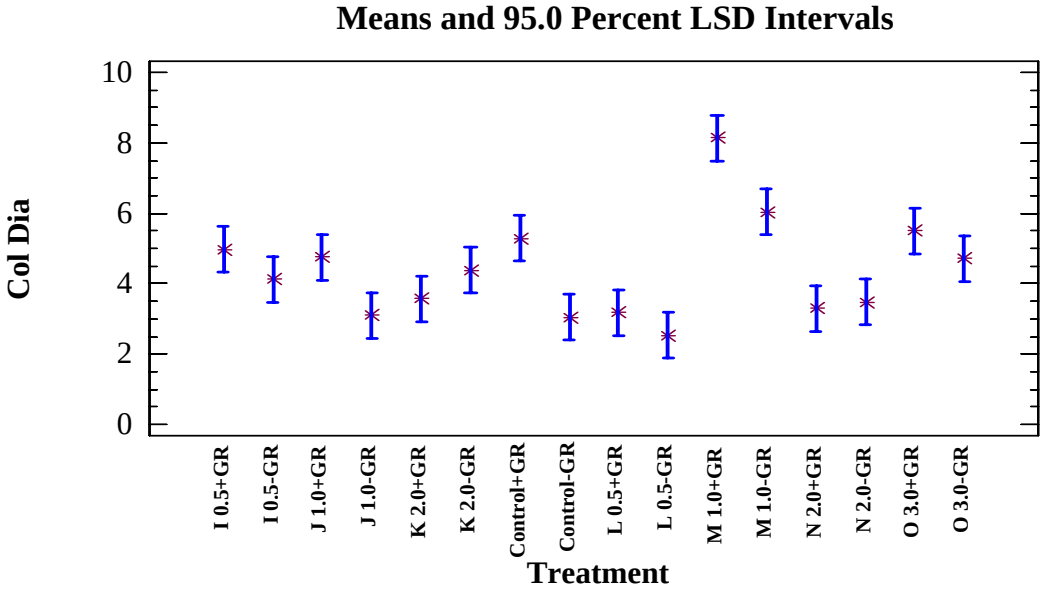

Figure 9. Optimization of growth media for selection of transformed early stage embryos. Media M promotes the highest rates of early embryo division

The transformation efforts in loblolly pine are ongoing at IPST as previously discussed. The system is however not yet reached a level of efficiency that allows for analyses of gene characterization in vivo. We have therefore established a collaboration with Dr. Armin Wagner at Forest research, Rotorua, New Zealand, to study the function of the cyclin D. Forest Research has developed a functional system for transformation of conifers (Walter et al. 2002, Plant Cell, Tiss Org Cult 70: 3-12) that has proven succesful for *Pinus radiata* and *Picea abies* (Walter et al. 1998, Plant Cell Rep. 17: 460-468), *Abies nordmanniana* (Find, in prep.), *Pinus taeda* (Grace, unpublished). We will supply the full length cDNA clone to Forest Research (non-disclosure agreement between Georgia Institute of Technology and Forest Research has been signed). The in house vector at Forest research will be used for making the construct (Walter et al. 1998, Plant Cell Rep. 17: 460-468). In addition, a newly characterized promoter with cambium specific activity will be added to the construct (Johansson et al. 2003, Plant Mol Biol. 52(2):317-29). This promoter is currenlty being tested at Forest Research for activity in conifers (Wagner. pers. comm.).

Task 6- Initiate analyses of cyclin expression, stem growth, vascular cell differentiation, and xylem cell properties

Accelerated Stem Growth Rates and Improved Fiber Properties of Loblolly Pine: Functional Analysis Of CyclinD from *Pinus taeda*

DOE

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SUMMARY

A sustained supply of low-cost, high quality raw materials is essential for the future success of the U.S. forest product industry. Enhancing stem growth rates, by concentrating the photosynthetically fixed carbon in the stem, is one of the more desirable goals. To maximize stem growth, a fundamental understanding of the molecular mechanisms that regulate cell dvisions within the cambial meristem is essential. It is well accepted that auxin is an essential regulator of cambial meristem activity. We hypothesize that auxin levels in the cambial meristem regulate cyclin

expression and this in turn controls cell cycle progression as occurs in all eucaryotic cells studied.

To date, we have isolated several cDNA clones showing similarity to cyclin genes. The expression of these clones have been studied in different types of xylem tissue, e.g. compression wood, side wood, early wood and latewood (data shown in previous report).

We are currently seeking a reverse genetics approach to further characterize one of the cyclin genes. The full length cDNA of the Pt cyclin D2 gene was isolated and work is underway to test the function of this specific cyclin in a trangenic pine system through the collaboration with Forest Resarch, NZ. The transformation system for *Pinus radiata* is well established (Walter et al. 2002).

PROGRESS REPORT IN BRIEF

Plant material

Isolation and characterization of PtCyclinD2 from xylem tissue of Pinus taeda.
Primers were designed based on previous sequence information on the consensus sequence for the cyclin D from *Pinus taeda* (Fig. 1). The full length cDNA of PtcyclinD2 cDNA was isolated. Sequencing from both ends revealed a full length cyclin sequence identical to the consensus sequence from cyclin D of Pt cDNA.The consensus sequence was previously constructed by aligning sequenced fragments encompassing partial sequences of the cyclin cDNA.

PtcyclinD>
ATGGCACCCAACTGCATAGACTGTGCCCCTAGTGATCTGTTTTGCGCGGAGGATGC
TTTTGGAGTTGTGGAATGGGGCGATGCAGAGACTGGAAGTTTGTATGGAGATGAGG
ATCAGCTGCATTATAATTTGGACATTTGTGACCAGCATGATGAGCATTTGTGGGATG
ACGGTGAACTTGTAGCTTTTGCAGAAAAAGAGACCCTCTATGTTCCTAACCCAGTTG
AGAAAAACAGTGCTGAAGCTAAAGCTAGGCAGGATGCTGTGGATTGGATTTTGAAG
GTTCATGCACATTATGGCTTTGGTCCTGTGACTGCAGTGCTCTCAATAAACTATCTT
GATCGGTTTTTGTCTGCAAATCAATTACAGCAAGATAAGCCATGGATGACTCAACTG
GCAGCTGTGGCTTGCCTCTCCCTCGCTGCCAAGATGGATGAGACAGAGGTTCCCC
TTCTCCTGGACTTTCAGGTTGAGGAGGCTAAGTATATATTCGAATCTCGCACCATTC
AGAGAATGGAATTACTGGTGCTCAGTACCCTTGAATGGCGAATGAGTCCTGTGACA
CCTCTTTCCTACATTGATCATGCCAGTCGTATGATTGGGTTGGAGAATCACCATTGT
TGGATTTTCACAATGCGCTGCAAGGAGATACTGTTGAATACACTCAGAGATGCAAAG
TTTTTGGGCCTTCTGCCCTCTGTTGTAGCTGCTGCAATAATGCTGCATGTGATCAAG
GAAACAGAGCTTGTTAATCCATGTGAGTACGAGAATCGCCTGCTCAGTGCCATGAA
AGTTAATAAGGACATGTGTGAAAGATGCATAGGACTACTCATAGCCCCTGAATCATC
ATCCTTGGGCAGTTTCTCTTTGGGTTTGAAAAGAAAGAGCAGCACCATCAATATTCC
TGTTCCTGGCAGCCCAGATGGAGTGCTAGACGCTACCTTTAGCTGCAGCAGCAGCA
GCTGTGGTAGCGGACAGAGCACCCCAGGGTCATATGATTCCAATAACTCCAGCATT
CTCTGCATCTCACCAGCGGTGATAAAGAAGAGAAAGCTTAATTACGAGTTTTGTAGC
GATCTTCATTGTTTGGAGGATTAGTAG

Figure 1. The predicted full length consesnus sequence of PtcyclinD2.

Homology searches against BLASTX (NCBI)

The PtcyclinD2 sequence showed sequence similarity to several other cyclins (Fig. 2). The highest similarity (E value $2e^{-69}$) was to a poplar (*Populus alba*) cyclin.

```
L.esculentum    1 -MAIENNDQ----S-FFLDVLYCEEEEEKWGDLLEDEEGVIINPLLLSSEGTTKTNSLLL
N.tabacum       1 -MAIEHNEQQELSQSFLLDALYCEEEEEKWGDLVDDETIITPLSSEVTTTTTTTTKPNSL
P.alba          1 MSFLQQQETHNQSPALALDGLYCEEDG-------FGEDYSCGLDDETSQVYDQNVKKEQN
P.taeda         1 -MAPNCIDCAP-------SDLFCAEDAFG---------VVEWGDAETGSLYGDEDQLHYN
consensus       1  ........   .  . ...*.*.*.............  .. ........ ..

L.esculentum   55 LPLLLLEQDLFWEDEELLSLFVKEKETRCCFESFGS-DPFLCSARVDVVEWILKVNAHYD
N.tabacum      60 LPLLLLEQDLFWEDEELLSLFSKEKETHCWFNSFQD-DSLLCSARVDSVEWILKVNGYYG
P.alba         54 LSSVLLEQDLFWEDSELLSLISKEKETHVVFDSVGSRDGSLMVVRREAVEWFLRVKAHYG
P.taeda        44 LDICDQHDEHLWDDGELVAFA--EKETLYVPNPVEK-NSAEAKARQDAVDWILKVHAHYG
consensus      61 *..........*.*.**......****...... .. .. ....*...*.*.*.*...*.

L.esculentum  114 FSALTAILAINYLDRFLSSLQFQKDKPWMTQLAAVTCLSLAAKVEETQVPLLLDFQVEDA
N.tabacum     119 FSALTAVLAINYFDRFLISLHYQKDKPWMIQLAAVTCLSLAAKVEETQVPLLLDFQVEDA
P.alba        114 FSALTGVLAVNYFDRFISSSRFRRDKPWMGQLAAVACLSLAAKVEETQVPLLLDLQVEDA
P.taeda       101 FGPVTAVLSINYLDRFLSANQLQQDKPWMTQLAAVACLSLAAKMDETEVPLLLDFQVEEA
consensus     121 *...*..*..** ***........*****.***** *******..**.******.***.*

L.esculentum  174 KYVFEAKTIQRMELLVLSSLKWRMNPVTPLSFLDHIIRRLGLKNNVHWEFLRRCESLLLS
N.tabacum     179 KYVFEAKTIQRMELLVLSSLKWRMNPVTPLSFLDHIIRRLGLRNNIHWEFLRRCENLLLS
P.alba        174 KYVFEAKTIKRMELWVLSTLHWRMNPVTSISFFDHIIRRLGLKTHMHWEFLWRCERLLLS
P.taeda       161 KYIFESRTIQRMELLVLSTLEWRMSPVTPLSYIDHASRMIGLENHHCWIFTMRCKEILLN
consensus     181 **.**..**.****.***.*.***.***..*..**..*..**.. ..*.*..**. .**.

L.esculentum  234 VMIDCRFVRYMPSVLATAIMLHVIHQIEPCNAIDYQNQLLGVLKISKENVNNCYELISEV
N.tabacum     239 IMADCRFVRYMPSVLATAIMLHVIHQVEPCNSVDYQNQLLGVLKINKEKVNNCFELISEV
P.alba        234 VISDSRFMSYLPSILATATMLHVIKEVEPRNQLQYQTQLMAVLKTNEDEVNECYRLILEQ
P.taeda       221 TLRDAKFLGLLPSVVAAAIMLHVIKETELVNPCEYENRLLSAMKVNKDMCERCIGLLIAP
consensus     241 .. *..*....**..*.*.*****. .*..*  ..*...*....*.... ...*..*....

L.esculentum  294 SSKPITS--------HKRKYDENPSSPSGVIDPIYTSESSNDSWDLDLPS---------F
N.tabacum     299 CSKPIS---------HKRKYENPSHSPSGVIDPIYSSESSNDSWDLESTSSY----FPVF
P.alba        294 PGSQNQR--------HKRKYLSTPSSPNGVIDASFSSENSNDSWAVASSISSSSS-VPQF
P.taeda       281 ESSSLGSFSLGLKRKSSTINIPVPGSPDGVLDATFSCSSSSCGSGQSTPGSYDSNNSSIL
consensus     301  . ....        .....   ..**.**.* ......*............ .   ...

L.esculentum  337 KKSKVQEQQMKMSSSLSRVFVEAVGSPH
N.tabacum     346 KKSRVQEQQMKLASSISRVFVEAVGSPH
P.alba        345 KRSRAQVQQMRLP-SLNRMCVDVLSSPH
P.taeda       341 CISPAVIKKRKLN---YEFCSDLHCLED
consensus     361 ..*. ....... ...... ........
```

Figure 2. Similarity of the PtCyclin D to other cyclins in the NCBI database. The three most similar cyclins are poplar (*Populus alba*; E value $2e^{-69}$), tomato (*Lycopesricon esculentum*; E value $2e^{-67}$), and tobacco (*Nicotiana tabacum*; E value $2e^{-67}$).

Transformation efforts

The full length PtCyclinD cDNA, was sent to Forest Research, NZ. Forest Research has a well established Constructs are being made with three different promoters: *Zea mays* ubi-1 promoter, an AGP promoter, and the *Pinus radiata* CCoAOMT promoter. The promoters come with introns, which are part of the original 5' UTR of the attached genes

FUTURE DIRECTIONS

The effects of up-or downregulating the PtCyclinD in *Pinus radiata* tissue will be evaluated in embryogenic cultures and plants regenerated from the somatic embryos. Phenotypic data and growth characteristics will be monitored. In addition, the construct will be tested in the alternative model systems available at Forest Research. The effect on global gene expression will be evaluated by microarray analysis.

REFERENCES

Walter, C., Charity, J., Grace, L., Höfig, K., Möller, R., Wagner, A. (2002) Gene technologies in Pinus radiata and Picea abies: tools for conifer biotechnology in the 21st century. Plant cell, Tissue Org Cult 70: 3-12.

Performance and Value of CAD-Deficient Pine

Mullin: North Carolina State University

ID14436, CPS#01869

QUARTERLY PROGRESS REPORT

Project Title: Performance and value of CAD-deficient pine

Covering Period: From: 04/01/04 through: 06/30/04

Date of Report: 07/30/04

Recipient: North Carolina State University
Campus Box 7514, Raleigh, NC 27695-7514

Award Number: DE-FC36-03ID14436

Subcontractors: Southern Institute of Forest Genetics
USDA – Forest Service
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Project Objective: The general objective of this study is to characterize the performance and value of partially CAD-deficient wood, arising from *cad*-n1 identified in descendants of an exceptionally fast-growing pine genotype. Specific objectives are:

1. to compare lignin formation in partially CAD-deficient and "normal" trees, ranging in age from 6 years to rotation age in multiple genetic and environmental backgrounds, in both juvenile and mature wood;
2. to identify associations between CAD genotype and growth performance (growth, stem form and defect in older trees, developmental traits in younger trees);
3. to conduct laboratory studies to confirm the value of partially CAD-deficient wood for energy savings in pulp production and impact on properties of solid-wood products; and
4. to develop approaches to marker-assisted breeding for partially CAD-deficient wood

Background: The southern US produces 58% of the nation's timber, much of it grown in intensively managed plantations of genetically improved loblolly pine. One of the fastest-growing loblolly pine selections made by the NCSU-Industry Cooperative Tree Improvement Program, whose progeny are widely planted, is also the only known natural carrier of a rare gene, *cad*-n1. This allele codes for deficiency in an enzyme, cinnamyl alcohol dehydrogenase (CAD), which catalyzes the last step in the biosynthesis of lignin precursors. Preliminary data for 4-year-old descendants from this fast-growing selected parent indicate that those carrying a single copy of *cad*-n1 (partially CAD-deficient) grow 14% faster and require less energy for pulping, producing higher brightness and paper strength. As a naturally occurring gene, acceptance of *cad*-n1 as a candidate for genetic engineering should be rather high. Before any such use can be considered, however, *cad*-n1 must be well characterized in harvest-age trees in a broad range of environments and in diverse genetic backgrounds. As a well-characterized candidate gene, marker-assisted selection and deployment should be possible in the breeding program. This research will enhance the sustainability of forest production in the South, where land-use pressures will limit the total area available in the future for intensively managed plantations. Furthermore, this research will provide information to establish higher-value plantation forests with more desirable wood/fiber quality traits.

Status:

1. Field sampling and growth/form assessment

1.2 Collect field data, cambium scrapings and cores

Field sampling of all presently identified CAD-deficient progeny of the cad-n1 founder was completed. Sampling of *cad-n1* segregating families and crosses identified in replicated field tests was completed, with cambium samples sent to SIFG for genotyping, and core samples brought back to our lab in Raleigh. A total of 2185 trees were sampled in these replicated tests. An additional 180 samples were also collected in a genetics x cultural treatment field test at the Southlands Forest near Bainbridge, GA (International Paper Co.). Preparation of cores from all diallel and OP test trees for X-ray densitometry was begun, with about 850 samples ready for scanning. X-ray scanning of these cores has begun.

2. Genotyping of informative crosses and individuals for CAD

Samples from 1116 additional progeny trees were sent to the Southern Institute of Forest Genetics for genotyping (plate 9 through plate 20). DNAs were isolated and PCRs were completed and analyzed by the procedures reported previously (12/31/03). To date, a total of 1847 progeny and 30 parental samples have been genotyped. Thirteen samples have failed to yield genotype data. For the 1834 progeny samples with data; 852 are heterozygous *Cad-n1* and 982 are homozygous wild type

3. Evaluation of wood structure

3.1 NIR analyses (lignin, cellulose)

Increment cores from 20 trees each from the four different groups: wild type control, wild type fertilized, CAD-nl control and CAD-nl fertilized have been collected from Scotland County. Ring 3-8 each of the increment cores have been cut into thin wafers for lignin and α-cellulose determinations. Our NIR was broken and had to be shipped back to the manufacturer for repair. We will finish this work during the next quarter.

3.4 Pulping

Ten trees each from the four different groups: wild type control, wild type fertilized, CAD-nl control and CAD-nl fertilized have been collected from Scotland County for pulping studies. Disks were obtained from each of the trees for chemical analysis. The logs were chipped separately and then classified by thickness into 0-2mm, 2-4mm, 4-6mm, 6-8, mm and 8+mm fractions. Four sets of chips have been prepared representing the four groups. The 6 and 8 mm chips were used to make up the mixed fractions. They have been pulped using the following conditions: 19%AA,

4:1 liquor to wood ratio, 170^{o}C and 25% sulfidity. The H factor was varied from 800-1800 to produce a wide range of kappa numbers.

The results of these pulping studies are shown in Table 1 and Figures 1 and 2. As shown in Figure 1, the rates of pulping appear to be similar among the four groups except that there are some indications that the CAD-nls (both control and fertilized) may be easier to pulp at lower H-factors. These results will be verified during the next quarter. As shown in Figure 2, the pulp yield at a given kappa number is comparable between the wild and the CAD. A 2% yield difference between the control and the fertilized is observed for both the wild and the CAD.

Table 1. Pulping Results

	H Factor	Total Yield	Kappa
CAD Control	800	51.2	84.5
	1200	46.8	48.2
	1600	45.2	40.2
	2000	44.3	37.2
CAD Fertilized	800	48.7	83.8
	1200	44.8	46.4
	1600	43.7	38.8
	2000	41.5	28.2
Wild Control	800	50.8	87.9
	1200	47.7	50.1
	1600	46.1	39.1
	2000	44.8	37.1
Wild Fertilized	800	48.6	85.7
	1200	44.8	50.7
	1600	44.3	38.7
	2000	42.8	31.0

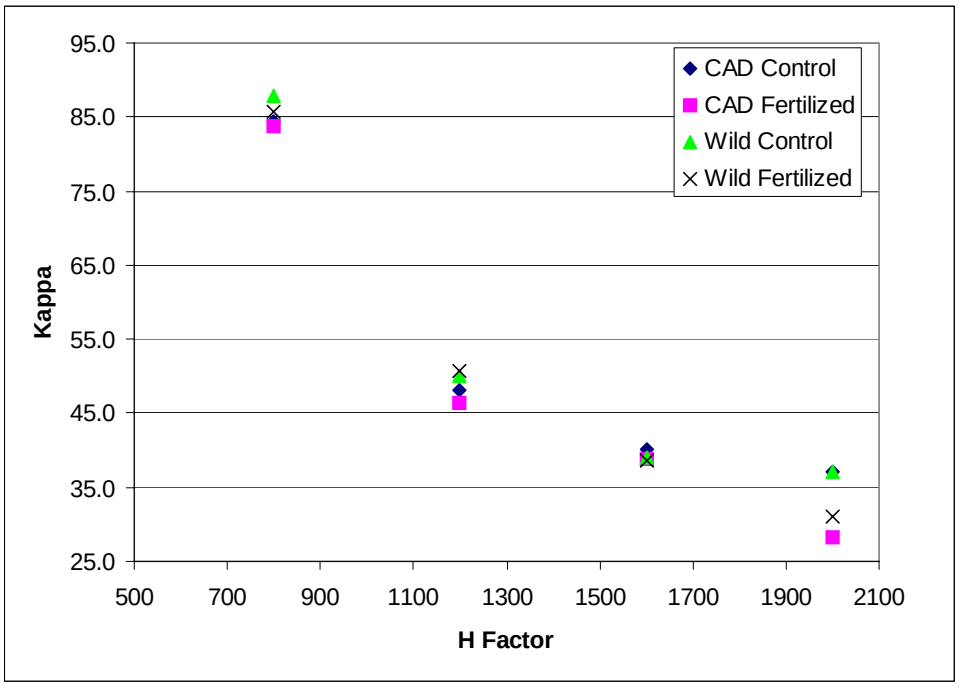

Figure 1. Rate of pulping

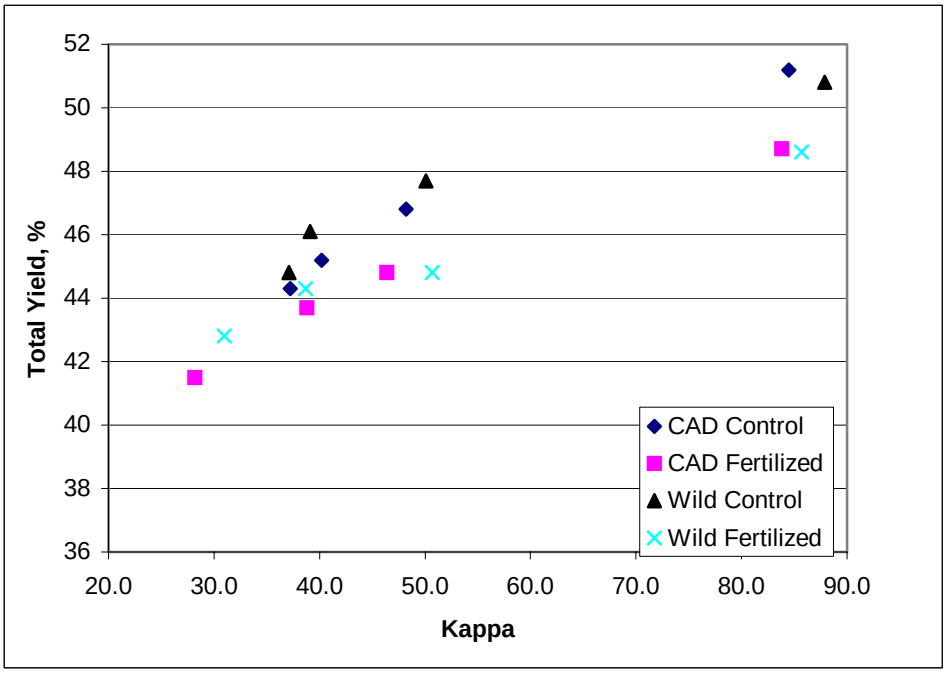

Figure 2. Pulp yield at a given kappa number

Lignin structural changes during pulping

Kraft lignins isolated from black liquor from pulping of CAD-deficient pine and the control (both non-fertilized) were comprehensively characterized using ^{13}C NMR of non-modified and acetylated samples (Table 2). Very little differences in the structure of the kraft lignin from CAD-deficient pine and the control one have been observed.

Table 2 Characterization of kraft lignins isolated from pulping of CAD-deficient pine and control wood (both non-furtilized). Amount of moieties is expressed per 100 Ar (can be considered as mole %).

Moieites	A2 (control)	C2 (mutant)
Total CO	6	5
Conjugated CO	3	3
Non-Conjugated CO	3	2
Total COOH	18	16
Aliphatic COOH	16	15
Aromatic COOH	1	1
Total OH	128 (118*)	131 (121*)
Aliphatic OH	64 (54*)	65 (55*)
Primary	36	38
Secondary	28 (18*)	27 (17*)
Phenolic OH	64	66
h-units	7	7
Degree of Condensation	77	76
OMe	82	83
Oxygen. aliph. (90-58 ppm)	115 (95*)	119 (99*)
Saturated aliphetic (35-10 ppm)	76	80
Phenylcoumaran (β-5)	4	5
Pinoresinol (β-β)	2.5	2.5
β-O-4	4	4
Sugars (Xylan)	5	5

* Corrected for sugar content (as xylan)

4. Quantitative analysis of dataset

Ten-year growth assessments for the trees at Scotland Co. were completed and the complete dataset analysed for growth performance and wood density. The results from this analysis were documented in a paper to presented at the Open Session of the TAPPI Summit in Atlanta in May, and in a poster presented at the IEG-40 meeting held in June at

Jeckyll Island, GA. A manuscript was drafted and is completing internal review prior to journal submission.

Project meetings

Four members of the project team participated in a Peer Review of the Project, conducted in conjunction with the TAPPI meeting in Atlanta in May.

Plans for Next Quarter:

The remaining genotyping from replicated field tests will be completed. Rotation-aged paired-tree samples (heterozygote and wild-type) from Good General Combiner test series will be identified and work will begin to harvest these trees for whole-tree pulping studies and wood-quality analysis.

Preparation of cores from these trees will be completed and an additional 1000 of these will be scanned for ring-by-ring densitometry. Site-by-site analyses of growth and wood density data and correlations with cad genotype will be carried out as scanning of cores is completed.

The 10-year growth and wood density analysis of the Scotland Co. material will be submitted for journal review.

The ring-by-ring scanning by NIR for an 80-core subset of these trees for lignin and alpha-cellulose, delayed last quarter due to equipment failure, will also be completed. Pulping results for bulked chip samples for each CAD genotype and fertilizer treatment will be verified.

Patents:

Publications/Presentations:

1. Mullin, T.J. 2004 . Tracking down the effects of a rare mutant gene in loblolly pine – a first report. Presentation at the TAPPI 2004 Paper Summit, Spring Technical and International Environmental Conference, 4 May 2004, Atlanta, GA.
2. Yu, Q., Capanema, E., Batista, V.B., Josserand, S., Johnson, G., Nelson, C.D., McKeand, S.E., MacKay, J.J., Kadla, J.F., Li, B., Jameel, H., Chang, H.-M., and Mullin, T.J. 2004. Tracking down the effects of a rare mutant gene in loblolly pine – a first report. Paper published on CD-ROM: "2004 Paper Summit, Spring Technical and International Environmental Conference", TAPPI, Norcross, GA
3. Yu, Q., Capanema, E., Nelson, C.D., McKeand, S.E., Li, B., Jameel, H., Chang, H.-M., and Mullin, T.J. 2004. Wood density, pulping and growth of partially CAD-deficient loblolly pine in fertilized and non-fertilized treatments. Poster and abstract presented at 2004 IEG-40 Meeting: Advancing Regeneration Technologies for the Deployment of Elite Southern Pine Germplasm, 22-24 June 2004, Jeckyll Island, GA.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Comments
1	Field sampling and growth/form assessment		
1.1	Identify candidate families and field sampling plots	01/31/04	Complete
1.2	Collect field data, cambium scrapings and cores	04/30/05	95% complete
2	Genotyping of informative crosses and individuals for CAD		
2.1	Process parental megametophyte tissues to identify informative crosses	04/30/04	Complete
2.2	Process cambium scrapings for genotyping	04/30/05	75% complete
3	Evaluation of wood properties		
3.1	NIR analyses (lignin, cellulose)	04/30/05	NIR calibration complete
3.2	Analyze lignin structure	04/01/06	
3.3	Analyze fiber morphology	10/30/05	
3.4	Pulping studies	07/31/05	First pulping tests complete and protocols established for additional samples
3.5	Analyze paper strength	04/01/06	
3.6	Analyze solid wood properties	04/01/06	Density profiles complete for 200 trees; sample preparation of 2185 cores is 50% complete
4	Quantitative analysis of dataset	04/01/06	Scotland Co. analysis for 10-year growth and wood density in manuscript; additional site analyses underway
5	Develop breeding strategies	04/01/06	
6	Reports		
6.1	Interim report year 1	04/20/04	Peer-review conducted May 4, 2004, Atlanta, GA
6.2	Interim report year 2	04/20/05	
6.3	Final report	04/20/06	

Budget Data (to date):

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	04/03	04/04	410,532	225,000	635,532	249,593	20,652	270,245
Year 2	04/04	04/05	400,491	225,000	625,491	68,550	623	69,173
Year 3	04/05	04/06	314,387	225,000	539,387	0	0	0
		Totals	1,125,410	675,000	1,800,410	318,143	21,275	339,418

Engineering of Syringyl Lignin in Softwood Species Through Xylem-Specific Expression of Hardwood Syringyl Monolignol Pathway Genes

Joshi: Michigan Technological University, NREL

ID14440, CPS#01870

QUARTERLY PROGRESS REPORT

Project Title: Improved Wood Properties Through Genetic Manipulation: Engineering of Syringyl Lignin in Softwood Species Through Xylem-Specific Expression of Hardwood Syringyl Monolignol Pathway Genes

Covering Period: April 1, 2004 through July 31, 2004

Date of Report: July 29, 2004

Recipient: Michigan Technological University
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Congressional District: MI Ist

Award Number: DE-FC36-03ID14440

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Richard B. Phillips, Senior Vice President-Technology
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(subcontract) Vincent L. Chiang, Forest Biotechnology Group, College of Natural Resources, North Carolina State University, 919-513-0098; vincent_chiang@ncsu.edu

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Project Objective:

Our long-term goal is to genetically engineer higher value raw materials with desirable wood properties to promote energy efficiency, international competitiveness, and environmental responsiveness of the U.S. forest products industry. The immediate goal of this project is to produce the first higher value softwood raw materials engineered with a wide range of syringyl lignin quantities.

Background:

The most important wood property affecting directly the levels of energy, chemical and bleaching requirements for kraft pulp production is lignin. Softwoods contain almost exclusively chemically resistant guaiacyl (G) lignin, whereas hardwoods have more reactive or easily degradable lignins of the guaiacyl (G)-syringyl (S) type. It is also well established that the reactive S lignin component is the key factor that permits much lower effective alkali and temperature, shorter pulping time and less bleaching stages for processing hardwoods than for softwoods. Furthermore, our pulping kinetic study explicitly demonstrated that every increase in one unit of the lignin S/G ratio would roughly double the rate of lignin removal. These are clear evidence that softwoods genetically engineered with S lignin are keys to revolutionizing the energy efficiency and enhancing the environmental performance of this industry.

Softwoods and hardwoods share the same genetic mechanisms for the biosynthesis of G lignin. However, in hardwoods, three additional genes branch out from the G-lignin pathway and become specifically engaged in regulating S lignin biosynthesis. In this proposed research we will simultaneously transfer aspen S-specific genes into a model softwood, black spruce, to engineer S lignin.

Status:

During this reporting period, research has been focused on subjects related to the planned Project Milestone (NCSU Tasks 1, 2, 3, 5 & 6) in the following three areas: (**A**) molecular biology, (**B**) tissue culture and spruce transformation and (**C**) lignin chemical characterization. For Area **A** (molecular biology), which includes NCSU Tasks 1 and 2, we have cloned spruce *CCoAOMT* and *4CL* cDNAs. Based on these cDNA sequences of and genome walking techniques, we have cloned promoters for *CCoAOMT* (~ 1 kb) and *4CL* (~ 0.8 kb) gene. We have also completed the construction of promoter::GUS expression cassettes for *CCoAOMT* and *4CL* promoters, respectively. Currently, the tissue specificity of these promoter sequences is being tested in tobacco. For tissue culture task (Area **B** or NCSU Task 3) we have constructed binary vectors harboring 35S-driven S lignin genes, *CAld5H*, *AldOMT* and *SAD*, which were transferred into spruce. For Area **C**, NCSU Tasks 5 and 6, we have developed a preliminary Near Infrared spectrometry (NIR) based high throughput protocol for determining lignin S/G ratio.

(A) Molecular Biology (NCSU Tasks 1 and 2): Characterization of spruce xylem specific promoter

Analysis of *4CL* and *CCoAOMT* gene promoter sequences

Based on the *4CL* and *CCoAOMT* cDNA sequences, we have cloned their cognate gene sequences including their promoter region. Sequence analysis showed that the final spruce *4CL* gene promoter fragment (pm4CL) is 751bp in length, containing 146bp UTR. The spruce *CCoAOMT* gene promoter fragment (pmCCoAOMT) is 954bp long, containing 88bp UTR and 198bp first intron region.

The two promoter sequences were analyzed by comparing with loblolly pine xylem-specific *4CL* and *CCoAOMT* promoter sequences. By using Blast engine in NCBI, common sequences have been found between cloned spruce promoter and loblolly pine xylem specific promoter. These analyses indicated that cloned pm4CL and pmCCoAOMT promoters are likely xylem specific.

Promoter–GUS fusion analysis of promoter activity in tobacco

To further confirm the xylem specific of the cloned promoters, binary vector of promoter::GUS expression constructs were made for pm4CL and pmCCoAOMT, as depicted in Fig. 1.

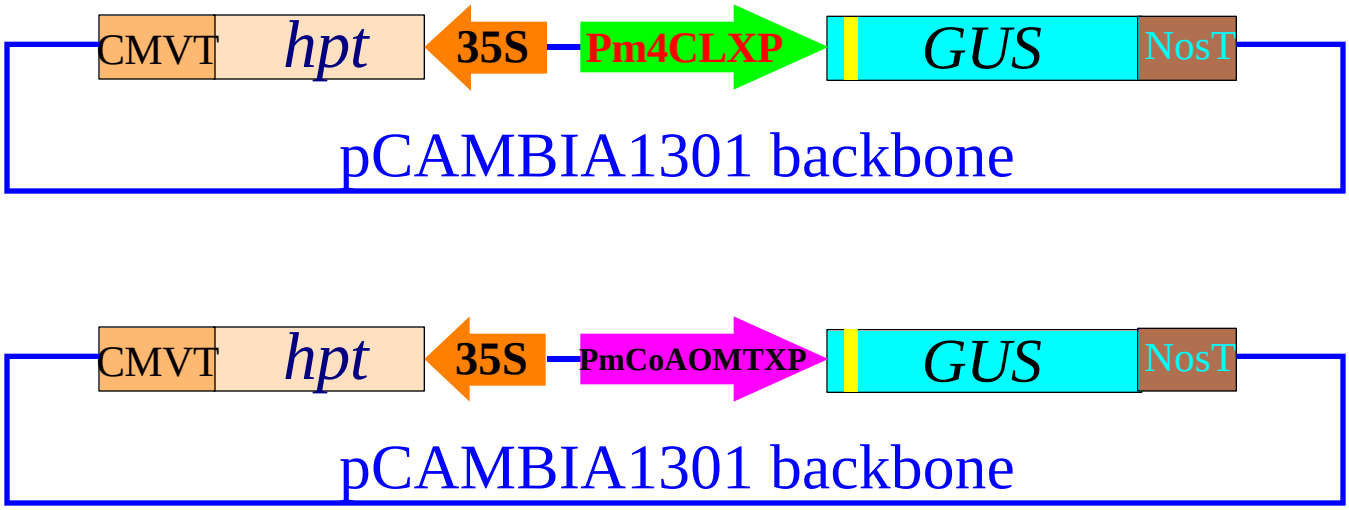


Figure 1. Binary vectors (pCAMBIA1301) for GUS expression under the control of spruce *4CL* (pm4CLXP, upper construct) and of *CCoAOMT* (pmCoAOMTXP) promoters.

Currently, these constructs have been transferred into tobacco via *Agrobacterim.* We have so far regenerated about 10 transgenic tobacco for pm4CL promoter construct and about 25 for pmCCoAOMT promoter construct. These transgenic plants have been maintained in our greenhouse and will be characterized for their GUS expression as the major tasks for the next reporting period.

Aspen syringyl lignin gene expression constructs

Binary vectors harboring aspen S lignin genes, *CAld5H*, *AldOMT* and *SAD*, under the control of double 35S promoter were constructed (Fig. 2) and are ready to be transferred into spruce.

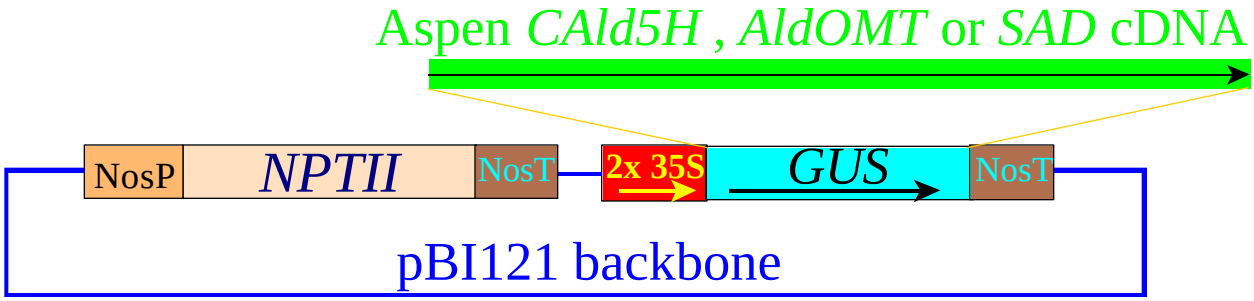


Figure 2. Binary vectors (pBI121) for expressing syringyl lignin genes under the control of double 35S promoter.

(B) Tissue culture and spruce transformation (NCSU Task 3):

Using our developed multiple gene transfer technique, the three S lignin gene constructs (Fig. 2) will be simultaneously transferred into spruce based on our spruce gene transfer protocols. Based on our experience, a high efficient transformation rate depends to a large extent on the callus conditions; rejuvenated and fresh callus always provides the best results. Therefore, we are now in the process of proliferating fresh callus as the explant materials, to which the 3 S lignin gene constructs will be transferred.

(C) Lignin chemical characterization

To determine lignin S/G ratio using NIR as a high throughput approach, we first determined the appropriate region in a regression NIR spectrum to be used. To do so we compared the NIR spectra of aspen and pine wood to identify peaks that are unique only to aspen wood because of the presence of syringyl lignin.

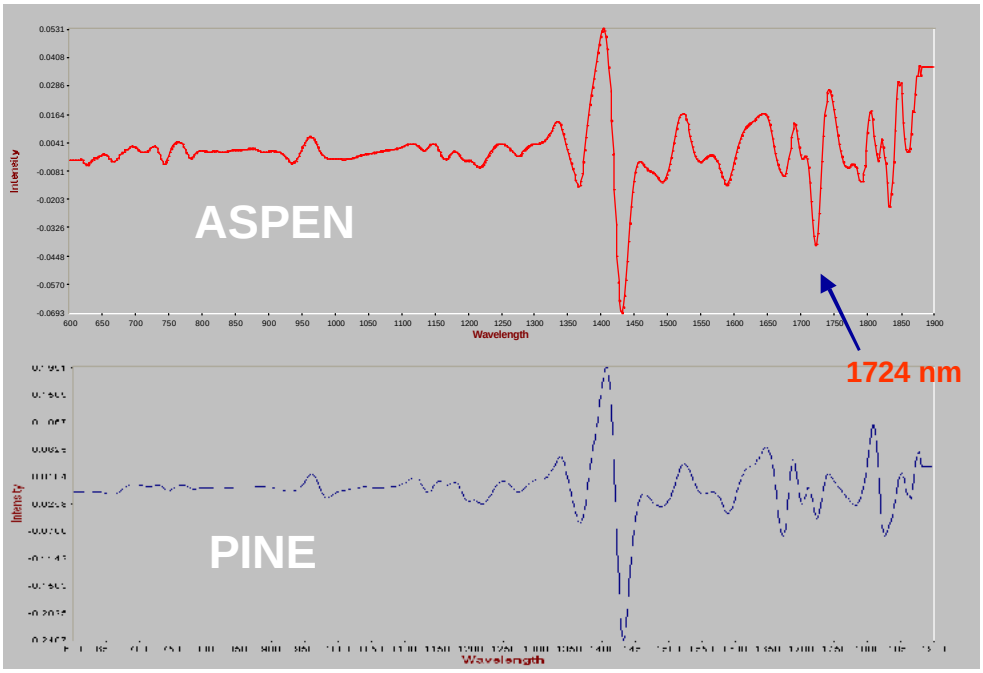


Figure 3. NIR spectra of aspen and pine wood.

As shown in Fig. 3, a unique NIR band at 1724 nm was found for aspen, which was absent from pine spectrum. Likely, this 1724 nm band is due to the presence of syringyl units providing a much stronger methoxyl signal. Therefore, the spectrum including this unique 1724 nm band was used to make lignin S/G ratio calibration line to estimate S/G ratio based on NIR data.

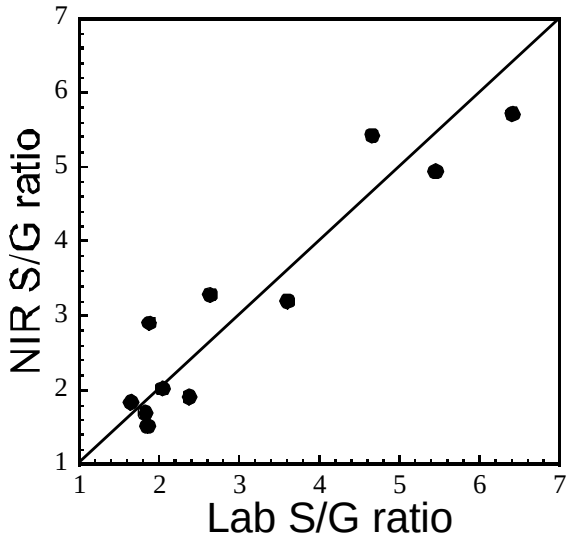


Figure 4. Correlation between lab S/G ratio (by thioacidolysis) and NIR S/G ratio. Y = 0.8796 X + 0.3766; R^2 = 0.8796; SEC = 0.69.

Using NIR we measured lignin S/G ratios for various transgenic aspen having a wide range of S/G ratio based on the quantitative thioacidolysis protocol. As shown in Fig. 4, a fairly good correlation existed between these lab S/G ratios and the S/G ratios obtained by NIR method. The correlation became greatly improved for samples with a similar lignin content (Fig. 5).

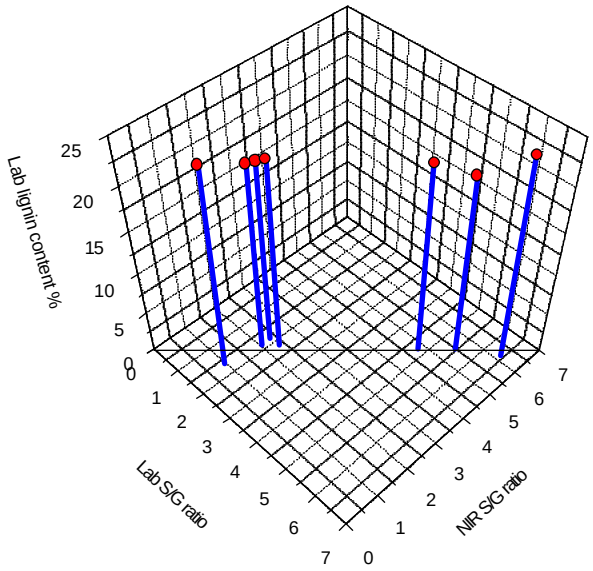


Figure 5. Correlation between lab S/G ratio (by thioacidolysis) and NIR S/G ratio for samples with a similar lignin content. Y = 0.9649 X + 0.1212, R^2 = 0.9649, SEC = 0.54.

This calibration curve should be adequate for testing the transgenic spruce trees with altered lignin S/G ratios and with lignin contents remain unchanged. However, we would like to establish a more universal calibration curve that would also applicable tree samples with a wide range of lignin content as well as a broad range of lignin S/G ratio. This will be one of the major tasks during the next reporting period.

Plans for Next Quarter

In the next reporting period, we will focus on the characterization of GUS expression in the 10 transgenic tobacco harboring the pm4CL promoter construct and in the 25 transgenic tobacco containing the pmCCoAOMT promoter construct. Once confirmed for their xylem-specific activity, *4CL* or *CCoAOMT* promoter fragments will be used to prepare xylem promoter driven S lignin gene expression constructs. At the same time we will simultaneously transform fresh spruce embryonic callus with the three 35S promoter driven S lignin gene expression constructs. For cell wall chemistry tasks, we will conduct further lignin structure analyses focusing on the methoxyl content using either wet chemistry or NMR. The purpose is to establish a more universal calibration curve for the analysis of lignin S/G ratios in a high throughput manner.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Comments
NCSU Task 1	Cloning of spruce xylem-specific promoter	6/1/04	Complete
NCSU Task 2	Preparation of aspen *CAld5H*, *AldOMT* and *SAD* gene expression constructs and *Agrobacterium* strains	8/1/04	35S promoter constructs have been complete
NCSU Task 3	Transformation of black spruce with aspen *CAld5H*, *AldOMT* and *SAD* gene expression constructs via *Agrobacterium*-mediated multigene transfer and regeneration and propagation of transgenics	6/1/06	In progress & on schedule
NCSU Task 4	Molecular genetic and biochemical characterization of transgenic black spruce trees	6/1/06	
NCSU Task 5	S/G protocol establishment	6/1/05	Basic calibration curve complete
NCSU Task 6	Characterization of lignin and cellulose contents, S/G ratio, and fiber morphology	6/1/06	In progress & on schedule
NREL Task	Py-MBMS quantification of the S/G ratios and other lignin structural details for the finalist transgenic spruce	6/1/06	
	Final Report	7/1/06	

Patents: None

Publications/Presentations: None

Budget Data (as of date): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total*
	From	To						
Year 1	4/23/03	4/22/04	$616,154	$159,062	$775,216	$241,582	$ 63,640	$305,222
Year 2	4/23/04	4/22/05	$370,599	$145,562	$516,161	$45,096	$70,003	$115,099
Year 3	4/23/05	4/22/06	$434,089	$145,563	$579,652			
		Totals	$1,420,842	$450,187	$1,871,021			

* The total does not yet include $243,610 for the equipment purchase recently complete.

Increasing Yield and Quality of Low-Temperature, Low-Alkali Kraft Cooks with Microwave Pretreatment

Compere: Oak Ridge National Laboratory

CPS#01164

QUARTERLY PROGRESS REPORT

Project Title: Increasing Yield and Quality of Low-Temperature, Low-Alkali Kraft Cooks with Microwave Pretreatment

Covering Period: April 1, 2004 through June 30, 2004

Date of Report: August 9, 2004

Recipient: Oak Ridge National Laboratory (ORNL), operated by UT-Battelle
P. O. Box 2008
Oak Ridge TN 37831-6150

Award Number: DE-AC05-00OR22725

Subcontractors: H. Jameel, North Carolina State University (NCSU)
A. L. Fricke, Emeritus Professor, University of Florida

Other Partners: D. Parent, Communications and Power Industries

T. L. White, W. L. Gardner, and W. L. Griffith, ORNL

G. Marrs, Weyerhaeuser

Contact(s): A. L. Compere (865-574-4970) compereal@ornl.gov

Project Team: Dickson Ozokwelu, DOE program manager, AF&PA program managers; and Energy Task Group (mentors)

Project Objective: The project goal is development of a predictive understanding of the effect of different microwave pretreatment parameters, including frequency, application pattern, and wood shape (logs or chips) and water content, on yield and quality of Kraft pulp produced using low-temperature or low-cooking-chemical digestion regimes. In addition to yield evaluation of Kraft pulps, pulp bleachability and handsheet quality (brightness, strength, freeness) will be evaluated for selected processing conditions. The ultimate project goal is development of proof-of-concept demonstration of a microwave/RF pretreatment process which could: 1) increase the yield of Kraft pulps, 2) decrease the cooking chemicals and cooking temperature required for production of a given quality pulp, 3) increase Tomlinson boiler throughput, or 4) decrease lime kiln energy usage.

Background: This project started six years ago as a two-year study supported by ORNL in-house funding to determine whether it was possible to develop “green chemistry” pulping technology. The project approach was to change the structure of wood to facilitate penetration

of cooking chemicals. Pulping studies to evaluate the effect of pretreatment on ORNL hardwood coppice were performed by Thomas Joyce of North Carolina State University through his small business, and Beloit and Bechtel staff provided advice on pulping technologies.

Initial proof-of-concept experiments were performed on small sections of wood (~200 g) in a small microwave unit, and later experiments evaluated pulp quality and yield of sycamore sections up to 3.75 inches in diameter treated with a high power microwave. The data consistently showed increased yield and lower Kappa number at conventional Kraft pulping conditions. Tom Joyce also found that a substantially smaller amount of cooking chemicals were required to achieve equivalent pulp quality. Bleaching and handsheet tests indicated that samples from pretreated wood were slightly brighter and slightly stronger than control samples. However, these proof-of-concept tests did not systematically evaluate processing schemes such as low-temperature or low-chemical cooks, which could minimize process energy and material requirements. Additionally, these tests did not systematically evaluate the effect of pretreatment on softwoods or address the ability to process chips. Both of the factors are critical to adoption of this process technology by the pulping industry.

Status: In the previous quarter, progress was made in three different areas: econometric analysis, larger pulp cooks, and evaluation of enzyme and surfactant treated chips. The econometric analyses were extended to cover mill costs where microwave pretreatment is used to extend mill capacity.

Microwave pretreatment permits significant decreases in inorganic chemical use and H-factor, which is a measure of process energy, to process the same type and grade of pulp. Together, these could significantly increase the amount of pulp which can be processed by a given mill because of decreases in recovery boiler load and in process temperature / time. These factors could be particularly useful in improving the production capacity of installed or older mills. Professor Arthur Fricke evaluated the decreases in batch digestion time facilitated by lower H-factor and changes in yield for bleachable softwood and hardwood chips, as well as linerboard. These were used to evaluate changes in economics and capacity of nominal 1000 air-dried ton/day mills which used microwave pretreatment as a head-end retrofit technology. A range of electrical costs were used to reflect national conditions. Standard times for loading and unloading operations were used in these studies. No credit for reductions in fines or the ability to use larger chips, which permit a higher packing density and less intensive chipping operations, were taken.

<u>Econometric evaluation of increased mill throughput from microwave pretreatment of chips</u>. Because it permits significant decreases in chemical use and, thereby, in chemical recovery load, microwave pretreatment of chips could find use in extending the working capacity of mills which have process limitations centering in mill chemical processes. This series of studies evaluates the economic consequences in batch mill throughput and/or chemical reduction facilitated by microwave pretreatment for bleachable grade softwoods, linerboard softwoods, and bleachable grade hardwoods.

The assumptions were that the mill staff and overhead were adequate to support the additional throughput possible based on the processing rate increases permitted by decreased H-factor and that the chemical process system would be able to manage the load. This is thought to be reasonable because similar cases evaluated in earlier years involved estimating incremental pulp production based on constant chemical process system loadings. It was also assumed that decreases in pulping chemicals would decrease boiler load. This is likely because inorganic chemicals are often the limiting factor in evaporation due to formation of precipitates. Additionally, experimental measurements of lignin molecular weight indicates it to be comparable for pretreated and control samples. The costing method selected is conservative in that credits for reductions in fines, decreased chipping and screening costs arising from the ability to use larger chips was not taken.

This series of cases evaluates the direct increases in batch mill throughput possible with microwave pretreatment using a nominal 1000 air dried tons/day (ADT)/day Kraft mill. The calculations are detailed in the paper referenced under, “Publications,” below.

For bleachable hardwood and using an electrical cost of $0.039/kWh, the mill variable cost savings per ton were calculated to be $14.30/ADT, while mill related cost savings (wood, operations, depreciation, microwave depreciation, etc.) were calculated to be $24.95. Together, these amount to ~ $39/ADT.

For bleachable softwood and using an electrical cost of $0.039/kWh, the additional mill variable costs per ton were calculated to be $1.18/ADT, while mill related cost savings (wood, operations, depreciation, microwave depreciation, etc.) were calculated to be $36.15. Together, these amount to ~ $35/ADT.

For softwood linerboard and using an electrical cost of $0.039/kWh, the mill variable cost savings per ton were calculated to be $6.30/ADT, while mill related cost savings (wood, operations, depreciation, microwave depreciation, etc.) were calculated to be $8.75/ADT. Together, the relative cost savings amount to ~ $15/ADT.

Larger pulp cooks. These tests were initiated to provide materials for larger handsheet tests at the end of the summer. Using the wide range of equipment available at NCSU, several different types of pulping and sizes of digester can be evaluated.

Enzyme and surfactant incorporation into chips. Microwave pretreatment permits the incorporation of a variety of different chemical modifiers into the wood prior to pulping. The initial tests indicated that surfactant or enzyme treated softwood chips could be readily pulped with no major difficulties and that the use of either enzyme or surfactant treatment decreased rejects slightly.

During this quarter, a variety of different studies were initiated and are continuing. Samples to complete a series of larger Kraft cooks have been prepared and are in progress. These are needed to support larger handsheet preparation and properties tests later in the summer. The

data from larger scale cooks is comparable to the data from the smaller cooks performed earlier.

After discussions with the industrial review committee and with Arthur Fricke, we changed the plan for the debarking experiment and will completed it shortly. Fricke's subcontract was extended to cover these studies.

We are also working with Art Fricke to plan some short tests to better evaluate the effects of microwave pretreatment on mill chemical recycle, including any increases in non-process elements which could be caused by the processing of larger amounts of wood and pulp, relative to process chemicals. The element of most concern is potassium, a cell constituent which can increase with increasing mill throughput.

We also prepared and are evaluating a series of sulfur-free softwood cooks. These will permit us to extend our process database significantly and will improve our ability to map data onto a larger response surface. In practical terms, this is a step toward creating a large enough database to permit use of industrial process modeling systems, such as GEMS or ASPEN, which require a large sample base to support calculations.

Plans for Next Quarter: Studies to evaluate the effect of microwave pretreatment on wood yield after debarking are in progress. A series of pulp cooks at progressively increasing sizes are planned to improve understanding of process scale up.

Patents: None.

Publications/Presentations: A paper, "Microwave pretreatment to decrease pulping energy and chemicals," was presented at the TAPPI 2004 Spring Technical Conference and Environmental Conference, May 2-5, and include in the conference proceedings. The paper formed part of the project annual industrial review.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1.1	Complete preliminary small digester experiments evaluating low-temperature and low-cooking-chemicals pulping	10/31/2001	11/02/2001	Presented as TAPPI Pulping Conference paper
1.2	Complete draft preconceptual design report	10/31/2001	09/30/2001	
1.3	Initiate softwood studies	09/30/2002	09/30/2002	
1.4	Larger cooks and papermaking evaluations	09/30/2002	09/30/2002	
2.1	Pretreatment tests of logs	03/31/2003	03/31/2003	
2.2	Complete initial handsheet and bleaching tests	09/30/2003	09/30/2003	
2.3	Initiate large cooks to prepare enough pulp for evaluation	12/31/2003	03/15/04	Funding received late, equipment problems.
2.4	Complete tests evaluating bark separation from wood	06/30/2004		Funding received late
2.5	Handsheet and bleaching tests	09/30/2004		
2.6	Softwood and hardwood cooks with larger test facility (TBD)	2005		

Budget Data (as of June 27):

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	10/99	9/00	200000	108000	308000	68391	108000	176391
Year 2	10/00	9/01	350000	108000	458000	251715	108000	359715
Year 3[a]	10/01	9/02	350000	108000	458000	279120	108000	387120
Year 4[a]	10/02	9/03	372000	122200	494200	238722	122200	360922
Year 5	10/03	9/04	395000	134200	529200	148979	100500	249479
Year 6	10/04	9/05	421000	104200	525200			
		Totals	2088000	684600	2772600	986927	546700	1533627

[a]Only $250,000 in DOE funding was received during FY.

Novel Pulping Technology: Directed Green Liquor Utilization (D-GLU) Pulping

Lucia: Institute of Paper Science and Technology

GO10626, CPS#01483

DOE QUARTERLY PROGRESS REPORT

For:	**NOVEL PULPING TECHNOLOGY: DIRECTED GREEN LIQUOR UTILIZATION (D-GLU) PULPING**
Covering Period:	May 1, 2003 to July 30, 2004
Date of Report:	July 28, 2004
Recipient:	Georgia Institute of Technology
Award Number:	**DE-FC36-01GO10626**
Subcontractors: (if any)	
Other Partners:	
GL&V-Impco-Jones 150 Burke Street Nashua, NH 03060 NH 2nd	Georgia-Pacific Corporation 133 Peachtree St., NE Atlanta, Georgia 30303 GA 5th
Ahlstrom Machinery Inc. 101 Ridge Street Glen Falls, NY 12801 NY 22nd	
Contact:	
Principal Investigator:	Lucian A. Lucia
	Georgia Institute of Technology; transferred to North Carolina State University tentatively at end of year
	500 Tenth Street, N.W.
	Atlanta, Georgia 30332-0620
Tel./Fax	404-894-9712 (Office)/404-894-4778 (Fax) 919-515-7707 (Office as of 8/1/04/919-515-6302 Fax as of 8/1/04)
E-mail:	lucian.lucia@ipst.gatech.edu lucian.lucia@ncsu.edu (as of 8/1/04)

Project Team:

Weiping Ban, Mark Turner

Project Objectives:

1. Identification of the viability of normal green liquor (GL) application to North American SW and HW chips.
2. Identifying the optimal addition level and the best pulping conditions that support enhanced pulp strength.

3. Performing an oxygen delignification and subsequent typical bleaching study of the pulps.
4. Use the experimental data to evaluate overall economics at a selected mill.
5. NEW (over next two years): The selected mill will implement the technology with the proper resources.

BACKGROUND

This work is going well, and is scheduled to coordinate a mill trial with the newest funding it has received from DOE (2005 – 2008).

The presentation of our work to the 2004 Paper Summit and Spring Technical Conference in Atlanta, GA garnered good support from industry representatives, government officials, and the general academic community.

STATUS

GL pretreatment has been shown to improve the efficiency of chemical performance for delignification. First, chemical consumption is well matched with lignin dissolution in each pulping stage, in which they mainly contribute to delignification; further, the function of hydrosulfide toward delignification is enhanced through GL pretreatment. A higher consumption ratio of hydrosulfide to hydroxide in the bulk phase pulping period correlates with a higher delignification rate. A linear relationship was shown to exist between lignin removal and hydrosulfide.

Delignification kinetics for GL-modified kraft pulping may also be modeled as a first-order process that includes three successive phases. Compared to conventional kraft pulping, the GL pretreatment pulping process has a higher delignification rate. The process accelerates the bulk delignification by 20 minutes and takes a shorter time for each consecutive stage. It is possible to reduce the whole pulping process by 30 minutes or longer. The average delignification rate may also be increased by as much as 30% compared to the kraft cook control.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
10626	Novel Pulping Technology: Directed Green Liquor Utilization (D-GLU) Pulping (1483) IPST, Lucia, PI	From 10/1/00 To 10/1/04		As of 7/30/04
	Year 1			
1.0	Literature Review	11/1/00	2/1/01	A review paper will be published soon.
1.1	Collect selected SW and HW chip samples from partner mills.	12/1/00	3/1/01	Have begun to use Northern HW; have been using Southern loblolly pine and Northern black spruce.
1.2	Evaluation of the value and proof of principle of this pulping technology for US hardwood and softwood furnishes.	4/1/01	6/1/01	4 research papers on the value and proof of principle have been written and submitted for publication; TAPPI presentation in this area will be delivered to North American personnel during 2002.
1.3	Characterize pulp products with respect to type of furnish and native lignin and carbohydrate content and subsequent structural changes as a function of cooking conditions and green liquor charge.	9/1/01	9/1/03	
1.4	Establish correlations between cooking conditions, structural changes, and preliminary pulp properties-Collect selected SW and HW chip samples from partner mills.	3/1/02	10/31/01	4 research papers on the value and proof of principle have been written and submitted for publication.
	Year 2			
2.1	Rationale for GL pretreatment with respect to preliminary pulp qualities and strength properties.	5/1/02	7/1/02	2 papers will be available regarding this work.
2.1.1	Analysis of sulfide absorption during pretreatment.	3/1/01	4/26/02	2 more research papers will be available from this work in the next several months
2.1.2	Establish mathematical mould using central composite experimental design.	5/1/02	6/1/02	2 papers have been submitted.
2.1.3	Rationale for GL pretreatment and cooking process.	5/1/02	1/1/04	
2.2	Determine optimal methods to increase yield of pulp based on previous results.	8/1/02	9/1/02	1 paper
2.2.1	Finalized investigation of economic additive to improve GL pretreatment pulping.	3/1/02	10/1/02	Prospect for patentable invention being explored; in process of invention disclosure.
2.2.2	Optimize the GL pretreatment process with respect to yield and strength.	6/1/02	6/30/02	2 research papers.
2.3	Complete characterization of GL modified pulp with respect to lignin structural changes and pulp quality.	6/1/02	6/1/04	1 research paper
2.3.1	NMR analysis for GL pulp.	3/1/02	1/1/04	1 research paper
2.3.2	Correlate oxygen delignification with residual.	6/1/02	1/1/04	
2.4	Provide fundamental analysis of pulping catalyst mechanisms	10/1/02		On-going; completed in newest award from DOE
2.4.1	Discuss potential mill trials with Georgia Pacific or suitable mill sponsor	9/1/02	3/1/04	Mill trial to be done at Samoa, CA
2.4.2	Develop WIN GEMS analysis of implementation at mill	9/1/02	12/31/02	
2.4.3	Specific economic simulations given mill schematics	11/1/02	1/31/03	Conference proceeding
2.4.4	OLI modeling of evaporator fouling	12/01/02		To be done in newest award
3.1	Complete characterization of GL modified pulp with respect to lignin structural changes and pulp quality	9/1/03	1/1/04	
3.1.1	IEC,NMR analysis for GL pulp.	6/1/04	4/1/04	
3.1.2	Correlate oxygen delignification with residual.	9/1/04		
3.1.3	Rational for GL modified pulping	2/1/04		
3.2	Provide fundamental analysis of pulping catalyst mechanisms	3/1/04		

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
10626	Novel Pulping Technology: Directed Green Liquor Utilization (D-GLU) Pulping (1483) IPST, Lucia, PI	From 10/1/00 To 10/1/04		As of 7/30/04
3.2.2	Develop WIN GEMS analysis of implementation at mill	3/1/04	1/30/04	
3.2.3	Specific economic simulations given mill schematics	3/1/04	1/30/04	
3.2.4	OLI modeling of evaporator fouling	5/1/04	5/1/04	
3.3	Final report and conclusion of project	10/1/04		

*The project was initially delayed by 3 months due to budgetary allocations and arrival of principal research scientist.

High Selectivity Oxygen Delignification

Ragauskas: Institute of Paper Science and Technology

ID13870, CPS#01153

QUARTERLY PROGRESS REPORT

Project Title: High Selectivity Oxygen Delignification

Covering Period: April 1 – June 30, 2004

Date of Report: July 31, 2004

Recipient: Institute of Paper Science and Technology
500 10th St., NW, Atlanta, GA 30318

Award Number: DE-FC07-00ID13870

Subcontractors: Hasan Jameel, North Carolina State University

Contact(s): Arthur J. Ragauskas, 404-894-970, Arthur.ragauskas@ipst.edu

Project Team: AF&PA Agenda 2020 Environmental Performance Task Group, United States Department of Energy, Elmer H. Fleischman//INEEL/US

Project Objective: The overall objective of this program is to develop improved extended oxygen delignification (EOD) technologies for current U.S. pulp mill operations. This will be accomplished by:

- Identifying pulping conditions (conventional, extended batch and/or continuous cooking) that optimize O and OO performance;
- Identifying structural features of lignin that enhance reactivity towards EOD of high kappa pulps;
- Identifying factors minimizing carbohydrate degradation and improve pulp strength of EOD high kappa pulps;
- Developing a simple, reproducible method of quantifying yield gains from EOD;
- Developing process conditions that significantly reduce the capital requirements of EOD while optimizing the yield benefits.

Background: Improving the overall economics of pulping and bleaching operations while simultaneously remaining in compliance with this nations environmental regulations is an important goal for the pulp and paper industry. Oxygen delignification is one of the most promising technologies available to achieve this goal. The well known higher selectivity and improved yield preservation for oxygen delignified low kappa pulps in comparison to pulps prepared by kraft cooking is now well established, as shown in Figure 1.

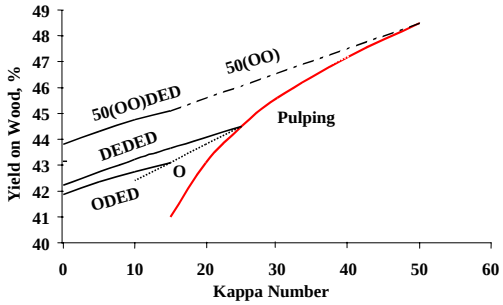
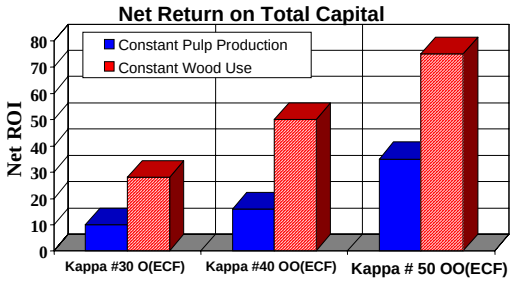


Figure 1: Yield kappa number relationship.



Note : reference is kappa # 20 bleached D(EOP)DE(EP)D:ECF

Figure 2: Projected cost benefits of EOD.

Recently, extended oxygen delignification processes have been developed that improve the typical delignification effects of an O-stage from approximately 50% to 70%. The use of 2-stage oxygen delignification in which the first stage temperature (80°-90°C) is lower than the second stage (105°-120°C) was shown to improve the overall selectivity and reduce alkali requirements. Mill results from 2-stage oxygen delignification have demonstrated the potential of this technology. Interestingly, it appears that EOD operates best when the temperature of the first stage is relatively low (ca. 85°C) with a high charge of alkali and oxygen applied. The second O stage then functions principally as a high temperature extraction stage. Following the above principals, the SCA mill in Ostrand, Sweden, employs a two-stage oxygen system to delignify a softwood kraft pulp from kappa # 26 to kappa # 9 with excellent strength properties. The Stora mill, in Skoghall, achieves slightly better results using interstage washing (i.e., OwO) between the two oxygen stages. Lab and mill trials have shown that EOD of high kappa kraft pulp can improve overall pulp yields by 1 to 4%. Economic evaluations of EOD technologies suggest that the payback for this type of process is between 16–26 months (see Fig. 2).

Fundamental studies have shown that oxygen delignification occurs principally by oxidizing free phenolics in lignin. Remarkably, studies by Moe et al., Senior et al., Gellerstedt et al., and others have shown that less than 50% of the phenolic sites of lignin are consumed during an O or OO-stage. These results suggest that the both the O and EOD technologies are operating far from optimal lignin degradation conditions and a tremendous opportunity exists for improving these stages. For conventional SW kraft pulps (kappa # less than 30) recent studies suggest that condensed lignin structures may be resistant to conventional oxygen delignification conditions and furthermore, these unreactive units may be formed during a conventional O-stage. Likewise, hexenuronic acids which contribute between 30–60% of the apparent kappa number for US HW kraft pulps can not be degraded by an O-stage. The removal of these components from conventional kraft pulps can *Not* be achieved using improved mixing or reactor design for an O-stage as their degradation chemistry is not influenced by oxygen mass transfer.

Halting the kraft cook above a kappa number of 20 can minimize the presence of hexenuronic acids in HW kraft pulps. Likewise, the content of condensed lignin structures in kraft pulps can be minimized by halting the cook at high kappa numbers (i.e., ca for HW>20; for SW> 35). These target kappa numbers should be ideal for the development of EOD technologies. This program will identify the optimal kraft cooking conditions for EOD and determine how the formation of condensed phenolics can be minimized during an O-stage.

Our knowledge of the fundamental processes contributing to the degradation of carbohydrates and how to minimize these reactions is even less understood. It is generally believed, that some oxygen – metal species is involved in degrading the carbohydrates in pulp during an O-stage although the exact mechanism and how this impacts strength properties is not known. The addition of $MgSO_4$ to an O-stage is believed to protect pulp carbohydrates during an O-stage but mill experiences vary widely with this additive.

In addition, the limitations of oxygen mass-transfer for EOD of high kappa pulps has not been fully studied nor optimized. This program will determine what the effects of mixing on the EOD process are so as to maximize lignin degradation and minimize carbohydrate degradation.

The development of an improved EOD system for high-kappa pulps will also require new, mill applicable, testing methods that provide for rapid determination of pulp yields so that mill operators will able to efficiently operate new EOD technologies. The investigators propose to develop a statistically valid EOD yield test method based to the physical properties of the pulps. Pulp properties to be correlated to yield will include α-cellulose content, total carbohydrate composition, and fiber coarseness.

In summary, future advances in EOD of high kappa pulps for improved yield capabilities will require an increased understanding of:

- How pulping influences the bleachability of an O or OO-stage;
- The selectivity of EOD of high lignin content pulps as a function of NaOH charge, O_2 – concentration, temperature, mixing, and additives (*i.e.*, role of $MgSO_4$);
- The factors controlling lignin, hemicellulose, and cellulose degradation during EOD;
- Development of a simple yield test designed for mill applications of EOD technology.

Status: Research Results Over Last Quarter

Research Highlights:

Several key outcomes from this past quarter's research efforts include:

- Research efforts are directed at completing the remaining deliverables and summarizing the outstanding experimental results for the final report.
- Experimental studies demonstrating the potential of oxygen delignification to modifying fiber charge has been summarized and will be presented an an upcoming TAPPI conference.

Research Details from Past Fiscal Quarter

Fiber charge of chemical pulps has been shown to be an important chemical parameter that influences the behavior of fibers in pulping, papermaking and the physical properties of paper products. As reported ((Scallan and Grignon 1979; Lindstrom and Carlsson 1982; Swerin, Odberg et al. 1990; Lindstrom 1992; Barzyk, 1997), the negative groups strongly affect the binding of metal ions to pulps, the swelling of fibers, water removal during wet press, the rate of beating, the adsorption of retention aids, and the strength and optical properties of the resultant papersheets. Carboxylic acid groups in cellulosic fibers are the main functional group responsible for surface and bulk charge of kraft pulps.

In light of these benefits, several different fiber modification technologies are being pursued to introduce carboxylic acid groups into fibers including carboxylmethylation, grafted polymerization, and chemical adsorption/precipitation (Barzyk, Page et al. 1997; Barzyk, Page et al. 1997; Barzyk, Ragauskas et al. 1997; Gellerstedt and Gatenholm 1999; Fors 2000; Laine, Lindstrom et al. 2001; Laine, Lindstrom et al. 2002; Chandra, Felby et al. 2004; Vander Wielen and Ragauskas 2004).

It is known that acidic groups can be introduced into fibers during chemical pulping and bleaching process (Sjostrom 1993). The amount and types of these acidic groups will change dependent upon the exact process conditions and chemical reagents employed. Recent studies suggest that oxygen delignification is a promising practical technology that introduces carboxylic acid groups into fibers and can beneficially impact fiber strength, fiber bonding, and fiber charge (Jiang, Genco et al. 1989; Snowman, Genco et al. 1996). The kinetic changes in fiber charge and its distribution between lignin and polysaccharides during oxygen delignification remain ill-defined and require further investigation. This study addresses these issues by characterizing the changes in acid group content for a softwood kraft pulp during oxygen delignification and clearly assigns how much of this charge resides with the lignin and carbohydrate components of oxygen delignified kraft pulps.

Experimental

Materials

All bleaching studies employed a commercial southern kraft pulp which was extensively washed and screened before use. Table 1 summarizes the chemical properties of this brownstock

Table 1. SW Kraft brownstock pulp properties

Kappa No.	Viscosity , mPa.s	Major transition metals, ppm				Sugar analysis,%				
29.6	24.6	Mn	Mg	Cu	Fe	Arab.	Gal.	Glu.	Xyl.	Man.
		44.7	473.9	9.2	21.8	0.71	0.44	77.48	12.65	8.73

All other chemicals and solvent were commercially purchased and used as received with the excerption of 1, 4-dioxane which was freshly distilled over $NaBH_4$ prior to use.

Oxygen delignification

All one stage oxygen delignification experiments were conducted in a 1 liter inclined rotary stirred par reactor filled with 30.00 O.D. grams pulp at 10% consistency. The $MgSO_4$ was

charged so that the molar ratio of Mg/Mn in the pulp was kept at 30-33 mol/mol to offset the detrimental effects of Mn^{2+} (Liden and Ohman 1997). The other varied experimental parameters include: 1.5-3.5% NaOH, 85-115˚C, 640-960 kPa oxygen, and 10-80 minutes of reaction time. The oxygen delignified pulps were washed and air dried or stored at 2 ^{o}C prior to analysis.

Holocellulose

The oxygen delignified pulp was holocellulose pulped following the procedure as follows. In brief, pulp samples (2.00 g) were dispersed into 75.00 ml deionized water, and treated with 0.50 ml glacial acetic acid, 0.60 g of $NaClO_2$. The resulting mixture was warmed to 75 ^{o}C. After stirring for 1 hour, additional glacial acetic acid (0.50 ml) and $NaClO_2$ (0.60 g) were added and the reaction was continued for another 1 hour. This process was repeated for a total 3 hours. The treated pulp was then cooled to 0 ^{o}C, filtrated, washed using deionized water and air dried for further determination.

Methods

Metal ion concentration Pulp samples were analyzed using Inductively Coupled Plasma Emission Spectroscopy following literature methods (Allison, Ragauskas et al. 2000).

Sugar analysis was determined using high performance anion exchange chromatography (H.P.A.E.C.) based on the method description in Tappi T-249 and utilized by Pronto (1998).

Bulk pulp acidic group content was determined based on the method developed by Chai *et al* using Head Space gas Chromatography (HSGC) (Chai, Hou et al. 2003). About 0.15 g air dried pulp was treated with 50.00 ml 0.1N HCl solution for 60 minutes under magnetic stirring. The treated pulp was then washed with 1.50 L deionized water until the filtrate was neutral. Air dried pulp (0.0500 g) was added to a 20.00 ml head space vial. The pulp was then treated with 4.00 ml of a reference solution consisting of 0.0025 M Na_2HCO_3 and 0.11 M NaCl. This mixture was immediately sealed and allowed to react for 10 min. HSGC was then employed to determine the amount of CO_2 peak generated. The acid group content was calculated based on the following equation:

$$R-COOH\,(\mu mol/g) = \frac{A_{CO_2} - A_{blank}}{f \times W} \times 1000$$

Where

A_{CO_2} = measured GC peak area for CO_2

A_{blank} = measured GC peak area for control

f = calibration constants and can be obtained through calibration

W = oven dry weight of pulp simple, g

Hexenuronic acid pulp analysis A sample of air dried pulp (~0.0500 g) was placed in a 20 ml vial and treated with 10.00 ml of an aqueous hydrolysis solution (0.60% $HgCl_2$ + 0.70% NaAc). The septum sealed vial was shaken for 5 minutes and then immersed in a heated water bath at 70ºC for 30 minutes. The hydrolysis solution was extracted, filtered, and cooled to room temperature. It was then analyzed by UV/Vis at the wavelengths of 260 and 290 nm. Determination of hexenuronic acid content in the pulp was calculated in terms of the following equation (Chai, Zhu et al. 1999).

$$HexA(\mu mol/g) = 0.287 \times \frac{(A_{260} - 1.2 \times A_{290}) \times 10}{W}$$

Where A_{260}/A_{290} = UV Adsorption at 260/290 nm; W = oven dry weight of sample, g

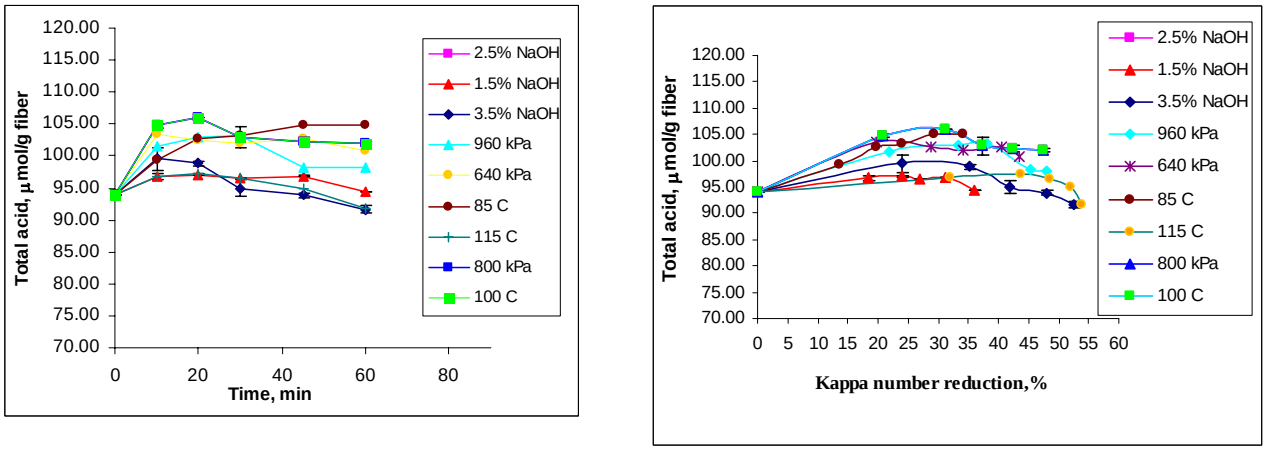
Residual lignin isolation Residual lignin was isolated from pulp by employing a mild acid hydrolysis procedure that had been described in the literature (Froass, Ragauskas et al. 1998).

Pulp properties: Tappi standard methods were used to determine Kappa number (T231cm-96 2002)) and tensile strength (T237 1996).

Results and Discussion: Total fiber acid group development

Recent literature reports indicate that oxygen delignification can enhance or slightly diminish fiber acid group content for the softwood kraft pulps (Laine 1997; Toven 2002). To determine how process parameters influence acid group formation a series of oxygen delignification experiments were conducted varying reaction time, oxygen pressure, caustic charge, and temperature (see Figure 1). From Figure 1a, an initial 3-13% rise in acid groups is observed for the first 10 minute of the reaction, with a fiber charge maximum usually observed after 20 minutes of reaction. After 20 minutes, fiber charge was found to either remain constant or begin to decrease depending on the process conditions. These varied results could be ascribed to the fiber chemical composition and different reactions with oxygen species under alkaline conditions.

As shown in Figure 1b, a plot of total acid content over Kappa number reduction indicates that total pulp acid group content is maximized when the pulps exhibit 25-35% kappa number reduction.



(a) (b)

Figure 1. Total acid content change during one stage oxygen delignification

Conditions: 1. Varied NaOH: 1.5, 2.5, 3.5%; temperature: 100 ˚C; O_2 pressure: 800 kPa
2. Varied temperature: 85, 100, 115 ˚C; NaOH: 2.5%; O_2 pressure: 800 kPa
3. Varied O_2 pressure: 640, 800, 960 kPa; NaOH: 2.5%; temperature: 100 ˚C

In general, the major source of total acid in oxygen delignified pulp is from residual lignin, HexA and other aldonic acids in carbohydrate, *i.e.*,
$A_{Total} = A_{Carb.} + A_{Lignin} + A_{HexA} + A_{others}$

Where A_{Total} = Total acid group content, μmol/g fiber ; A_{Lignin} = Acid group content in residual lignin, μmol/g fiber [A_{Lignin} = acid concentration (μmol/g lignin amount of residual lignin (% on fiber)]; A_{HexA} = Hexenuronic acid content, μmol/g fiber; $A_{Carb.}$ = acid group content in carbohydrate not including HexA, μmol/g fiber [$A_{Carb.}$ = acid concentration (μmol/g carbohydrate× amount of carbohydrate (% on fiber)]; A_{others} = acid group content from other compounds, mainly extractives. For oxygen delignified pulps, they are eligible.

As reported, HexA content does not change during oxygen delignification (Dahlman, Jacobs et al. 1999; Toven 2002), which is also shown in Figure 2 and the HexA content in oxygen delignified pulps is stable at around 28 umol/g fiber. From Figure 1a, the total acid group content in the same oxygen delignified pulps ranges from 94 to 106 μmol/g fiber. Among them, 26-30% is contributed by HexA. However, hexenuronic acids will be oxidatively removed with electrophilic bleaching chemicals such as ClO_2 and O_3 (Laine 1997). Therefore, these units will not significantly contribute to the final fiber charge of ECF or TCF bleached pulps.
Figure 2 also shows that HexA contents drop to 1.5-3.5 μmol/g holocellulose (equivalent to 1.7-3.7 μmol/g fiber for oxygen delignified pulps studied) due to the mild ClO_2 treatment from holocellulose preparation.

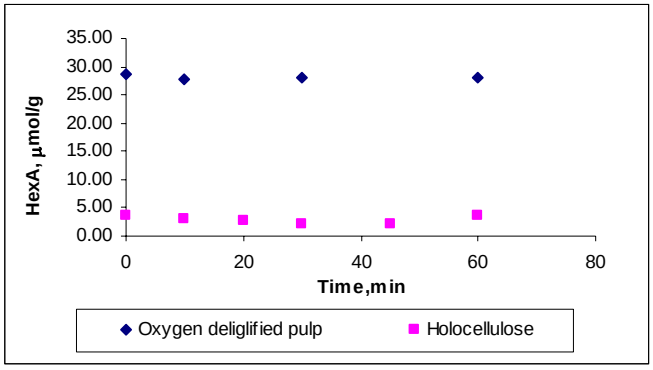


Figure 2. HexA content in oxygen delignified pulp and corresponding holocellulose
Oxygen delignification conditions: NaOH: 2.5%; temperature: 100 ˚C; O_2 pressure: 800 kPa

Since HexA content is unchanged during oxygen delignification, accordingly, the total acid content change in alkaline oxygen delignified pulps should vary mainly with the change of acid group in residual lignin and carbohydrate (
Figure 3).

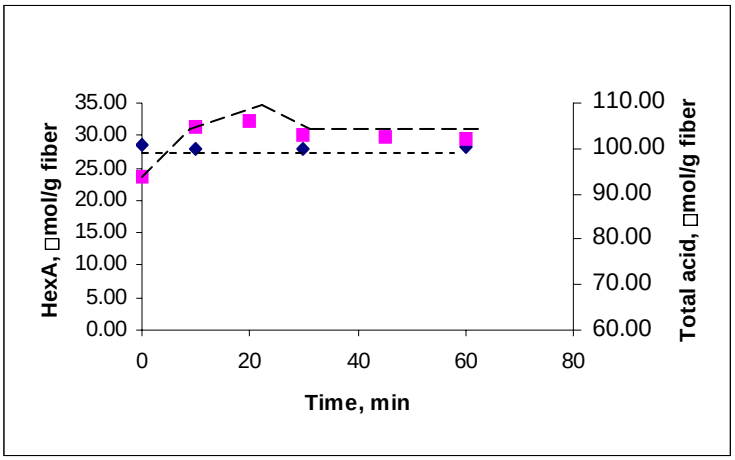


Figure 3. The change of total fiber acid and HexA in oxygen delignified pulps
Oxygen delignification conditions: NaOH: 2.5%; temperature: 100 ˚C; O_2 pressure: 800 kPa

Previous literature studies (Dence and Reeve 1996) have shown that residual lignin will experience a series of reactions during oxygen-alkaline delignification, such as ring opening, side chain cleavage, hydroxylation, demethylation *etc.* As a result, the molecular weight of residual lignin is reduced and its hydrophylicity increases.. The newly formed lignin acid groups during oxygen delignification will contribute to fiber charge. Similarly, cellulosic and hemicellulose adolic acids formed during oxygen delignification will also contribute to fiber charge. The total fiber charge for oxygen delignified pulps is the sum of acid groups both on residual lignin and pulp carbohydrates.

However, as previously described the extraction of lignin occurs simultaneously with oxygen reactions in the first 10 minutes during oxygen alkali delignification (Van Heiningen and Violette 2002). To determine if alkali-induced lignin removal during an O-stage influences fiber charge, a series of experiments were conducted employing O-delignification conditions with exception that nitrogen was employed instead of oxygen. The kappa number reduction (K_N) is within 1.74 - 2.80 kappa units as shown in Table 2.

Table 2. Alkali-induced Kappa number reduction

	NaOH,%	K_N
100 ˚C, 800 kPa N_2, 10 min	1.5	2.09
	2.5	2.31
	3.5	2.33
	Temperature, ˚C	K_N
2.5% NaOH, 800 kPa N_2, 10 min	85	1.76
	100	2.31
	115	2.67
	Nitrogen, Psi	K_N
2.5% NaOH, 100 ˚C, 10 min	640	1.74
	800	2.31
	960	2.24
	NaOH(%)/Temp(˚C)	K_N
800 kPa N_2, 10 min	3.5/115	2.80

K_N = caustic-induced kappa number reduction

It is also found that alkali-induced Kappa number reduction (lignin removal) does not lead to change of the acid group content in fiber (Table 3). Therefore, the oxygen-mediated Kappa number (K_C) will be the difference of pulp Kappa number (K) and K_N ($K_C = K - K_N$).

Table 3. Acid group content for alkali extracted pulps

	Control	CMN	THCN
Total acid, μmol/g	93.98	93.80	93.67
Kappa number	29.55	27.17	26.69

CMN: 2.5% NaOH, 100 ˚C, 800 kPa N_2, 10 min.
THCN: 3.5% NaOH, 115 ˚C, 800 kPa N_2, 10 min.

When we plot the change of oxygen-mediated total acid [(Total acid – HexA)/K_C] over oxygen-mediated Kappa number reduction ($\Delta Kc = K - K_o$, K_o: initial pulp Kappa number), an exponential correlation between them was found (Figure 4), which indicates that the acid concentration of residual lignin increases with the more lignin removal since the amount of residual lignin decreases during oxygen delignification.

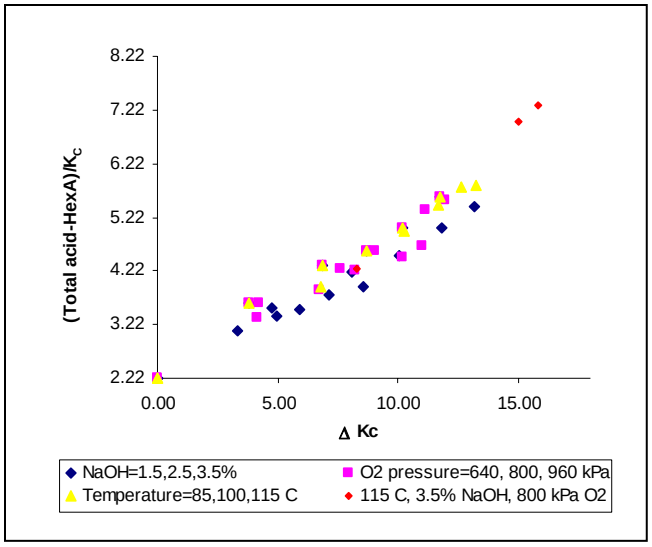


Figure 4. Oxygen-mediated acid group change with Kappa number reduction

Effects of Parameters on oxygen-mediated fiber acid group content

Alkali charge

It is known (Dence and Reeve 1996) that increase the alkali charge will increase lignin removal during oxygen delignification. One of the important changes is the increase in lignin hydrophilicity due to the acid group formation by oxidative reactions. This may lead to the acid group increase in oxygen delignified fiber. As shown in Figure 5, an increase alkali charge from 1.5% to 2.5% apparently raises the oxygen-mediated acid group content. However, further an increase in alkali charge to 3.5% does not show any additional acid group increase effect. As reported (Dence and Reeve 1996), a higher alkali usage will be beneficial to lignin removal. However, when the amount of residual lignin is significantly reduced to a low level, its contribution to total acid group increase may be no longer significant even though the acid concentration in residual lignin may be still very high. Therefore, high alkali usage does not necessary lead to a high fiber acid content.

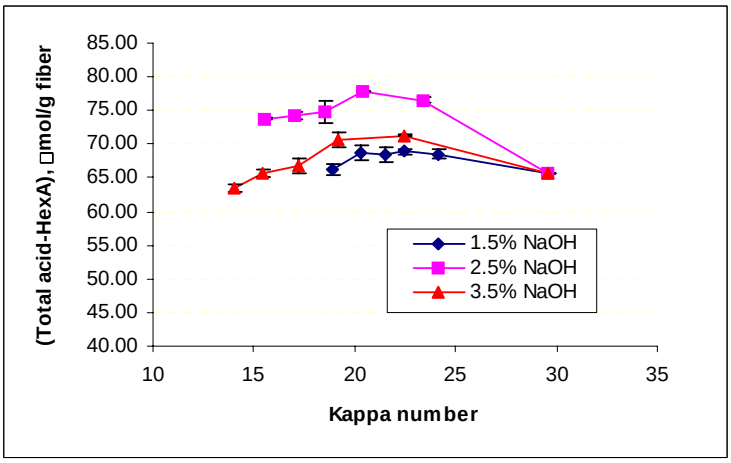


Figure 5. Effect of alkali charge on oxygen-mediated fiber acid group content

Conditions: 1.5-3.5% NaOH, 800 kPa O_2, 100 ˚C, 0-60 mim

Temperature

As previously reported (Dence and Reeve 1996) an increase of reaction temperature will greatly raise the rate of oxygen delignification. However, the temperature rise from 85 ^{o}C to 100 ^{o}C does not result in an oxygen-mediated acid content increase as shown in Figure 6. At 115 ^{o}C, the oxygen-mediated acid content even decreases.

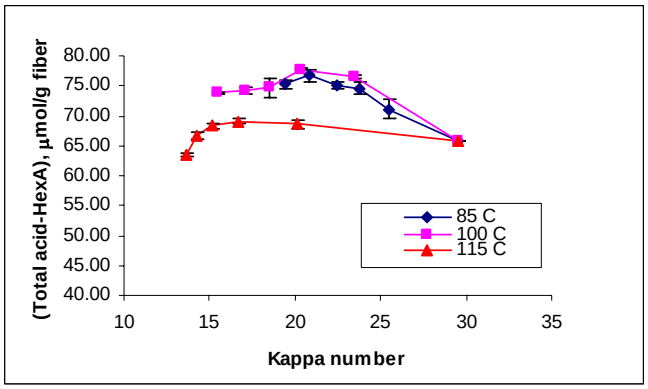


Figure 6. The effect of temperature on oxygen-mediated fiber acid formation
Conditions: 2.5% NaOH, 800 kPa O_2, 85-100 ˚C, 0-60 mim

Oxygen pressure

As shown in Figure 7, an increase oxygen pressure does not appear to have any major effect on acid group content within the experimental limits examined.

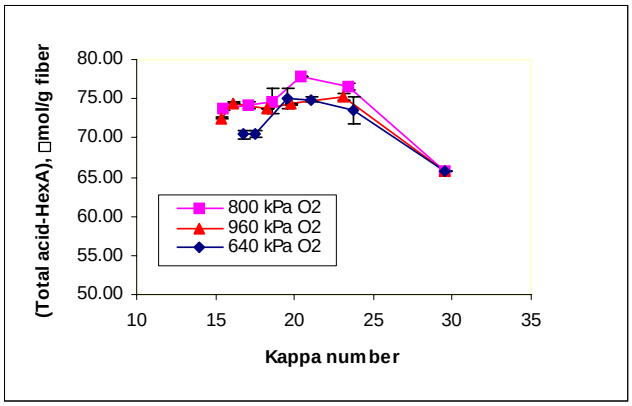


Figure 7. The effect of charged oxygen on oxygen-mediated fiber acid formation
Conditions: 2.5% NaOH, 640-960 kPa O_2,100 ˚C, 0-60 mim

Acid group content in holocellulose

The acidic groups introduced into lignin will not contribute to the fiber charge of fully bleached pulps although they can facilitate lignin solubility by increasing the hydrophilicity and increase the total acid group content for oxygen delignified pulps.

Research studies by Laine, *et al* (Laine and Stenius 1995; Laine 1997) reported total fiber charges of 58, 56, 51, and 57 μeq/g for softwood kraft pulps bleached via OZEP, OPZEP, ODEDED and DEDED, respectively. The corresponding kappa numbers/HexA contents for fully bleached pulps are 2.9/12.1, 0.8/4.0, 0.4/2.3/, and 0.8/3.2 (%/%) respectively. Since the remaining residual lignin and HexA in these fully bleached pulps are so low, their fiber charge must predominantly come from carbohydrates

In order to investigate the acid group development in carbohydrates during oxygen delignification, holocellulose samples from oxygen delignified pulps were prepared. The data in Table 4 showed that the process of making holocellulose did not affect acid group content in the pulp. Therefore, it is reasonable to assume that the acid group in holocellulose can represent the acid group in pulp carbohydrates excluding hexenuronic acids.

Table 4. Acid group content in softwood kraft ECF pulp and holocellulose of ECF

	ECF of softwood kraft pulp	Holocellulose from ECF
μmol/g fiber	43.31	43.18

As summarized in Figure 8, three phase of acid group change in holocellulose from oxygen delignified pulps were apparent during one stage oxygen delignification: an initial 10-39 % of decrease was followed by a small gradual increase and then flat or small decrease. The initial rapid decrease of acid group most likely occurred because of the removal of oxidative lignin and easily accessible amorphous cellulose with acid group due to the alkali dissolution. Due to the selectivity, lignin oxidation is dominant at this stage and acid groups may not form in carbohydrate at this phase; the gradual increase of acid should may involve direct oxidation of

exposed carbohydrate through oxygen or radicals since the rapid delignification starts to slow down; and the flat or slow decrease of acid group formation is thought to be the oxidized and slow elimination of amorphous cellulose hairs and formed by opening the crystallite structures. These changes were oppositely paralleled by the reported changes of cellulose crystallinity (De SouZa, Bouchard et al. 2002).

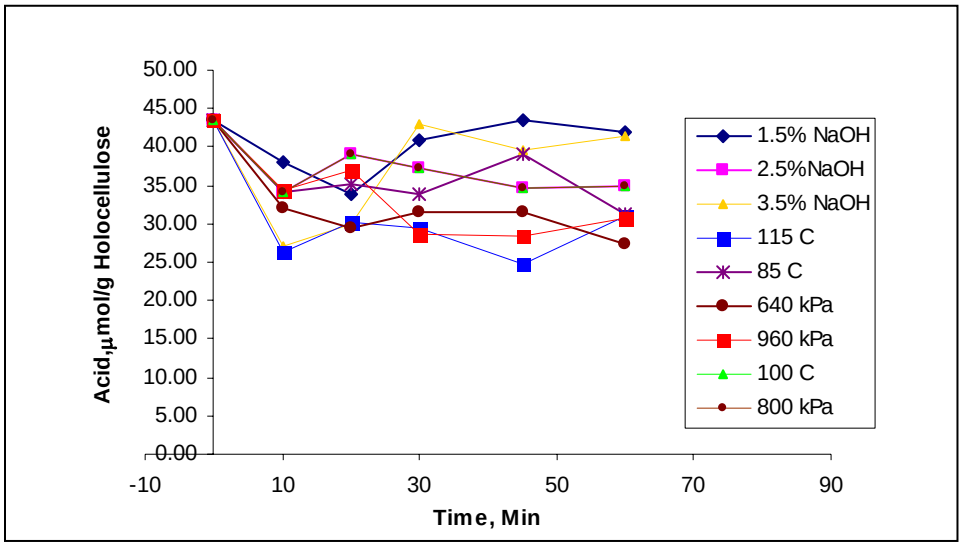


Figure 8. Acid group content in holocellulose

From Figure 1a, it is found that the total acid increase initially. Therefore, the acid group content in residual lignin must be high enough during the initial stage to compensate for the initial drop of the acid in carbohydrate, which was shown in Figure 9 for one of the oxygen delignification streams. More experiment need to be conducted to verify this trend.

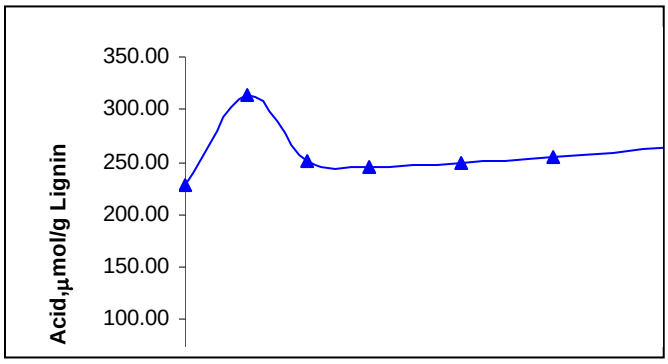


Figure 9. Acid group in residual lignin during oxygen delignification
Conditions: 2.5% NaOH, 800 kPa O_2,100 ˚C, 0-60 mim

The effect of acid group in holocellulose on sheet strength

From Table 5, it was observed that holocellulose with higher acid content (42.94 μmol/g holocellulose) shows higher tensile strength than those with lower acid group content (26.99 and 29.96 μmol/g holocellulose). The other three post O-samples yielded close tensile strength values because, in part, of their similar acid group contents. Certainly, the higher delignification rate will inevitably affect the fiber strength especially at higher alkali charge. However, it is still a safe assumption to believe that the sheet tensile strength can be raised by significant acid group increase in the pulp.

Table 5. The effect of acid content in Holocellulose on sheet strength

NaOH %	Kappa reduction %	Acid μmol/g holocellulose	Tensile strength index N.m/g
2.5	20.7	34.18	11.88
	31.1	39.12	11.61
	47.5	35.01	11.18
3.5	23.9	26.99	8.04
	35.1	29.96	8.82
	41.4	42.94	10.45

Other conditions: 800 kPa O_2, 100 ˚C, 10-60 minutes

Conclusions

Based on the experimental results from a series of one stage oxygen delignification on southern pine kraft pulps, the following conclusions on acid group development in oxygen delignified pulps can be obtained.

1. An initial increase followed by a level off or small slow drop exist for the total fiber acid group development. When the delignification rate is within 25-35%, the total acid content in oxygen delignified pulps develops with a maximum.
2. The acid group content in residual lignin will significantly affect the total fiber charge, which is also influenced by the amount of residual lignin in oxygen mediated pulps and further affected by the oxygen delignification parameters. Increase alkali charge (1.5-2.5%) can raise the acid contribution from residual lignin to total fiber acid content. However, the increase of oxygen charge and reaction temperature does not show positive effect on oxygen mediated fiber acid group development.
3. For the acid group development in carbohydrates (*i.e.*, holocellulose), there exists an initial decrease for the acid content change during first 10 minute. A small rise followed by a flat or slow drop is also found after first 10 minute.

These results suggest that acid groups in pulp carbohydrates are formed and destroyed simultaneously. Depending on which effect is dominant effect will determine the final acid group content in the pulp carbohydrates.

References

- Allison, L., A. J. Ragauskas, et al. (2000). "Metal Profiling of Southeastern U.S. Softwood and Hardwood Furnish." Tappi **83**(8): 97.
- Barzyk, D., D. H. Page, et al. (1997). "Acidic group topochemistry and fiber-to-fiber specific bond strength." Journal of Pulp and Paper Science **23**(2): J56-J61.
- Barzyk, D., D. H. Page, et al. (1997). "Carboxylic acid groups and fiber bonding." Fundamentals of Papermaking Materials, Transactions of the Fundamental Research Symposium,11th. **2**: 893-907.
- Barzyk, D. L., A. J. Ragauskas, et al. (1997). "The effect of acid group content on the properties of cotton fibers." AIChE Symposium Series (1996). Fundamentals and Applications in Pulping, Papermaking, and Chemical Preparation: 146-151.
- Chai, X. S., J. Y. Zhu, et al. (1999). "A simple and rapid method to determine hexenuronic acid groups in chemical pulps." 10th ISWPC.
- Chai, X.-S., Q. X. Hou, et al. (2003). Carboxyl Groups in Wood Fibers: Part II. The Fate of Carboxyl Groups during Alkaline Delignification and Its Application for Fiber Yield Prediction in Alkaline Pulping.
- Chandra, R. P., C. Felby, et al. (2004). "Improving Laccase-Facilitated Grafting of 4-Hydroxybenzoic Acid to High-Kappa Kraft Pulps." Journal of Wood Chemistry and Technology **24**(1): 69-81.
- Dahlman, O., A. Jacobs, et al. (1999). "Xylan structure and distribution in kraft pulping." 10th ISWPC **2**: 186-189.
- De SouZa, L. J., J. Bouchard, et al. (2002). "Carbohydrate in oxygen delignification Part I: Changes in Cellulose Crystallinity." Journal of Pulp and Paper Science **28**(5): 167-170.
- Dence, C. W. and D. W. Reeve (1996). Pulp Bleaching, Principle and Practices. Atlanta, Georgia, Tappi Press.
- Fors, C. (2000). The effect of fiber charge on web consolidation in papermaking. Pulp and Paper Chemistry and Technology. Stockholm, Royal Institute of Technology**:** 78.
- Froass, P. M., A. Ragauskas, J., et al. (1998). "NMR studies. Part 4: Analysis of residual lignin after kraft pulping." Industrial Engineering and Chemistry Research **37**(8): 3388.
- Gellerstedt, F. and P. Gatenholm (1999). "Surface properties of lignocellulosic fibers bearing carboxylic groups." Cellulose **6**(2): 103-121.
- Jiang, H., J. M. Genco, et al. (1989). "Strength of oxygen delignified Northeastern kraft hardwood pulp." AIChE Proceedings,1989 and 1990 Forest Products Symposium: 67-73.
- Laine, J. (1997). "Effect of ECF and TCF bleaching on the charge properties of kraft pulp." Paperi Ja Puu. **79**(8): 551-559.
- Laine, J., T. Lindstrom, et al. (2001). "Studies on topochemical modification of cellulosic fibers. Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibers." Nordic Pulp & Paper Research Journal. **15**(5): 520-526.
- Laine, J., T. Lindstrom, et al. (2002). "Studies on topochemical modification of cellulosic fibers. Part 3. The effect of carboxymethyl cellulose attachment on wet-strength development

by alkaline-curing polyamide-amine epichlorohydrin resins." Nordic Pulp & Paper Research Journal. **17**(1): 57-60.

- Laine, J. and P. Stenius (1995). "Surface properties of bleached kraft pulp fibers and their comparison with properties of the final paper products." 8th ISWPC **2**: 589-596.
- Liden, J. and L.-O. Ohman (1997). Journal of Pulp and Paper Science **23**(5): J193-199.
- Lindstrom, T. (1992). "Chemical factors affecting the behavior of fibers during papermaking." Nordic Pulp and Paper Research Journal. **7**(4): 181-192.
- Lindstrom, T. and G. Carlsson (1982). "The effect of chemical environment of fiber swelling." Svensk Papperstidn **85**(3): R14.
- Pronto, M. (1998). "Carbohydrate analysis of pulp using high performance anion-exchange chromatography with Pulsed Amperometric detection: a comparison of two detector settings." 1998 Tappi Pulping Conference.
- Ragauskas, A. J., C. Courchene, et al. (2003). Fiber modification/fiber-fiber bonding. Atlanta, Institute of Paper Science and Technology**:** 61.
- Scallan, A. M. and J. Grignon (1979). "Effect of Cations on Pulp and Paper properties." Svensk Papperstidning **82**(2): 10.
- Sjostrom, E. (1993). Wood Chemistry. Fundamentals and Applications. San Diego, Academic press.
- Snowman, V. R., J. M. Genco, et al. (1996). "Bond strength of oxygen delignified hardwood kraft pulps." 481-489.
- Swerin, A., L. Odberg, et al. (1990). "Deswelling of hardwood kraft pulp fibers by cationic polymers. The effect on wet pressing and sheet properties." Nordic Pulp and Paper Research Journal. **5**(4): 188-196.
- T231cm-96 (2002). 2000-2001 Tappi Test Methods. Atlanta, GA, Tappi press.
- T237 (1996). "Tappi Test Methods 1996-1997." .
- Toven, K. (2002). "Swelling and physical properties of ECF/ECF light bleached softwood kraft pulps." 2002 International Pulping Bleaching Conference: 189-192.
- Van Heiningen, A. and S. Violette (2002). "Selectivity improvement during oxygen delignification by adsorption of a sugar-based polymer." PAPTAC 88th Annual meeting: B151-161.
- Vander Wielen, L. and A. J. Ragauskas (2004). "Grafting of acrylamide onto lignocellulosic fibers via dielectric-barrier discharge." European Polymer J. **40**(3): 477-482.

Plans for Next Quarter: Research efforts this next quarter will be directed at research tasks 3.IPST/NC.2, 3.IPST.3, .5 and .6.

Milestone Status Table:

Milestone Status Table High Selectivity Oxygen Delignification

ID No.	Description	Planned * Completion Date	Actual Completion Date	Comments As of (Date)
1.NC.1	Prepare SW and HW kraft (conventional, extended modified and batch)	June 30, 2000	Sept/2000	Completed
1.NC.2	Single Stage EOD: Examine effects of NaOH, temperature	September 30, 2000	June, 2001	Completed
1.NC/IPST.3	Single Stage EOD: Examine effects of mixing, NPEs and MgO_4	September 30, 2000	September 2000	Completed
1.IPST.4	Pulp strength studies before and after EOD	September 30, 2000	March 2001	Completed
1.IPST.5	Characterize lignin and carbohydrates before and after EOD	September 30, 2000	March 2001	Completed
1.NC/IPST.6	Develop Model Predicting EOD Yield & Strength Properties based on fundamental chemistry	December 31, 2000	May, 2001	Completed
1.NC/IPST.7	Experimental verification of improved EOD conditions	December 31, 2000	June, 2001	Completed
1.NC/IPST.8	First Year Report	December 31, 2000	May, 2001	Completed
2.NC.1	Investigate OO as a function of incoming pulp kappa #	Oct 30, 2002	April 2002	Completed
2.NC.2	Evaluate temperature profile effects of single EOD stage to match performance of OO	Dec.31, 2002	Dec. 2002	Completed
2.IPST.3	Develop yield test method for EOD based on gravimetric yield results of year I & II	December 31, 2002	Dec. 2002	Completed
2.IPST.4	Measure kinetics of lignin removal for EOD using O and OO	September 30, 2002	Dec. 2002	Completed
2.IPST.5	Determine lignin & carbohydrate degradation pathways for 2-stage EOD	September 30, 2002	Feb. 2003	Completed
2.NC/IPST.6	Model new EOD system and perform preliminary economic assessment	December 30, 2001	Dec. 2003	Completed
2.NC/IPST.7	Second Year Report	December 31, 2001	Dec 2001	Completed
3.NC.1	Test and refine new EOD system	Dec 31, 2003	Jan. 2004	Completed
3.IPST/NC.	Evaluate ECF bleachability of improved	April 30,		Ongoing

2	EOD bleached pulps	2003		
3.IPST.3	Measure papermaking properties of fully bleached pulps	April 30, 2003		Ongoing
3.IPST.4	Evaluate EOD yield testing procedure	June 30, 2003	March 2003	Completed
3.IPST.5	Economic assessment of new EOD system	July 31, 2003		Ongoing
3.NC/IPST.6	Final Report Task	Oct. 1, 2003		Initiated

*Project initiation was delayed by 4 months required to get the necessary research staff at IPST and NC State University. A one year no-cost extension has been granted till Dec. 2004

Project Publications:

Manuscript titled “Tailoring fiber properties during one-stage oxygen Delignification. Fiber acid group content development.” has been accepted for presentation at the upcoming 2003 TAPPI Fall Technical Conference: Engineering, Pulping & PCE&I in Atlanta (2004).

Higher Selectivity Oxygen Delignification

Lucia: Institute of Paper Science and Technology

ID14261, CPS#01695

DOE QUARTERLY PROGRESS REPORT

For:	**HIGHER SELECTIVITY OXYGEN DELIGNIFICATION**
Covering Period:	May 1, 2004 to July 30, 2004
Date of Report:	July 28, 2004
Recipient:	Institute of Paper Science and Technology
Award Number:	**DE-FC07-02ID14261**
Subcontractors: (if any)	
Other Partners:	
SAPPI (formerly Potlatch) Research Center Cloquet, Minnesota 55720-0503	Sunoco Chemicals Frankford Plant Margaret & Bermuda Streets Philadelphia, PA 19137-1193
International Paper Coporate Research Center 1422 Long Meadow Road Tuxedo, NY 10987	Alabama River Pulp Company, Inc. P.O. Box 100 Claiborne Mill Perdue Hill, Alabama 36470
Contact:	
Principal Investigator:	Lucian A. Lucia
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Tel./Fax	404-894-9712 (Office)/404-894-4778 (Fax)
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Project Team:

Kevin Schanilec, Mark Turner

Project Objective: The objectives of this project are as follows:

- Examine the physical and chemical characteristics of a partner mill pre- and post-oxygen delignified pulp and compare them to lab generated oxygen delignified pulps
- Apply the chemical selectivity enhancement system to the partner pre-oxygen delignified pulps under mill conditions (with and without any predetermined amounts of carryover) to determine how efficiently viscosity is preserved, how well selectivity is enhanced, if strength is improved, measure any yield differences and/or bleachability differences
- Initiate a mill scale oxygen delignification run using the selectivity enhancement agent, collect the mill data, analyze it, and propose any future plans for implementation

BACKGROUND

We have been trying to solidify our work plan with the new company in Cloquet, but communication has been slow since our contacts are missing, the former company, Potlatch has been acquired by SAPPI, the softwood fiberline is no longer the main furnish (it has been switched to hardwood) and IPST has been acquired by the state of Georgia. We have established a relationship with Vinod Gupta (Vinod.Gupta@na.sappi.com) who is now our liaison at SAPPI. Since our last report in April, we have had no activity in this project due to a move of our resources to North Carolina State Univeristy. We will complete several experiments on hardwood samples in the next few months and complete our project by September 2004.

Status of Current Work and Plans

1. We have determined from Mr. Kevin Schanilec of the US EPA that we have a very cheap and abundant resource of phenol for our additive work.

2. We have acquired from SAPPI maple brownstock from the second stage wash press as well as pulp from the 2PO post oxygen wash press as a benchmark for our work.

3. Mr. Mark Turner has been unable to perform all of the final hardwood oxygen delignification runs given his schedule. What remains to be done at North Carolina State University is as follows (before September 30, 2004):

    - Measure the hexenuronic acid levels in the pre- and post-oxygen pulps

    - Use three levels of phenol (0%, 1.0%, and 5.0% on an o.d. basis) while varying the base levels from 1% to 5% and the times (15 min. and 60 min.) to get a range of kappas

    - Compare the changes in selectivity between the control and the test pulps and make a final determination of conducting a mill trial

MILESTONES

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
14261	*Higher Selectivity Oxygen Delignification IPST, Lucia, PI	Fr 10/1/01 To 12/31/03		As of 04/30/04
	Year 1+Year 2 (No Cost Extension)			
1.0	Literature Review	11/1/01	1/15/02	We have ten papers as a result of this work.
1.1	Collect selected SW post and pre-oxygen pulp from Potlatch, IP, and APP for laboratory analysis	11/15/01	1/15/02	Have been able to receive pre- and post-oxygen SW delignified pulps from Potlatch; recently received HW
1.2	Character pulp with respect to kappa, viscosity, metals, and preliminary response to initial set of oxygen delignification	2/1/02	8/1/02	Completed
1.3	Analyze pulp carbohydrates and lignin of mill pulps and pulps generated in the laboratory	3/1/02	8/1/02	Completed
1.4	Examine the physical and chemical effects of the added organic/inorganic catalyst system on the pre-oxygen pulps after a series of oxygen delignification experiments (controls and test pulps).	6/1/02	10/1/03	Completed
1.5	Examine effect of various levels of black liquor carryover on the efficacy of the oxygen selectivity	7/15/02	11/1/03	Completed
1.6	Propose an economic and mill model for use in an actual oxygen delignification tower	8/1/02		Not able to begin at this time
1.7	Begin logistical and economic deliberations with partner mill for commencing the mill trial based on the collected laboratory data	8/15/02		Not able to begin at this time
1.8	Initiate the mill trial	5/01/03		In process of negotiating proprietary data collection with SAPPI
1.8	Collect mill data, interpret, propose new trial(s)	9/01/03		Not able to begin at this time
1.8	Final Report	9/30/04		

*The project was delayed by 3 months due to budgetary allocations and arrival of principal research scientist. We are currently under a longer delay due to the takeover of Potlatch by SAPPI and the loss of our principal contact, Gopal Goyal which delayed the project an additional 6 months. We have lost the primary postdoctoral fellow for this work and are seeking assistance internally and externally. We have obtained an extension of this project until June 30, 2004.

Yield Improvement and Energy Savings Using Phosphonates as Additives in Kraft Pulping

Tschimer: University of Minnesota

ID14433, CPS#01871

QUARTERLY PROGRESS REPORT

Project Title: Yield Improvement and Energy Savings Using Phosphonates as Additives in Kraft pulp

Covering Period: 3/31/04-6/30/04

Date of Report: July 31, 2004

Recipient:
University of Minnesota
Office of Sponsored Projects
McNamara Alumni Center
200 Oak Street SE, Room 450
Minneapolis, MN 55455
Congressional District:5

Award Number: DE-FC36-03ID14433

Subcontractors: none

Other Partners:
Solutia Inc. (Company)
Cost sharing, in-kind contributions of salary, travel, chemicals and supplies at $15,000/year
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Project Team:
DOE-HQ contact: Joseph Springer, Project Officer
Beth Dwyer, Financial Assistance Officer
Sheldon Verrett (Industry contact)
Sharon Bartlett (U of Mn grant and Contract Administrator)

Project Objective: Develop a commercially viable modification to the Kraft process resulting in energy savings, increased yield and improved bleachability. Evaluate the feasibility of this technology across a spectrum of wood species used in North America. Develop detailed fundamental understanding of the mechanism by which phosphonates improve KAPPA number and yield. Evaluate the North American market potential for the use of phosphonates in the Kraft pulping process. Examine determinants of customer perceived value and explore organizational and operational factors influencing attitudes and behaviors. Provide an economic feasibility assessment for the supply chain, both suppliers (chemical supply companies) and buyers (Kraft mills). Provide background to most effectively transfer this new technology to commercial mills.

Background: The project is to advance the development, optimization, and potential commercialization of a new Kraft pulping process using phosphonates as additives that promises opportunities for substantial energy savings, increased yield, and bleaching cost

reduction. Our preliminary studies suggest energy savings in the digester of up to 10%, increased yield of 4-6%, increased ratio of delignification and improved pulp strength. As the predominant pulping technology worldwide for producing chemical pulps of high strength, the Kraft process is used to produce approximately 51 million metric tons of pulp per year in the US. The approach of using phosphonates as additives in the Kraft cook is entirely new. Phosphonates are acids or salts with highly anionic charges, containing at least one functional group, $-P(=O)(OH)_2$, attached to a carbon atom. Their complex structures are characterized by phosphoryl bonds and multiple metal ion chelating sites. Phosphonates are soluble and stable in aqueous systems to high temperatures, pressures and extreme pH values. Phosphonates have surfactant and dispersing properties and are expected to facilitate penetration of chemicals into chips as well as prevent re-deposition of lignin. In addition their chelating properties are expected to favor brightness improvements in subsequent bleaching processes since bleaching sequences such as oxygen, chlorine dioxide or peroxide are negatively influenced by presence of transition metals. Preliminary experiments performed in our lab far exceeded our expectations with respect to increased lignin removal, improved yield, conservation of pulp viscosity and bleached brightness.

Status:

Wood Species characterization:

As planned we obtained spruce and birch samples to be evaluated. As seen before for other softwoods, spruce showed no favourable response to phosphonate addition in the Kraft digester with respect to lignin removal. Some improvement in bleaching response could be observed (1-2 points). This effect has been seen before and is attributed to the reduced content of metals in the phosphonate treated pulps.

Birch chips have not been processed yet, but will be part of next quarters study.
It was suggested by our reviewers (April/04) to consider measuring Guaiacyl/Syringyl ratio in the hardwoods we are studying. It is reasonable to suspect that the G/S ratio has an impact on the reponse of the wood sample in question to our process. After an extensive literature review we selected pyrolysis/GC as an analytical test. Arrangements have been made to test our aspen, birch, maple and alder chips. We are hoping to be able to correlate the response of these species to our process to their G/S ratio.

Solid-state (SS) NMR

Aspen pulp samples from different cooks (with and without phosphonate addition, different H-factors, different KAPPA numbers) were characterized using SS-NMR. Due mainly to the angular dependence of the C-H dipolar coupling in solid state, the resolution of SS-NMRs is relatively low in comparison with solution state NMRs. Nevertheless, it is simple, fast, and can give valuable information about the chemical structure and composition of wood and pulp samples. Some sample spectra of CP/MAS ^{13}C-NMR at 400MHz are illustrated in **Fig. 1** (two aspen pulp samples and aspen wood). Assignments of principal resonances in the spectra are summarized in **Table 1**.

Signals occurring between 60 and 110ppm are attributed primarily to carbohydrate carbon atoms, while including contributions from lignin side-chains and Lignin-Carbohydrate functionalities. Resonances in the region of 110 to 160ppm are indicative of lignin structures. In addition, the most characteristic peak for the methoxyl group at 56ppm is contributed by lignin.

Prominent signals for hemicelluloses appear at 173ppm for the carbonyl group and at 20ppm for the methyl group.

Table 1 Assignments of peaks in the CP/MAS ^{13}C-NMR spectra of wood and pulp samples

δ, ppm	Lignin (S=Syringyl, G=Guaiacyl)	Cellulose and hemicelluloses
173.0	C_α=O (trace)	C=O in acetyl and -COOH groups of xylan
153.0~148.0	S 3/5 (4-O-R) (downfield)	
	S 3/5 (4-O-H), G 3/4 (upfield)	
135.0~132.0	Condensed structures: S 1/4 (4-O-R), G 1 (4-O-R) (downfield)	
	S 1/4 (4-O-H), G 1 (4-O-H) (upfield)	
ca. 120.0	G 6	
ca. 114.0	G 2/5	
ca. 110.0	S 2/6	
105.0~103.0		C-1 in cellulose (downfield) and hemicelluloses
88.0		C-4 (crystalline)
84.0	C_β in β-O-4	C-4 (amorphous)
73.0 (strong)	C_α-OH in β-O-4	C-2,3,5 in cellulose and hemicelluloses
ca. 65.0	C_γ-OH	
64.0		C-6 in cellulose (crystalline)
56.0	Aryl methoxyl C	
50.0~15.0		Aliphatic C not attached to oxygen
20.0		Methyl C in acetyl groups of xylan

Signals of carbon atoms from carbohydrates (both cellulose and hemicelluloses) can be assigned without any difficulty. Carbon-1 occurs at ~105ppm in the most downfield range of 60~110ppm, due to two adjacent electron-donating oxygen atoms. Carbon-4 is the next, at 88~84ppm, followed by the doublet at ~73ppm of C-2, 3, 5 in the six-member ring. The doublet results probably from the minor difference in structure between cellulose and hemicelluloses. The aliphatic C-6 shows up in the most upfield area, i.e., at 64ppm with an upfield shoulder. Crystallinity is known in nature as a major characteristic of cellulosic microstructure. It can be accurately quantified by X-ray diffraction. In the SS ^{13}C-NMR spectra, the crystallinity of cellulose can be measured by the integral ratio of the C-4 peak at 88ppm (crystalline) over the C-4 peak at 84ppm. In fact, the same interpretation holds for the C-6 signals with the upfield shoulder representing the disorder or amorphous part in its structure. Results show that the crystallinity increases steadily from 0.58 of the wood sample to 0.84~0.85 of the pulp samples, whereas little difference is identified between the control, Na_4HEDP, and AQ treated pulps. Alkaline treatment and exposure to an elevated temperature are believed to be the fundamental factors explaining this phenomenon It is known that amorphous areas in cellulose are preferentially attacked and dissolved during Kraft pulping, giving rise to the crystallinity increase with growing yield losses.

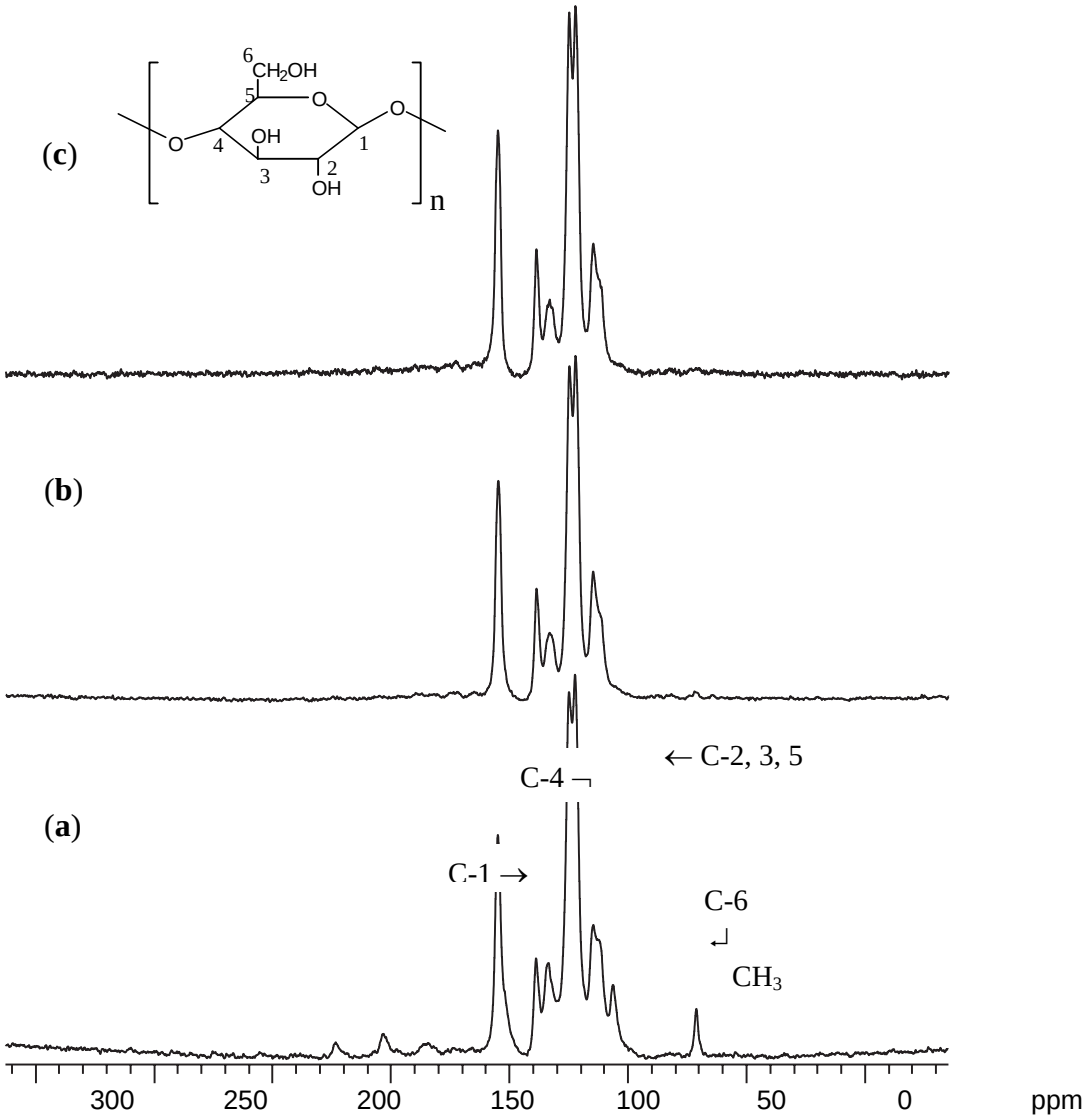

Figure 1 CP/MAS ^{13}C-NMR spectra of : (**a**) the aspen wood, (**b**) the control and (**c**) Na_4HEDP(0.2%) treated pulps at H-factor 853.

As a result of removal of hemicelluloses during pulping, two peaks at 173 and 20ppm for acetyl groups are strong in the wood sample, but become too weak to be visible in pulp samples. Signals at 153~148ppm indicate changes in the lignin content and its structure. Corresponding to C-3, 5 in syringyl units and C-3, 4 in guaiacyl units respectively, the peak at 153ppm is slightly stronger than that at 148ppm in the wood sample, probably a sign that the syringyl type outnumbers the guaiacyl type in the native aspen lignin. However, the signals become no longer detectable in pulp samples of lignin contents lower than 3%. Similarly, the $-OCH_3$ signal at 56ppm is firm in the wood sample, but it turns out to be weaker and weaker from the control

toward the phosphonate treated pulp due to increasingly stronger delignification. In addition, integration values (**Table 2)** at 105~103ppm, 88~84ppm, 73ppm and 64ppm are consistent with represented carbon numbers, i.e., 1:1:3:1 in order.

Table 2 Integration (total 100) of peaks in the CP/MAS ^{13}C-NMR spectra of wood and pulp samples

Chemical shift, δ (ppm)	Wood	Pulp		
		Control	Na_4HEDP(0.2%)	AQ(0.1%)
173.0	0.8	0.3	0.0	0.0
153.0~148.0	2.0	0.8	0.0	0.0
135.0~132.0	1.6	1.1	0.0	0.0
105.0~103.0	15.8	16.1	15.9	16.3
88.0	4.8	6.3	6.3	6.2
84.0	8.4	7.5	7.4	7.4
73.0	42.5	44.4	46.3	46.3
64.0	14.6	14.9	15.3	15.7
56.0	5.3	2.1	0.0	0.0
35.0~10.0	1.9	0.7	0.0	0.0
Ratio ($\frac{I\_at\_88ppm}{I\_at\_84ppm}$)	0.57	0.84	0.85	0.84
Kappa number	n/a	20.5	14.2	16.9

Note: All pulps cooked at H-factor 853; I=Integration

Molecular Weights by HP-SEC

Kraft lignin was separated from several cooks (with and without Phosphonate addition, different H-factors and different KAPPA numbers) by acidifying the black liquor. Some of the samples were acetylated before analysis. We attempted to characterize molecular weight distribution of these lignins using HP-SEC (High pressure size exclusion chromatographie).

A representative elution spectrum of acetylated lignin is shown in **Fig. 2**. After comparison with a standirization curve molecularweights were calculated (Table 3). As shown in **Table 3** we found almost all low-molecular-weight molecules [$\overline{M}_n$, lower than 750 and 475g/mol for acetylated and nonacetylated lignins, respectively]. Polydispersity indexes (PDIs) are 1.35~1.41 for nonacetylated samples, and up to 2.15~3.92 when subjected to acetylation, implying broader and more diversified distribution of molecular weights. Unfortunately these numbers are not realistic. It has been shown in literature that molecular weight of Kraft lignins are considerably larger. We assume that the higher molecular material precipitated on the colum material. We are presently setting up a sephadex colum to repeat these tests. Nevertheless, it was interesting to note that both acetylated and non-acetylated samples from the phosphonate treated cooking are showing higher molar masses at given H-factors than the respective control lignins. AQ pulps show similar molecular weight distribution than phosphonate pulps. There appears to be a distinct difference between control and HEDP treated cooks.

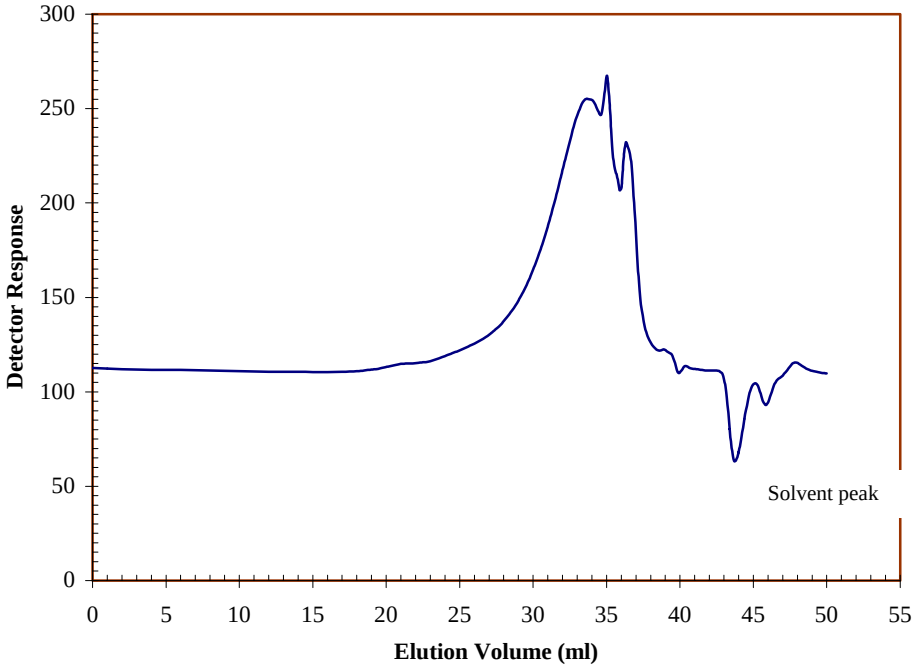

Figure 2 A typical HP-SEC elution spectrum of aspen kraft lignin in solvent THF with the calibration conducted using polystyrene standards.

Table 3 Relative molar masses (g/mol) of aspen kraft lignin by HP-SEC

Corresponded pulp (charge, %)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	PDI ($\overline{M}_w / \overline{M}_n$)	$\overline{N}_{free\_-OH}$
	Acetylated samples:				
Control-I	738.0	2839.4	36938	3.85	--
Na_4HEDP(0.2)-I	749.6	2936.9	34921	3.92	--
Control-II	692.0	2080.3	27285	3.01	--
Na_4HEDP(0.2)-II	714.1	2238.4	26610	3.13	--
Na_5DTMPA(0.2)-II	704.2	2358.4	29670	3.35	--
AQ(0.1)-II	705.4	1517.0	98562	2.15	--
	Non-acetylated samples:				
Control-I	459.7	623.1	902.2	1.36	6.6
Na_4HEDP(0.2)-I	469.0	653.6	978.8	1.39	6.7
Control-II	450.5	609.7	880.9	1.35	5.8
Na_4HEDP(0.2)-II	464.3	642.2	951.8	1.38	5.9
Na_5DTMPA(0.2)-II	459.3	637.1	947.8	1.39	5.8
AQ(0.1)-II	474.8	667.7	985.0	1.41	5.5

Note: I and II — H-factor 558 and 853 applied respectively;

Market Study
Qualitative data collection associated with phase I of the marketing research study is now complete, and focus has now turned toward analysis of this data and the further development of construct measures to be employed in the quantitative research to be completed in 2004-2005. Phase I interviews involved nine senior and operational managers at the mill and corporate offices. These interviews were conducted across four companies engaged in pulping operations in the upper Midwest region and represent functional responsibilities which include: research and development, pulping operations, mill management, and market development.

Constructs explored through phase I qualitative interviews are organized into environment, technological, and organizational dimensions. The intent is to understand the relationships between the constructs, gauge their relative contribution to technology adoption, and surface industry-specific catalysts and/or barriers impacting the adoption of incremental process innovations, specifically the adoption of phosphonate additives. Based on data captured in this phase, we are currently developing a quantitative questionnaire utilizing a combination of previously validated multi-attribute scales and unique measures related to the Kraft pulp industry to accomplish the objectives of the study.

Given low response rates associated with mail survey techniques in recent years. We are currently exploring the option of employing a web-based approach to facilitate a more convenient and less cumbersome data collection process for respondents. We have identified resources to assist us in the development and implementation of a web-based instrument and are currently in the process of attempting to identify accurate email addresses for the sample targeted by the study. Phase II survey efforts are expected to begin by January 2005.

Plans for next quarter:
We are planning to repeat molecular weight distribution analysis using a better suited system. Digester cooks using birch chips will be performed and analysed. S/G ratio for the four hardwoods we used in lab cooks (aspen, alder, maple, birch) will be determined using pyrolysis techniques. In addition we are in the process of setting up a protocol for ^{31}P NMR to be used to determine stability of our phosphonates in the Kraft process.

For the market study, given the low response rates associated with mail survey techniques, we are currently exploring the option of employing a web-based approach to facilitate a more convenient and less cumbersome data collection process for respondents. We will attempt to identify accurate email addresses for the sample targeted by the study.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Comments
1	Evaluation of different wood species	4/1/04	On-going
2	Characterization of fundamental background	3/31/06	On-going
2.1	Dispersion properties	10/1/03	Completed
2.2	Penetration into wood chips	4/1/04	On-going
2.3	Characterization of residual lignin	8/1/04	On-going
2.4	Characterization of black liquor lignin	10/01/04	On-going
2.5	Comparison of phosphonate responses	4/1/05	On-going
2.6	Optimization of process	10/1/05	On-going
2.7	Fate of phosphonates in the process	3/31/06	On-going
3.	Market study	3/31/06	On-going
3.1	Secondary Literature review	3/31/04	completed
3.2	Model development	3/31/04	On-going
3.3	Interview with mill personal	3/31/04	completed
3.4	Survey design and implementation	3/31/05	On-going
3.5	Economic feasibility assessment	3/31/06	
4.	Analysis and final report	3/31/06	

Approved Budget Data:

Phase / Budget Period			DOE Amount	Cost Share	Total
	From	To			
Year 1	4/1/03	3/31/04	$157,680	$ 41,145	$ 198,825
Year 2	4/1/04	3/31/05	$106,682	$ 42,190	$ 148,872
Year 3	4/1/05	3/31/06	$105,956	$ 43,277	$ 149,233
Year 4	NA				
Year 5	NA				
		Totals	$ 370,318	$ 126,612	$ 496,930

Design and Demonstration of Multiport Cylinder Dryers

Choi: Argonne National Laboratory

CPS#00785

QUARTERLY PROGRESS REPORT

Project Title: Development and Full-Scale Demonstration of Multiport Dryer Technology for the Forest Products Industry.

Covering Period: April 1, 2004 through June 30, 2004

Date of Report: July 30, 2004

Recipient:
Argonne National Laboratory
Energy Technology Division, #335
9700 S. Cass Avenue
Argonne, IL 60439

Award Number: 49682

Subcontractors:
Ability Engineering
Design Solutions, Inc.

Other Partners:
The University of Illinois at Chicago
Eastern Pulp and Paper
The Johnson Corporation

Contact(s):
Steve Choi
630-252-6439
630-252-5568 (fax)
choi@anl.gov

Project Team: DOE-HQ contact: Dickson Ozokwelu

Project Objective: The objectives of the proposed research are to design and fabricate a prototype multiport dryer and to conduct multiport dryer performance tests in a full-scale test dryer for retrofit applications.

Background: Argonne National Laboratory (ANL) has already developed a multiport dryer design concept that could create breakthroughs in drying pulp and paper. In a proof-of-concept test, ANL demonstrated the feasibility of this concept. A series of steam condensing tests in ANL's Multiport Dryer Heat Transfer Test Facility showed that the condensing heat transfer coefficient for multiport dryers is about 7 times greater than that in a conventional dryer with spoiler-bar enhancement and about 20 times greater than that in a conventional dryer without spoiler bars. Furthermore, the tests showed that dryer shell surface temperatures are more uniform in multiport dryers than in conventional dryers. With the

feasibility of the concept already proven in ANL's unique Multiport Dryer Heat Transfer Test Facility, the next step is to continue the project into full-scale tests that lead to commercial demonstration of the technology. At the same time, additional testing in the Multiport Dryer Heat Transfer Test Facility is scheduled to allow the development of predictive heat transfer relations for multiport dryers over a range of operating and design conditions.

Status: During the reporting period, ANL presented a technical paper in the open session of the Spring 2004 TAPPI Paper Summit on May 3 in Atlanta. The paper was focused on the Multiport dryer prototype design for testing in the JOCO full scale steam dryer facility. The paper was well received and generated interesting discussions. Following the open session presentation, the Multiport Dryer Demonstration project was reviewed in the closed session by the AF&PA's Agenda 2020 Energy Performance Task Group. We don't have the review team's recommendations at the moment. Also, ANL submitted a proposal titled "Development and Full-Scale Demonstration of Multiport Dryer Technology for the Forest Products Industry," requesting funding to complete the full-scale demonstration project. We have not been updated yet whether DOE has selected the Multiport Dryer project for continued support.

Plans for Next Quarter: Efforts will continue to complete the full-scale demonstration project when requested funding is available.

Milestone Status: no change since last report.

Budget Data (as of 7/30/04): no change since last report.

On-Line Fluidics Controlled Headbox

Aidun: Institute of Paper Science and Technology

GO10416, CPS#00975

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

Quarterly Progress Report

For: Improving Paper Machine Efficiency Through On-Line Control of Stock Delivery, Headbox and Forming Hydrodynamics

Covering Period: January 1 – March 31, 2004

Date of Report: May 10, 2004

Recipient: Institute of Paper Science and Technology at Georgia Tech., Atlanta, GA

Award Number: DE–FC36–99GO10416

Subcontractors: None

Other Partners: None

Contact:	Cyrus K. Aidun	(404) 894-6645	cyrus.aidun@me.gatech.edu
	Minami Yoda	(404) 894-6838	minami.yoda@me.gatech.edu

Project Objective: The main objective of this project is to retrofit a current headbox with an on-line controlled hydrodynamic system for uniform dispersion and distribution of fibers on the moving wire. The project will proceed in three phases with the third phase requiring a new project for commercial implementation. These are:

1. generation and control of axial vorticity in a tube bundle using "smart materials" for on-line actuation;
2. pilot machine implementation and trials (collaboration with industry)
3. commercial implementation on a small hydraulic headbox (collaboration with a company)

Background: This project involves implementing a new technology, *microforming*, in a headbox to produce an isotropic sheet with significant reductions in the MD/CD stiffness ratio (increasing CD specific STFI by 10 to 25%) and improved sheet uniformity. Microforming involves generating axial vorticity (*i.e.*, swirl) prior to the converging nozzle of the headbox by retrofitting an existing tube block with swirl generation devices. The objective of this project is to implement microforming by developing the retrofit technology for generation and on-line control of axial vorticity in the tubes to optimize turbulent scale and intensity, and consequently, fiber network structure properties in the sheet. This technology will result in significant improvements in the performance and capital effectiveness of the paper machine (PM) for a fraction of the cost to replace a headbox.

After completing the first phase milestone of the project—a commercial demonstration of the Vortigen system—the project is now focusing upon controlling the axial vorticity on-line using "smart materials" (shape memory alloys or SMAs) and an imposed electric field to adjust the geometry of the swirl generators with no moving parts. Dr. Yoda was co-Investigator on this project from July 2001 through April 2004 while Dr. Aidun was serving as program officer for the Multiphase and Particulate Processes Program at the National Science Foundation. Mr. Akay Islek, a graduate student in Mechanical Engineering at the Georgia Institute of Technology,

Figure 1. (a) A sketch of the SMA fin shown in its unheated, relatively soft martensite phase at a temperature below T_c. (b) The same SMA fin shown in its heated, relatively stiff austenite phase at temperatures above T_c. (c) Photo of an assembly of four such SMA fins in the new Vortigen concept.

joined this project in May 2003; his Master's thesis on experimental testing and characterization of the Vortigen system will be completed in Summer 2004.

Status: Over the last year, we have designed, built and tested an SMA-based actuation system for twisting a single vane through a twist angle up to 170º. This actuation system has been demonstrated in a working prototype of an adjustable twist rubber vane in a tube housing fabricated using sterolithography rapid prototyping.

A more robust system has been designed for pilot trials and final commercial implementation. The system uses four thin SMA vanes spaced evenly around the circumference of the Vortigen tube that twist through a fixed angle when heated above their transition temperature T_c (Fig. 1a) and return to an untwisted or straight configuration at temperatures below T_c (Fig. 1b). SMA of various compositions are commercially available with transition temperatures T_c ranging from about 20°C up to 90°C. Four of these vanes will be mounted symmetrically in the Vortigen tube (Figure 1c) and when twisted, will generate the axial vorticity or swirl required for microforming. This new Vortigen concept is more robust than the single-vane system because the vanes themselves are composed of the SMA, thereby greatly simplifying the vane actuation and swirl control systems.

We have presented the initial laser Doppler velocimetry (LDV) results comparing the mean streamwise velocity and its rms fluctuations at a Reynolds number of 75,000 based on average axial velocity and inner tube diameter for the new Vortigen concept at the 2004 TAPPI Paper Summit and Spring Technical Conference [C. K. Aidun, A. A. Islek, M. Parsheh and M. Yoda, The impact of turbulence and swirl on the flow in the tube bank part of a paper mill headbox, 21-1, 2004].

Currently, the SMA fins easily assume their "twisted" configuration when heated above their transition temperature. Returning the SMA fins to their straight configuration below this temperature, however, requires an external restoring force. We have evaluated two ways to obtain such a restoring force. First, we have fabricated a single prototype leaf spring from 0.60 mm thick stainless steel 304 that can be soldered to the SMA fin. Initial tests with the leaf spring alone, however, showed that the leaf spring would not be able to return the SMA fin to a straight configuration due to hysteresis. We are therefore focusing upon making SMA fins that are thin enough to be returned to their straight configuration by the hydrodynamic force

generated by the flow as it is turned by the twisted fins. Initial estimates suggest that the fins should be about 100 μm in thickness. We have therefore ordered three custom-fabricated thicknesses (100, 150 and 250 μm) of SMA fins from Memory-Metalle GmbH (Weil am Rhein, Germany) and expect delivery in 6 weeks.

We are also exploring two-way shape memory alloys, which do not require an external force to achieve reversible shape change. Components made of two-way SMAs assume a "twisted" configuration when heated to a temperature above their transition temperature (like one-way SMAs), but then return to their original shape on cooling without applying any external force (unlike one-way SMAs). Although the strains achieved in two-way SMAs are significantly less than those in one-way SMAs, these materials appear to be a promising technology for the new Vortigen concept. We are currently in discussions with a company, @ Medical Technologies NV (Herk-de-Stad, Belgium), that claims to have the capability to create two-way SMA fins using a proprietary thermo-mechanical process for "training."

We are also continuing LDV studies of the flow downstream of the SMA fins as well as the single-vane Vortigen concept, focusing upon measuring the azimuthal (*vs.* streamwise or axial) velocity component, which is critical for characterizing the swirl flow and accurately determining the swirl number at various downstream locations. Refractive index matching is required to overcome lensing effects due to the curved wall of the pipe and obtain accurate LDV measurements of this velocity component. We have just assembled a rectangular tank of optical glass filled with glycerin, a liquid whose refractive index is virtually identical to that of the pipe wall, and attached this box to the curved wall of the pipe, and plan to start measuring radial profiles of the azimuthal velocity component in the next week (Fig. 2).

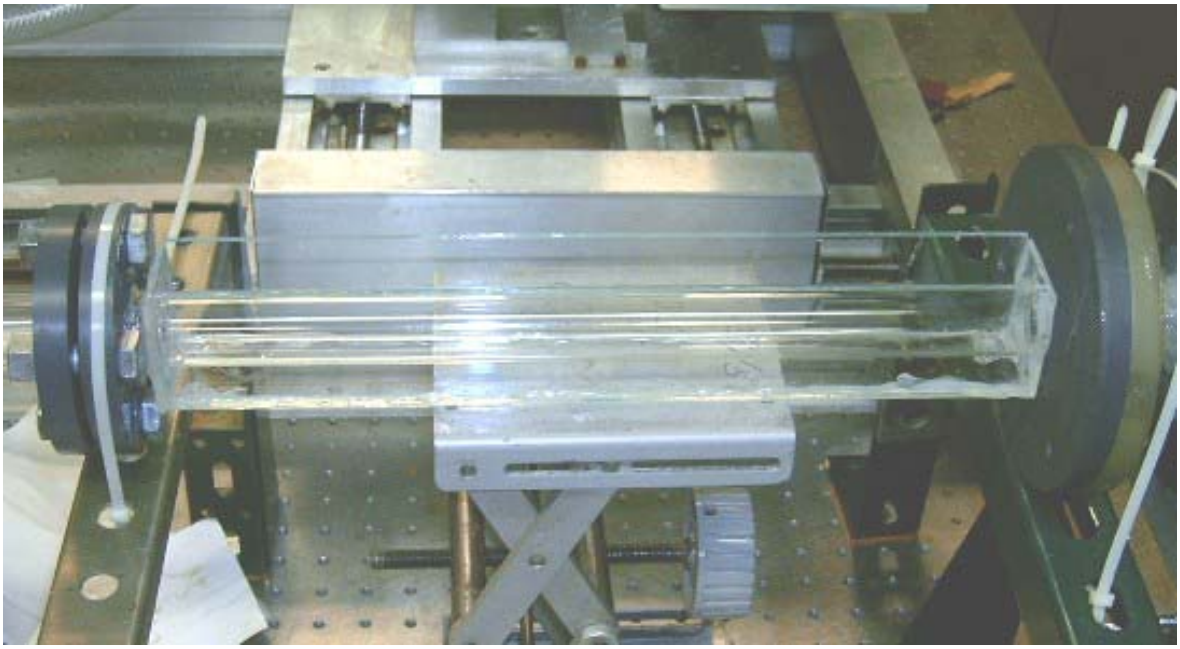

Figure 2 Flow loop test section with new refractive index matching tank. Most of the 34 cm long (axial extent) test section is contained within this glycerin-filled tank.

Plans for Next Quarter

We plan to finalize the design of the new Vortigen concept by: 1) exploring fabricating the SMA fins from two-way SMAs, thereby eliminating the requirement of an external restoring force to "straighten" the fins; and 2) testing SMA fins that are thin (100–250 μm thick) enough so that the hydrodynamic force generated by the flow as it is turned by the twisted fins will be sufficient to return the fins to their straight configuration.

We also plan to complete LDV studies of the flow downstream of the SMA fins in the new Vortigen concept as well as the single-vane Vortigen concept. These LDV studies, along with the final design of the new Vortigen concept, will be the basis of Mr. Akay Islek's Master's thesis (expected in August 2004) and a journal paper to be submitted to either the *Journal of Fluids Engineering* or *Experiments in Fluids*.

Milestone Status Table for the Development of the On-Line Field Control System

We have made good progress last quarter, exploring various design concepts for the new Vortigen geometry. To make sure the unit is practical for eventual commercial trials, we are spending more time than planned in lab experiments prior to pilot trials. The table for the updated schedule therefore reflects the additional time spent with the laboratory experiments.

TASKS	2003				2004			
Quarters→	1	2	3	4	1	2	3	4
Laboratory Experiments:								
Design/Fabricate Headbox & Tubes for the Tube Bundle (Complete)								
Headbox & Flow loop System Installation/Optimization (Complete)								
CFD Characterization (Complete)		√	√	√				
Laser-Doppler Turbulence Characterization								
System Installation/Optimization in Lab, Concept A		√	√	√	√	√	√	
Pilot Trials:								
Design/Fabrication for Pilot Trials, Concept A	√						√	√
Pilot Machine Installation/Trials, Concept A								√
Report at each milestone				√				√

The Lateral Corrugator

Schaepe: Institute of Paper Science and Technology

GO10616, CPS#01481

DOE QUARTERLY REPORT

For: An Improved Method of Manufacturing Corrugated Boxes: Lateral Corrugator

Covering Period: April 1, 2004 – June 30, 2004

Date of Report: August 2, 2004

Recipient: Institute of Paper Science and Technology at Georgia Tech

Award Number: DE-FC36-01GO10616 M3

Subcontractors:

Other Partners:

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Joseph Springer, joseph.springer@go.doe.gov
Carrie Capps, carrie.capps@go.doe.gov

Project Objective:

The goal of this project is to develop a commercially viable lateral corrugating process. This includes designing and building a pilot lateral corrugator, testing and evaluating the pilot machine, and developing a strategy for commercialization.

Background:

Since paper is non-isotropic and fibers tend to orient in the machine direction, machine direction (MD) compressive strength of paper exceeds that of the cross-machine direction (CD). In a conventional corrugator, the paper machine direction is perpendicular to the flute direction. Therefore, a typical corrugated container cannot take advantage of the stronger compressive strength of the paper machine direction.

Experiments conducted at IPST demonstrated that combined-board with the linerboard MD orientation in the transverse direction of the combined-board generated box compression strength improvements of 30% over conventionally oriented board. Yet, with the medium MD orientated conventionally, flat crush, handling toughness, and board rigidity were maintained. It was found

that a box utilizing 15% lighter materials with the linerboard transversely oriented generated a comparable stacking strength to a conventional box.

A method to produce combined-board with the linerboard oriented in the transverse direction has been considered. This method of box manufacturing could reduce fiber consumption 15% and improve the compressive strength to weight ratio of corrugated shipping containers considerably, thereby **significantly reducing energy usage both in manufacturing and transportation**. The technology to produce such a sheet would involve conventional fluting of the medium. The transverse orientation of the linerboard would be achieved through a sheeting operation. Single-facing and double-backing would again involve conventional but state-of-the-art corrugating technologies.

This project has been undertaken to construct a lateral corrugator and evaluate the resulting combined-board. The project will entail the development of a testing program, the design and construction of a pilot lateral corrugator, and the evaluation of conventional and lateral combined-board samples and boxes.

During the first year of this project two major program objectives were initiated. Heat transfer model development t aid in the design of the lateral corrugator preheating and adhesive curing systems was begun. Heat transfer modeling associated with this project is limited to the heat transfer mechanisms directly related to the lateral process. Heat transfer modeling is intended only as an aid for designing the unique aspects of the adhesive curing section of the lateral corrugator at the splicing and forming section. The heat transfer model is necessary for the design of the lateral corrugator.

Secondly, lateral corrugator design has been initiated. The design will proceed as a retrofit to the newly completed double-backer at the IPST Industrial Engineering Center. The glue applicator system will be a unique design to allow the use of high solids adhesives and single-face festoons will be eliminated from the corrugating process. Both of these unique design features will **reduce the energy requirements** to produce combined-board. Blanks produced on the pilot lateral corrugator will be of sufficient size to manufacture small boxes.

Budget Data:

Fourth Quarter: April 1, 2004 – June 30, 2004

Cost share this quarter:	$103,110
Total cost share:	$268,254
Federal dollars spent this quarter:	$ 80,454
Total federal dollars:	$166,637

Status:

To more clearly explain the advantages of lateral corrugating, the following general description of the results of an earlier experiment has been prepared. To achieve transverse orientation of the linerboard, paper rolls were sheeted, then turned 90 degrees and taped together to form butt splices. The rolls were converted on the commercial corrugator to produce combined board. In this fashion, lateral corrugated samples were obtained. It is noteworthy that the simulated lateral corrugated board was subjected to the entire converting process including corrugating, slitting and scoring, and printing on a flexo-folder-gluer.

Figures 1 and 2 present the results of these experiments. The figures show the relationship between combined board weight and performance. Therefore, the comparative strength of conventional and lateral corrugating can be determined. In Figure 1 for example, at 121 lbs/msf combined board weight (42-26-42 construction) the BCT strength for a shipping box made conventionally would be approximately 750 lbf. The lateral corrugated box would provide the 750 lb strength at 107 lb/msf (35-26-35 construction). That is 11.6% less fiber in total and 16.7% less linerboard fiber. Figure 2 shows the result if only the inside linerboard is turned transversely. Using the same example, the 121 lb/msf conventional box could be achieved with a 111 lb/msf lateral box (37-26-37 construction). That is a fiber savings of 8.3% in total and 11.9% linerboard savings.

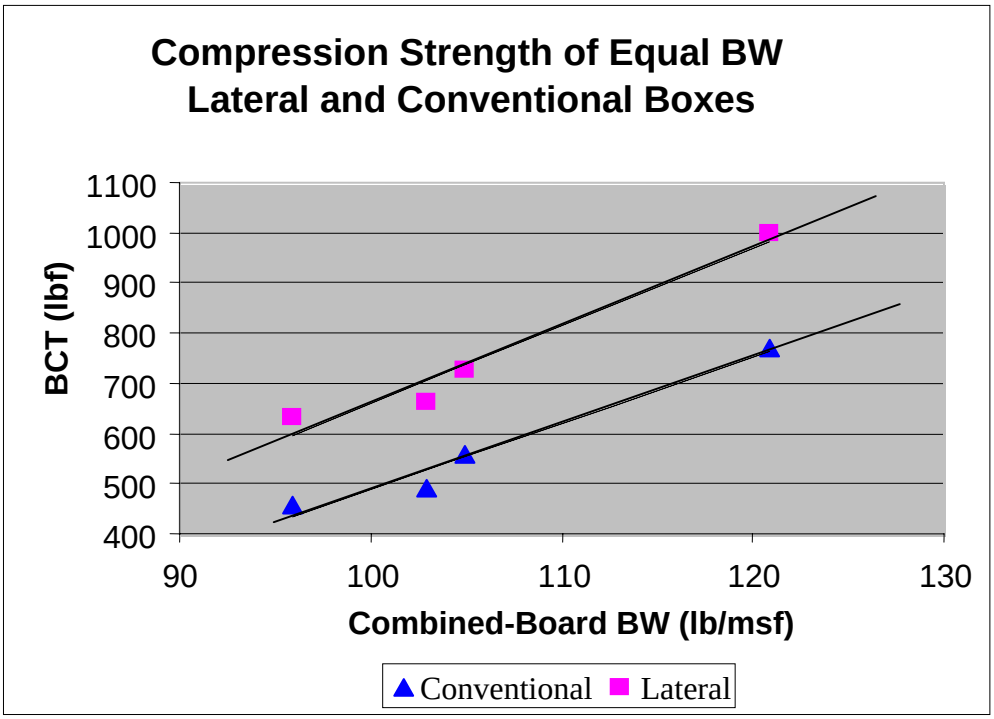

Figure 1) Box Compression strength of Conventional and Lateral Corrugated Boxes (Both Linerboards Transversely Oriented)

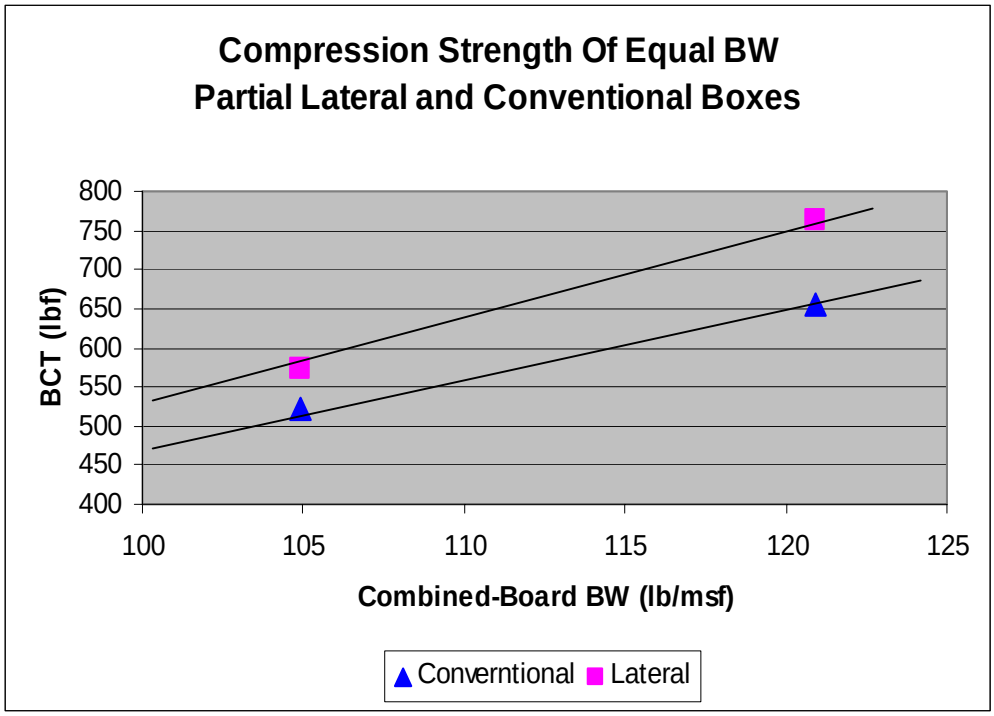

Figure 2) Box Compression strength of Conventional and Lateral Corrugated Boxes (Inside Linerboard Transversely Oriented Only)

With a lateral corrugator, single-face festoons will be eliminated. This unique design feature of the lateral corrugator will result in a reduction in the energy required to produce combined-board. Regarding productivity and waste, two factors will considerably influence the performance of the lateral corrugator. The first factor is the speed of present day sheeters and sheet feeders. The other is the ability to form usable splices. Sheeting and sheet feeding technology is well established in the paper industry. Existing equipment will be used for these operations on the lateral corrugator. It is expected that the sheeting and sheet feeding operations will not limit the speed of the lateral corrugator. The ability to form viable splices is the second factor influencing productivity and waste on the lateral corrugator. If usable splices are generated, waste will be reduced. With the cut-to-width sheeting operation of the lateral corrugator, paper roll management will be simplified and trim waste will be minimized. Since the paper is sheeted, matching paper roll widths will not be not necessary and trim waste can be precisely controlled.

Figure 3, with Cases 1 and 2, shows the advantages of the lateral corrugator cut-to-width concept. Case 1 shows the trim loses in conventional corrugating when roll widths are not matched and when order changes are made. Case 2 shows that for lateral corrugating these variables do not affect trim waste. With lateral corrugating trim waste remains optimal. Box plant waste is 3% to 10%. Trim waste is 2% to 4%. Lateral corrugating will save 50% to 75% of the trim waste presently generated at a box plant.

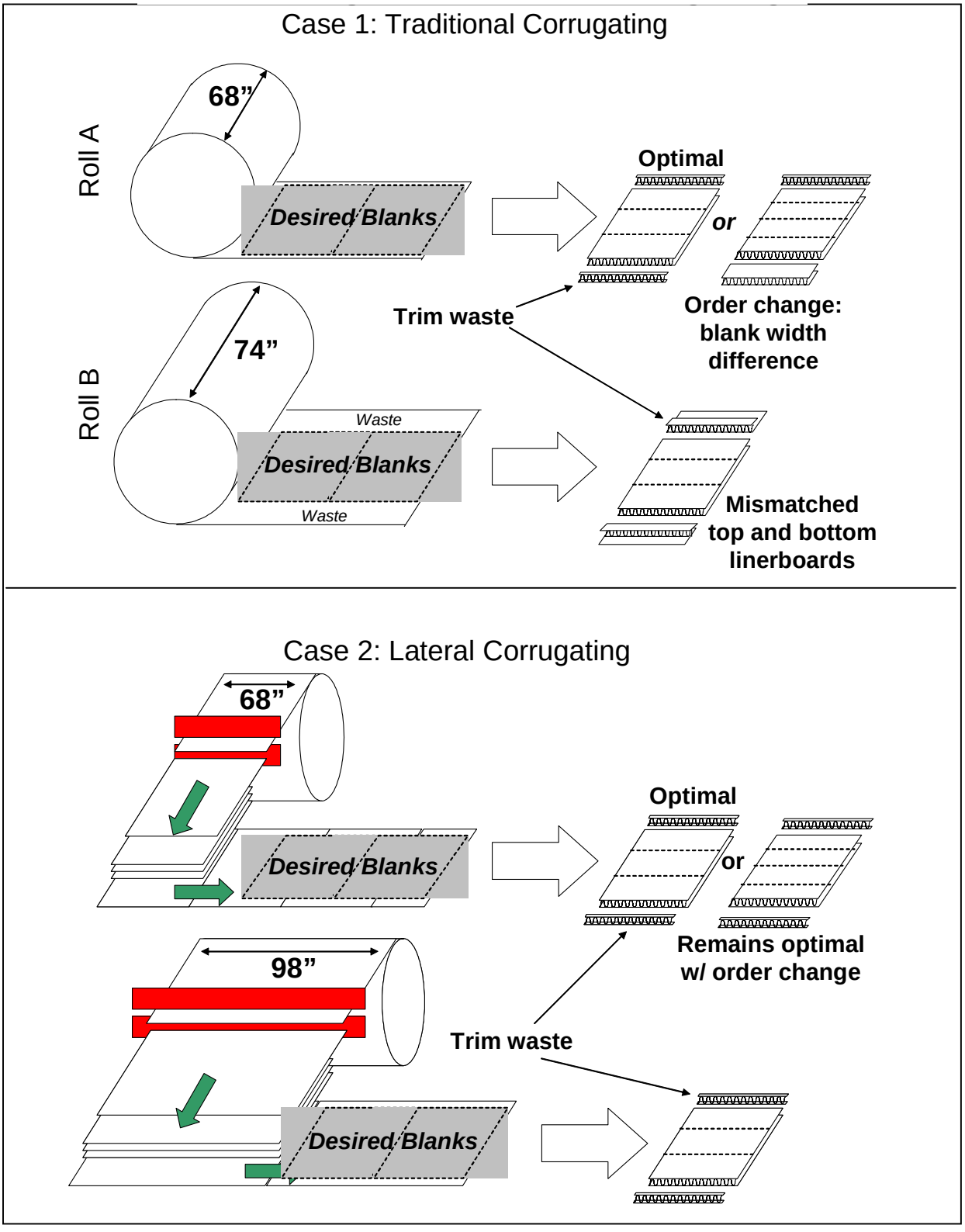

Figure 3) Trim Savings with Lateral Corrugating

The Institute of Paper Science and Technology will design a pilot lateral corrugator to retrofit its newly completed double-backer section. The design of the corrugator roll stack will be based on existing fluted rolls as originally fitted to the IPST pilot single-facer. Presently, IPST is building the pilot lateral corrugator. When completed the pilot machine will produce a finished combined-board sheet with a maximum width of 13 inches. The length of the sheet will be fixed at 66 inches based on the size of the double-backer cutoff section. Fingers will be used to hold the medium to the lower fluting roll. Pressure will be applied to the top and bottom rolls of the roll stack by a hydraulic system similar to that used on the existing pilot single-facer. Figure 4 is a recent picture showing the lateral corrugator frame, corrugating roll stack supports, and pre-heat rolls.

Figure 4) Lateral Corrugator Construction

Future Plans:

IPST will design feeding systems for precut linerboard sheets for the inner and outer facings of the combined-board. The systems will be designed to feed the sheets with overlapping edges to form a continuous web. The sheet feeding section and splicer will be integrated into the corrugating section presently under construction.

When completed, the pilot lateral corrugator will produce combined-board sheets about 13 inches wide by about 66 inches long as a finished product. The sheets will be of sufficient size to make small boxes. A test program will included the manufacturing of lateral corrugated and control boxes. The combined-board will be tested for flexural stiffness, flat crush, edge compression, and pin adhesion. Printability of the lateral corrugated material will also be investigated. Blanks will be converted into boxes and box compression testing will be performed. The performance of the lateral corrugator, evaluation of lateral corrugated boxes, and a comparison of lateral and conventional boxes will be provided in a final report.

Acknowledgements:

This research is made possible through a grant from the U.S. Department of Energy, the financial support of Inland Paperboard and Packaging and Smurfit-Stone, and contributions and consultation provided by the following companies: MarquipWardUnited, Corrugated Gear, Albany International, Armstrong, Container Graphics Corporation, CUE, Harper-Love Adhesives, The Johnson Corporation, and Corn Products International.

This research is the result of the hard work and efforts of the following individuals at IPST: Mark Szlemko, Robert Hall, Mark Urbin, Perry Arrington, Dr. Fred Ahrens, Dr. Timothy Patterson, and Dr. David White.

Laboratory Development of a High Capacity Gas-Fired Paper Dryer

Chudnovsky: Gas Technology Institute

GO10621, CPS#01484

QUARTERLY PROGRESS REPORT

Project Title: Laboratory Development Of A High Capacity Gas-Fired Paper Dryer

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 29, 2004

Recipient: Gas Technology Institute, 1700 S. Mount Prospect Road, Des Plaines, IL 60018

Award Number: DE-FC36-01GO10621

Subcontractors: Purdue University (professor R.Viskanta)

Other Partners:

Partner Company	Contact	Mailing Address	Cofunding
GTI Sustaining Membership Program	Vince Fiore Managing Director	1700 S. Mt.Prospect Rd. Des Plaines, IL 60018	CASH
Boise Paper Solutions	Donald E. Harrison Task Force Leader	P.O.Box 50 Boise, ID 83728	IN-KIND
Flynn Burner Corporation	Joseph DiGiacomo Sales Director	425 Fifth Avenue New Rochelle, NY 10802	IN-KIND
GL&V USA Inc.	Stan Green Engineering Manager	27 Allen Street Hudson Falls, NY 12839	IN-KIND

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Project Objective:

The primary objective of this project will be to provide experimental confirmation of the technical and economic feasibility of an innovative, low cost, natural gas-fired cylinder paper dryer which would be suitable for both retrofit and new installations.

Background:

The drying of paper requires the evaporation of 1.0 to 2.0 pounds of water per pound of paper or paperboard produced. The conventional drying method uses a series of approximately 5 ft diameter by up to 30 ft long metal cylinders, which are heated, from the inside by condensing steam. The use of steam requires the drums to meet ASME codes for pressure vessels, which limits the steam pressure to about 160 psig. Consequently, the shell temperature and the drying capacity are also limited. In practice, most cylinders operate at an even lower pressure and temperature, further reducing their drying capacity.

Paper drying is the most energy-intensive and temperature-critical aspect of papermaking. It is estimated that about 67% of the total energy required in papermaking is used to dry a paper[1]. Paper machine speeds, and therefore production rates, are frequently limited by dryer capacity. A great deal of activity has therefore been devoted to development of new, high efficiency, high rate paper drying equipment. One of the most effective approaches to improving paper machine drying capacity involves the use of natural gas-fired heating technology in place of and/or in addition to conventional steam cylinder dryers.

GTI is developing innovative approaches to natural gas-fired combustion systems designed for applications in paper dryers drying that can significantly improve the drying efficiency, decrease specific energy consumption and overcome the limitations of pre-mixing while still producing stabilized combustion. As illustrated in Figure 1 below, one of the approaches involves combusting natural gas and combustion air in hemi-spherical dimples. Natural gas is injected inside the cavity, while combustion air is supplied on the outside. As shown in Figure 1, the flow of combustion air generates a vortex in the cavity, which result in good mixing of natural gas and air and stabilize the combustion. Each fired cavity forms its own flame as shown in the photograph in Figure 2 that interact with the flames from other cavities forming the vortex flame pattern. Preliminary tests[2] have shown that combustion is stable over a wide range of air velocities.

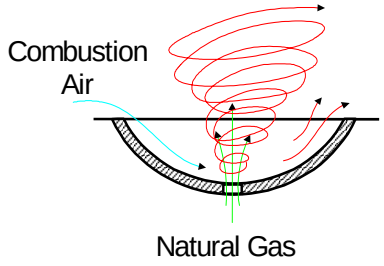

Figure 1. Vortex formed by combustion air flow results in intense gas-air mixing

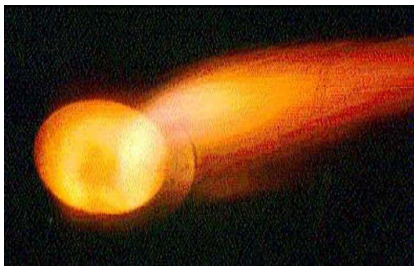

Figure 2. A highly stable flame is formed within each dimple

[1] B.Wilhelmsson. An Experimental and Theoretical Study of Multi-Cylinder Paper Drying. Ph.D.Thesis, Lund University, February 1995.

[2] Ya.Chudnovsky, A.Kozlov et al. Combustion Enhancement and Flame Stabilization Due to Vortex Generation. Proc. 1997 AFRC International Symposium "Combustion Technology for Improving Productivity and Product Quality", Chicago, IL, September 21-24, 1997

Another approach (see Figure 3) is comprised of the combination of sheet flame and a dimpled surface to provide low-emission recirculation flow and a high heat transfer rate from the combustion zone to the drying drum surface.

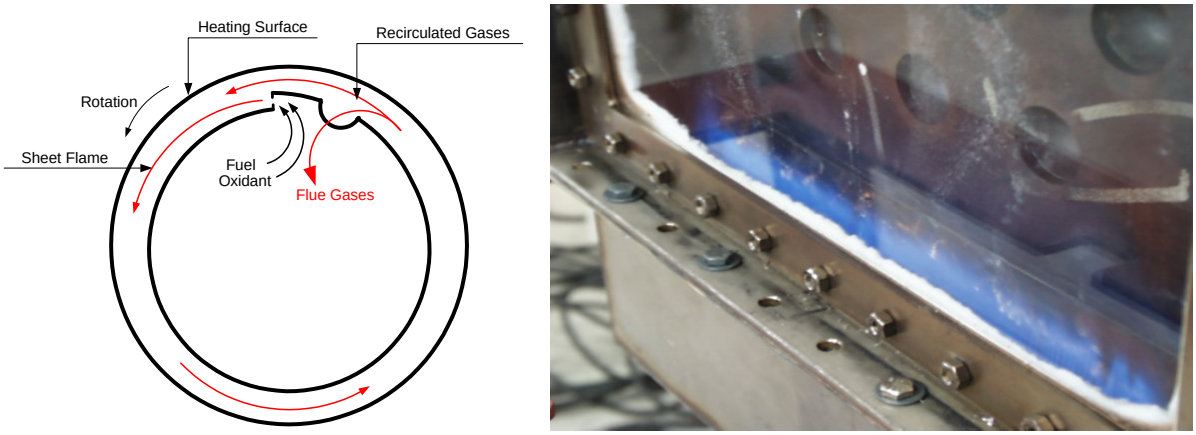

Figure 3. Concept and flame image of annulus combustion approach

Summary Status:

Two combustion concepts were developed and experimentally evaluated during the Phase I of the project. The results of Phase I were reported to Sponsors and Industrial Partners at the Project Review meeting that was held on 11-18-02 at GTI Headquarters, Des Plaines, IL and at the AF&PA Agenda 2020: Forest Products Breakthrough Technologies was held on 01-27-03 at Georgia Pacific Center, Atlanta, GA. The obtained results were considered as promising to proceed to Phase II.

Phase II was initiated and project partners GL&V USA and Flynn Burner Corporation (FBC) engineered a design of Gas-Fired Paper Dryer (GFPD) based on preliminary concept developed by GTI. The GFPD design review meetings were hold on 04-04-03, 07-10-03 and 08-15-03 (final design review) at FBC facility (New Rochelle, NY).

GTI reviewed the specifications of the Western Michigan University (WMU) pilot paper machine in which the GTI gas-fired drum to be installed and tested. Pilot-scale GFPD was fabricated and successfully evaluated at GTI Applied Combustion Laboratory using a specially designed simulation rig prior the installation at WMU paper machine. GTI has performed a baseline testing of drying section as well as pilot-scale testing of GFPD at WMU Pilot Plant:

- December 2003 – extensive two-weeks testing at drum #3 location;
- March 2004 - additional two-weeks testing at drum #7 location to explore the effect of GFPD optimal position in the drying section.

The results of entire pilot-scale GFPD testing were summarized in Technical Summary Report that was forwarded to project partners review.

Project results were presented at 2004 Paper Summit and DOE Peer Review Meeting (Georgia World Congress Center, Atlanta, GA, May 3-5, 2004).

The major findings of the project are to be presented at 2004 International Gas Research Conference (Vancouver, Canada, November 2004). The abstract was submitted and accepted for oral presentation.

Schedule Performance:

PHASE I: CONCEPT FEASIBILITY

Task 1. Bench-scale unit (BSU) design	– completed
Task 2. BSU fabrication	– completed
Task 3. BSU laboratory testing	– completed
Task 4. Data processing/analysis	– completed
Task 5. Technical report on Phase I	– completed

PHASE II: DEVELOPMENT TESTING

Task 6. Design of pilot-scale unit	– completed
Task 7. Fabrication of pilot-scale unit	– completed
Task 8. Laboratory testing of pilot-scale unit at GTI	– completed
Task 9. Pilot-scale testing at WMU's pilot-scale paper machine	– completed
Task 10. Data processing and analysis	– completed
Task 11. Technical report on Phase II /Final	– in progress

Plans for Next Quarter:

- Prepare final paper and presentation to be presented at 2004 IGRC (Vancouver, Canada)
- Draft Final Report preparation and forwarding it to project Sponsors' review
- Final Report is to be submitted to DOE for approval

Patents:

There no patent application was filed during the reporting quarter. US Patent Application for "Process and Apparatus for Indirect-Fired Heating/Drying" (No.10/454,021) was filed on 6-4-03. The first patent office action was received and response is under preparation.

Publications/Presentations:

Final results of the project were presented at US DOE/ITP Peer Review meeting (2004 TAPPI Paper Summit) in May 2004, Atlanta, GA

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
	PHASE 1			
1	Design of bench-scale unit	6/30/01	6/30/01	Completed
2	Fabrication of bench-scale unit	9/30/01	9/30/01	Completed
3	Laboratory bench-scale testing	12/31/01	5/28/02	Completed
4	Data processing and analysis	3/31/02	6/5/02	Completed
5	Technical report on PHASE 1	4/30/02	11/19/02	Completed
	PHASE 2			
6	Design of pilot-scale unit	6/30/02	08-15-03	Completed
7	Fabrication of pilot-scale unit	9/30/02	11-15-03	Completed
8	Laboratory testing of pilot-scale unit	12/31/02	12-05-03	Completed
9	Pilot-scale testing at WMU	3/31/03	12-19-03	Completed
10	Data processing and analysis	2/11/03	06-30-04	Completed
11	Technical report on PHASE 2 /Final	3/31/03	In progress	Expected by 09-30-04

Note:

The NCTE to 6/30/2004 (Final Report due by 9/30/04) was approved by US DOE (Contract Amendment No. M006 fully signed on 12/16/03)

Budget Data:

Phase / Budget Period			Approved Spending Plan, $			Actual Spent, $		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share*	Total
	From	To						
1	2/12/01	2/11/02	$300,000	$175,000	$475,000	$292,833	$ 98,972	$391,805
2	2/12/02	6/30/04	$400,000	$375,000	$775,000	$403,772	$435,390	$839,162
		Totals	$700,000	$550,000	$1,250,00	$696,605	$534,362	$1,230,967

* Actual spending of GTI-GRI-SMP budget for reported quarter was $21,020 (actual spending to 6/30/04 was $268,878). Industrial Partners' in-kind during the reported quarter: Flynn Burner (per J.DiGiacomo) confirmed their in-kind contribution as $6,813 (as of 6/30/04 - $58,870 adjusted with Eclipse's contribution). Boise Paper (per D.Harrison) confirmed their in-kind contribution as $200 (as of 6/30/04 - $93,941); GL&V (per S.Green) confirmed the in-kind as $17,900 (as of 6/30/04 - $112,673).

Acoustic Forming for Enhanced Dewatering and Formation

Aidun: Institute of Paper Science and Technology

ID14267, CPS#01703

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

QUARTERLY REPORT

Agenda 2020 Research Area(s): **Energy Performance,**
Area 1: New Approaches to Drying and Water Removal

Project Title: ACOUSTIC FORMING FOR ENHANCED DEWATERING AND FORMATION

Covering Period: Jan 1, 2004 through April 1, 2004

Date of Report: June 22, 2004

Recipient: Institute of Paper Science and Technology at Georgia Tech.
500 Tenth St., NW; Atlanta, GA 30332-0620

Award Number: DE-FC07-02ID14267

Contact: Cyrus K. Aidun, PI

Principal Investigator: Cyrus K. Aidun,
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Georgia Institute of Technology
500 10th St. NW, Atlanta, GA 30332-0620,
(404) 894-6645, Fax 4778, **cyrus.aidun@me.gatech.edu**,
Georgia 5th Congressional District.

ABSTRACT:

The next generation of forming elements based on acoustic excitation to increase drainage and enhances formation both with on-line control and profiling capabilities will be developed in this project. The system will be designed and optimized based on the fundamental experimental and computational analysis and investigation of acoustic waves in a fiber suspension flow.

PROJECT TITLE:

ACOUSTIC FORMING FOR ENHANCED DEWATERING AND FORMATION

PRINCIPAL INVESTIGATOR: Cyrus K. Aidun, Professor, School of Mechanical Engineering, Georgia Institute of Technology, 500 10th St. NW, Atlanta, GA 30332-0620, (404) 894-6645, Fax 4778, **cyrus.aidun@me,gatech.edu**, Georgia 5th Congressional District.

RESEARCH AREA(S) IN THE SOLICITATION TO WHICH THIS WORK IS FOCUSED: ENERGY PERFORMANCE, Area 1: New Approaches to Drying and Water Removal

1. Introduction

When ultrasonic waves are applied to pulp fibers in a liquid suspension, the fibers move away from the source due to the acoustic force acting on the fibers. The acoustic force consists of three major forcing mechanisms acting on a fiber. These are acoustic radiation, acoustic streaming, and cavitation bubble-induced force. These mechanisms are inter-dependent and nonlinear as well as frequency-dependent. It is the combination of all three forces that contributes to the manipulation of pulp fibers suspended in liquid. We propose to use this effect at the early stages of the forming table to generate controlled normal force on the fiber mat in the forming section to: (a) re-fluidize the fibers in the fiber mat to increase the drainage rate, (b) generate controlled activity on the forming wire to enhance formation, and (c) through sectional excitation, profile the sheet for more uniform moisture profile.

In the forming section, foils and suction boxes are used for dewatering of the pulp suspension delivered from the headbox. As soon as the forming jet impinges on the forming board, a layer of concentrated fiber mat forms on the forming wire. It has been demonstrated that by re-fluidizing the fiber mat at the early stages of the forming table, the dewatering rate increases resulting in additional drainage capacity along the same length of the forming section. Furthermore, it is demonstrated that this action enhances formation of the sheet by generating additional activity on the wire with benefits in quality and fiber savings (1). This application is currently limited to the use of undulating foils on slow speed machines. Although effective, there is lack of control on the current system once the foils are placed in the forming section. These limitations make the current technology to be effective only from time to time depending on the process conditions. Replacing the undulating foils with the acoustically excited foils has the advantage of superior control and on-line optimization capability for any given grade or process condition.

Impedance matching between the acoustic transducer, the forming wire and the fiber mat is critical to the success of this technique. There is a fundamental impedance mismatch

between the three components and the interaction between the three is driven by acoustic frequency and intensity, wire wetting (2, 3), wire weave (4) and fiber geometry (5). As this interaction is highly complex and non-linear it must be investigated experimentally. This paper presents the results of a series of experiments to quantify the effect of high intensity ultrasound on a wood fiber mat in water. The results presented in this paper provide information on power intensity and pulse duration. Additional experiments are required to optimize the system for actual commercial wires.

2. Method

Results from earlier work indicate that the acoustic pressure exerted by a transducer on an absorber in the near field, 5-15 cm from the transducer face, increases exponentially with decreasing distance from the face and is at a maximum at a transducer frequency of 150 kHz. Thus for these tests the setup is confined to 150 kHz transducer mounted immediately beneath the forming wire.

A clear Plexiglas test cell was constructed with a 5 cm by 10 cm rectangular 150 kHz Sonic Concepts hydro-acoustic transducer mounted at the bottom. The cell was filled with plain tap water and the top surface was left open to the air. A fiber mat was formed by moving a 5 cm by 10 cm forming wire sample vertically through a suspension of softwood pulp resulting in a mat about 1 mm thick resting on top of the wire. The wire was placed at the bottom of the water filled cell, resting on the transducer surface, and tacked to the cell wall around its edges. A sequence of four identical acoustic pulses, triggered at one second apart, was emitted beneath the wire and the resulting fiber mat disruption was recorded using a Kodak Model 1000 HRC high speed digital video camera at 250 frames per second. Pulse duration was varied between 30, 60 and 90 milliseconds to simulate changes in wire speed or transducer size, and thus residence time of the fibers above the emitter on a paper machine, and transducer power input were varied from 2 to 10 Watts per square centimeter of transducer surface. Two different forming wires were tested. The first wire, a 4.5 mil 150 mesh metal wire, was chosen to minimize the wire impedance and investigate acoustic interaction with the fiber mat. The second wire, an 18 mil 80 mesh synthetic wire, was chosen to more closely model a commercial forming wire.

A refluidization parameter, α, was developed based on analysis of each frame of the high speed digital video. After each test the camera contained 1365 frames of 512 by 384 pixel 8 bit grayscale image data showing the test cell, fiber mat and surrounding area. Each frame in turn was cropped to show only those pixels inside of the test cell. The frame was then binarized and a pixel count established the ratio between the image space occupied by fibers and that occupied by fluid. The refluidization parameter was then defined such that it was equal to zero, when this pixel ratio was equal to the ratio before the first impulse was triggered, and one if every pixel in the image was occupied by a fiber. This allowed a quantitative comparison between the relative ability of the different pulse durations and strengths to disrupt the fiber mat.

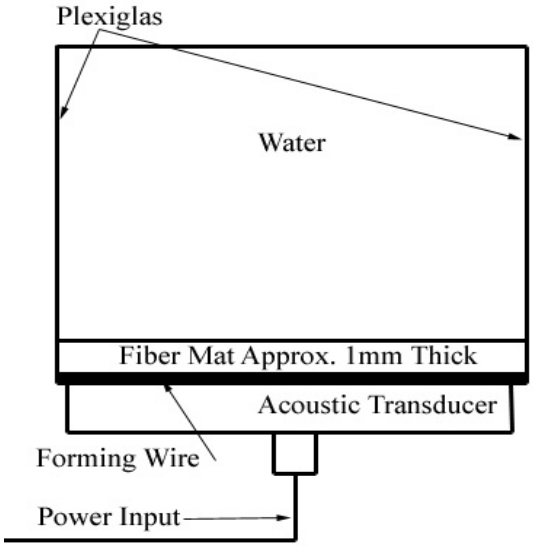

Figure 1. Schematic of the test setup.

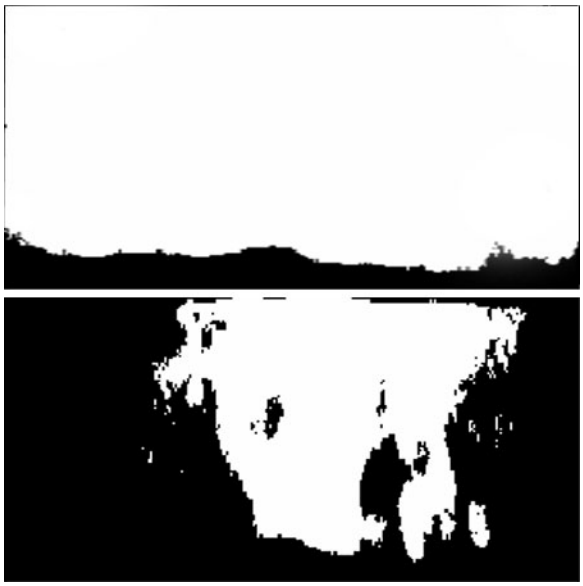

Figure 2. Comparison between an undisturbed mat, $\alpha = 0$, at the top and a refluidized mat, $\alpha = 0.5$, on the bottom after four pulses.

3. Results

The most extensive tests were conducted on the 150 mesh wire with each pulse duration tested at each power level. It was shown that holding power constant at 8 Watts/cm^2 a pulse duration of 60 ms or longer was sufficient to substantially refluidize the mat after four impulses. No additional refluidization was realized by longer pulses. A pulse duration of 30 ms served to somewhat refluidize the mat but the effect was much less than the 60 ms pulse. Holding the pulse duration constant at 60 ms, a power of 8 Watts/cm^2 or greater was sufficient to substantially refluidize the mat with no noticeable refluidization at 2 Watts/cm^2 and only minor effects at 4 or 6 Watts/cm^2.

With the second wire we considered the effect of wire impedance and the consequent reduction in acoustic energy reaching the fiber mat. The increased impedance was enough to prevent refluidization at all but the highest power levels and longest impulse times with a greater than 50% reduction in refluidization even at these levels.

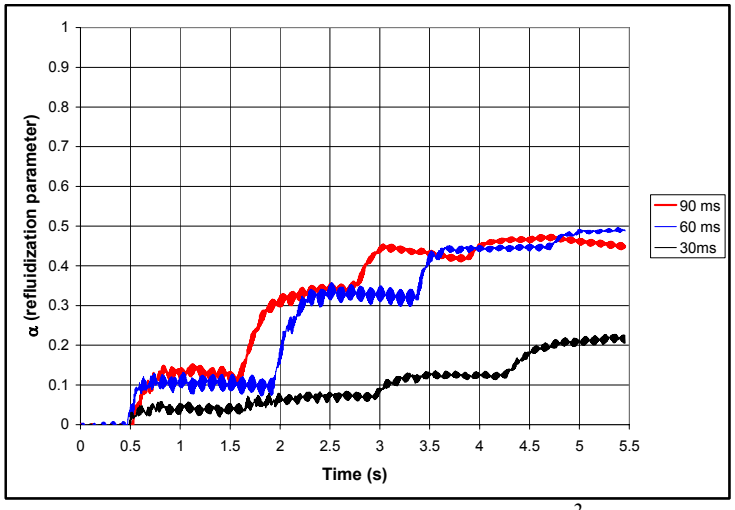

Figure 3. Refluidization on the metal wire at 8 Watts/cm^2 varying pulse duration.

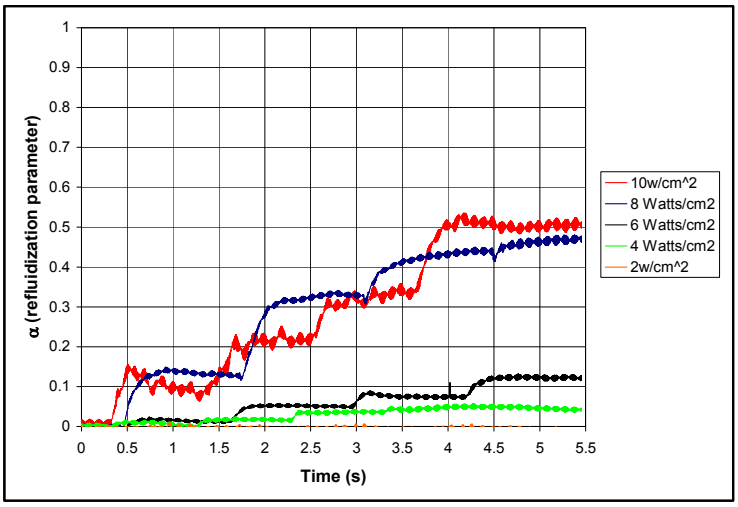

Figure 4. Refluidization on the metal wire with a 60 ms pulse duration varying power.

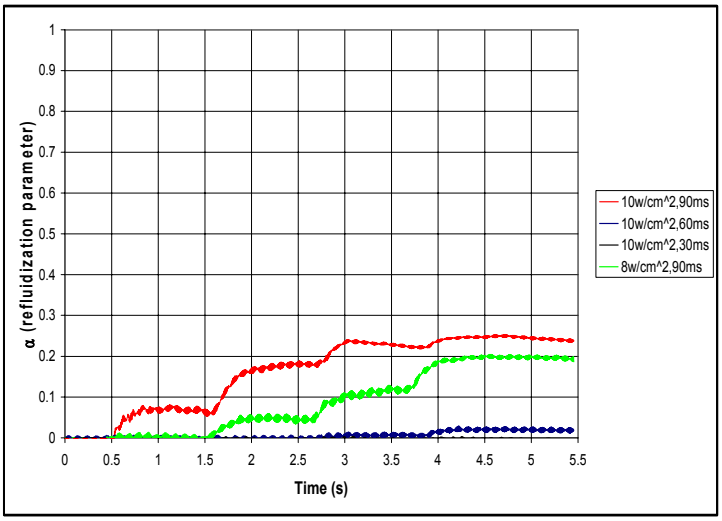

Figure 5. Refluidization on the 80 mesh wire at varying power and impulse durations.

4. Conclusions

It has been shown that pulsed 150 kHz ultrasound has the ability to significantly disrupt and refluidize a wood fiber mat in water with pulse durations of 60 ms or greater and power input levels of 8 Watts/cm^2 or greater. The imposition of a wire with characteristics of a commercial forming wire between the transducer and fiber mat causes an impedance mismatch which significantly attenuates the refluidization but does not completely prevent it at high power levels and long pulse durations. Further work to match the transducer impedance to the forming wire and to increase the efficiency of converting electrical power to acoustic power should greatly enhance the ability to disrupt mats through realistic forming wires and at pulse durations comparable to the residence time of a fiber over the transducer head on a high speed forming section.

5. References

1. Sondegren, O. F. and J. A. Neun, 'Developments in Activity Generation on Fourdriners', TAPPI Journal, Vol 83 (10), 2000
2. Datar, G. V., P. Banks-Lee and P. L. Grady, 'Acoustical Properties of Fabrics in Low-Intensity Ultrasound', Applied Acoustics, Vol 47, 345-350, 1996
3. Datar, G. V., P. Banks-Lee and P. L. Grady, 'Acoustical Properties of Fabrics in High-Intensity Ultrasound', Applied Acoustics, Vol 48, 33-45, 1996
4. Shoshani, Y. and G. Rosenhouse, 'Noise Absorption by Woven Fabrics', Applied Acoustics, Vol 30, 321-333, 1990
5. Brodeur, P. 'Motion of Fluid-Suspended Fibres in a Standing Wave Field', Ultrasonic, Vol 29, 302-307, 1991

PROGRESS DURING THE LAST PERIOD

During the last three months we have focused on setting up the experiments for investigation of the acoustic wave with the wire. A microscope with appropriate optics and visualization methods are being assembled to visualize the flow of fluid due to acoustic wave interaction in a porous surface, simulating the wire of a paper machine. The new Ph.D. student, Hong Sun is working on this project with assistant engineer Paul McKay and the PI.

QUANTIFIED BENEFITS TO THE INDUSTRY SHOULD THE RESEARCH YIELD PROMISING RESULTS:

The economic benefits of the acoustic dewatering technology are machine and grade dependent. The estimated savings with this technology are based on conservative numbers of 10% improvement in formation, 10% reduction in MD/CD tensile ratio, and 5% improvement in rate of drainage. The IPST economic model contracted from Jaakko Pöyry is used by Dr. David White, Assistant VP of Technology Transfer at IPST, as presented in Attachment I.

It is estimated that the drainage on the wire can be increased by 5% or more with the addition of an acoustic foil. The increase in drainage results in increased productivity and lower cost. Also, formation can be improved by 10% or more and the MD/CD ratio in tensile can be decreased by about 10%. Formation improvement results in enhanced quality in printing and other converting processes, as well as increase in strength properties, such as burst, with consequent reduction in basis weight. This would yield fiber savings (per unit area of product), a commensurate reduction in drying energy, and some further energy savings due to reduced over-drying of lighter weight areas in the sheet. The savings in fiber cost are estimated at $5.4 million Dollars per year ($3.4 MM in fiber savings and $2 MM in energy savings) for a 1000 ton/day machine. The benefits of 5% increase in drainage, based on use of the IPST Economic Model, results in increase in operating profit (revenues – costs – depreciation) of 12 million Dollars per year or $34/FMT. The annual cost of the electric power to operate the acoustic foil is estimated at $10,880 (= .0035 KW/$cm^2$ * 20x600 cm^2* 24Hx360D * $.03 per KWH). The cost of an acoustic foil is estimated at $250K per element; a small capital investment with an ROI of 2 to 3 months.

SCHEDULE, Milestones, Go/No-Go Decision Points, and Other Measures of Success Including a Path to Commercialization

Project Description / Tasks	Research Tasks for Oct. 1, 2003 to Oct 2004															
	1st				2nd				3rd				4th			
1. Laboratory experimental setup, and experimental investigation of the impact of acoustic waves on individual fibers in a dilute fiber suspension flowing over a porous surface **(IN PROGRESS)**	-	-	-	-	-	-	-	-	-							
2. Development of the lattice-Boltzmann method for analysis of the impact of acoustic waves on individual fibers in the fluid **(COMPLETED LAST YEAR)**																
3. Application of the lattice-Boltzmann method for investigation and optimization of the parameters in fiber suspension flow during forming (IN PROGRESS)				-	-	-	-	-	-	-	-	-	-	-	-	-
4. Experimental setup, and experiments with a microscope to evaluate the acoustic wave interaction with the wire, and on a slow moving screen with an acoustic foil to design and optimize the most effective acoustic foil system					-	-	-	-	-	-	-	-	-	-	-	-
5. Design of an acoustic foil for pilot applications															-	-
6. Implementation on a pilot machine **(2005)**											-	-	-			
7. Implementation on a high-speed pilot machine **(2005)**														-	-	
8. Design of a system for commercial implementation **(2006)**															-	-
9. Final report **(2006)**																-

Fibrous Fillers to Manufacture Ultra High Ash / Performance Paper

Mathur: G.R. International, LLNL

ID14439, CPS#01872

As of August 16, 2004, the PI has not submitted an updated status report for the period ending June 30, 2004. The following is the most recent report submitted:

QUARTERLY PROGRESS REPORT

Project Title: Fibrous Fillers to Manufacture Ultra High Ash/Performance Paper

Covering Period: January 1st, 2004 through March 31st, 2004

Date of Report: April 30th, 2004

Recipient:
G.R. International
32918 6th Ave. S.W.
Federal Way, WA 98023

Award Number: DE-FC36-013ID14439

Subcontractors:
Lawrence Livermore National Laboratory
Livermore, CA 94550
Contact: Brian Vianni (925 423-2001)

Western Michigan University
Kalamazoo, MI 49008-5162
Contact: Margaret Joyce (269 276 3500))

Other Industrial Partners:
Weyerhaeuser Company
Federal Way, WA 98063-9777
Contact: Dr. Larry D. Erickson (253 924-6957)

Grays Harbor Paper Company
Hoquiam, WA 98550
Contact: Bill Quigg (360 538-5636)

Ferenco Corporation
Vancouver, WA 98685
Contact: William G. Ferguson (360 573-1123)

Contact(s):
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Phone: (253) 874-1067
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Project Team: Ozokwelu (DOE Hdqtr), Springer (CO), Dwyer (CO), Campell (AF&PA), Thorp (Ind)

Project Objective (FY03): The main objective of this project is to verify the techno-economic viability of manufacturing GRI's novel calcium silicate "Fibrous Fillers" in paper industry.

The other objectives of this project are:

a) to manufacture a paper composite where up to 40 - 50% natural fiber is replaced with calcium and silica based pigments ("Fibrous Filler");
b) to reduce the cost of production of paper;
c) to reduce environmental load in the paper mill; and
d) to reduce overall energy consumption.
e) to produce value-added paper products;

Additional Project Objective (FY 04): Based on input from the DOE/AF&PA Review Team, we have added yet another objective. This is to develop a low cost calcium silicate, which will cost equal to, or lower than, pulp delivered to the headbox (~ $300/ton).

Additional Project Objective (FY 04): In order to meet the main objective we need to build a prototype plant to manufacture "fibrous fillers."

Background:

- Industry Needs

The paper industry is faced with escalating costs of manufacture, shrinking margins, and challenges to reduce energy consumption and environmental load. The industry needs a breakthrough technology solution to meet these challenges.

- GRI's Solution

GRI has developed a series of calcium and silica based fillers, collectively referred to as **"Fibrous Fillers"**. These products share similar properties, such as low bulk density and a large secondary particle size. It is the primary structure, however, which sets our two products apart. The first product, Silicate Nano-Fibers (SNF), consists of long, thin, needle-like "nano-fibers" with aspect ratios between 50:1 to 100:1, joined together into spherical agglomerates. The second is referred to as silicate macro-particles (SMP), characterized by a series of nano particles intergrowths, formed into a continuous, globular structure. The unique product attributes of SNF provide much improved optical properties with minimal strength loss, while SMP provides exceptional sheet bulk with higher strength and stiffness. The combination of these fillers imparts superior paper properties, which include improvements in sheet bulk, smoothness, porosity, stiffness, brightness and opacity, simultaneously. These "Fibrous Fillers" have also been shown to outperform conventional fillers at equivalent and higher usage levels.

- GRI's Approach

GRI has already succeeded in producing these pigments in lab scale and industrial scale. It is has also demonstrated their unique performance attributes in paper. Our current focus is to scale up the manufacturing of "Fibrous Fillers" on a commercial scale reactor, the application of "Fibrous Fillers" in paper (proof of concept), and to increase the fundamental knowledge of pigment manufacturing and the mechanism of its performance in paper. With this in view, our approach is to run a parallel program consisting of the following:

a) to scale up production of "Fibrous Fillers" to commercial scale
b) to evaluate the performance of "Fibrous Fillers" on a commercial paper machine; and

c) to study the reaction mechanisms of pigment preparations and interactions.
d) To study the mechanism of pulp and fibrous filler interaction

GRI has entered into an agreement with another pigment manufacturer to carry out experiments necessary to scale up the manufacturing of "Fibrous Fillers" from GRI's 30 gallon pilot reactor to a full commercial scale, 10,000 gallon reactor. The material produced from the full scale reactor will then be used for production scale paper machine trials. These trials are conducted with our industry partners like Gray's Harbor Company and Weyerhaeuser Company. GRI is collaborating with Lawrence Livermore National Laboratory to study the mechanism of silicate formation and fiber-"Fibrous Filler" interactions. Western Michigan University has agreed to work with GRI to examine the application of "Fibrous Fillers" in paper coatings.

Status:

The major work done during this quarter is described below.

TASK I (GRI): Optimization of Manufacture of Silicate Nano-Fibers (SNF, TiSil, or T-8) and Silicate Macro-Particle (SMP, or T-4)

Task I.2.1 Process Modeling: Empirical process models and response surface analysis employing the technique of designed optimization experimentation (DOE)

Objective:

To evaluate the effect of Calcium / Silica Ratio, reaction temperature, batch concentration, and agitator RPM on all paper properties – both physical and optical.

Design of Experiment:

This was a 4 factor experiment at 2 levels. Three center points were ran to detect curvature of the responses. This gave us a total of 11 runs. This is fractional factorial design (Resolution IV) - which means that all main effects were evaluated independently. Interactions were confounded with one another (see alias structure below). However, there are several statistical tools that can help evaluate interactions independently after the experiment. This was a randomized design. The table below outlines the run conditions. The responses for the experiment were all fibrous filler and paper properties. Results were evaluated in Minitab at the 90 percent confidence level.

Table 1. The design of experiment conditions.

Run Order	Batch Number	Ca/Si Ratio	Temperature C	Concentration (lbs/gallon)	Reactor RPM
1	WX065	1.25	250	0.25	350
2	WX066	1.35	250	0.25	150
3	WX067	1.35	230	0.25	350
4	WX069	1.25	250	0.4	150
5	WX070	1.25	230	0.4	350
6	WX071	1.35	250	0.4	350
7 (center)	WX072	1.3	240	0.325	250
8	WX073	1.25	230	0.25	150
9 (center)	WX074	1.3	240	0.325	250
10	WX075	1.35	230	0.4	150
11 (center)	WX076	1.3	240	0.325	250

Fractional Factorial Design Specifics

Factors: 4
Runs: 9
Blocks: 1
Base Design: 4, 8
Replicates: 1
Center pts (total): 1
Resolution: IV
Fraction: ½
Centerpoint repeated twice for a measure of error.

Design Generators: D = ABC

Alias Structure
A + BCD
B + ACD
C + ABD
D + ABC
AB + CD
AC + BD
AD + BC

Fibrous Filler (SNF) Testing:

The results of testing the product produced according to the experimental plan are given in Table 2.

Table 2. Product testing results.

Log #	Sample	Particle Size Distribution (micron)			XRD Analysis	Surface Area (m^2/g)
		D10	D50	D90		
29765	WX 065	13.7	20.5	29.3	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	11.31
29766	WX 066	22.1	35.8	50.7	Pure Foshagite ($Ca_4(SiO_3)_3(OH)_2$)	6.27
29767	WX 067	12.7	19.6	30.1	Amorphous Phase + Foshagite ($Ca_4(SiO_3)_3(OH)_2$)	11.48
29768	WX 068	13.6	20.5	29.0	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	11.15
29769	WX 069	16.8	24.3	37.7	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	11.49
29770	WX 070	9.1	14.9	21.9	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	21.34
29771	WX 071	8.4	14.5	21.8	Pure Foshagite ($Ca_4(SiO_3)_3(OH)_2$)	16.01
29772	WX 072	15.2	21.9	30.4	Pure Foshagite ($Ca_4(SiO_3)_3(OH)_2$)	12.54
29773	WX 073	17.8	31.2	45.5	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	11.84
29774	WX 074	16.6	23.0	31.8	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	11.16
29775	WX 075	17.4	27.1	41.8	Pure Foshagite ($Ca_4(SiO_3)_3(OH)_2$)	11.16
29776	WX 076	17.0	23.0	31.5	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Unidentified crystalline phase	12.10
29777	WX 077	16.4	21.9	30.0	Foshagite ($Ca_4(SiO_3)_3(OH)_2$) + Slight unidentified crystalline phase	11.66

The silicate nano-fibers were tested for particle size distribution, different phase composition by x-ray diffraction analysis (XRD) and surface area using a B.E.T. analyzer.

Testing and Key Findings

Particle Size Distrubition. The mean particle size (d_{50}) of the secondary agglomerate of silicate nano-fiber varied from a low of 14.9 microns to a high of 35.8 microns depending upon the experimental conditions employed.

X-Ray Diffraction Analysis. The phase composition of silicate nano-fibers varied considerably. In most cases, the predominant phase, as desired, was foshagite (with some other minor crystalline phases). However, in the experimental condition employed in reaction WX067 gave predominantly an amorphous phase with only some foshagite.

Surface Area (m^2/g) (B.E.T. Method). The surface area of the SNF varied from a low of ~6.27 m^2/g to a high of 21.34 m^2/g, once again depending upon the experimental conditions employed.

In summary, the SNF product quality responded to variation in process conditions as expected.

Silicate Nano-Fiber Performance in Paper

These eleven batches of SNF were used to make handsheets at 15, 20 and 25% ash levels. The resulting sheets were conditioned, calendared and tested for various key paper properties like sheet opacity, brightness, scattering coefficient of the filler, bulk, porosity, smoothness, etc. The test data was interpolated to a 20% ash level. The results are placed in Table 3a and Table 3b.

Table 3a. Paper testing data used for the statistical modeling.

Description	Ash Level (520 C) (%)	Basis Weight (gsm)	Calendered Caliper (mils)	Calendered Bulk (cc/g)	Calendared Gurley Porosity (sec/100cc air)	Calendared Haggerty Smoothness (Sheffiled Units)		Gurley Stiffness (mg)
						Front	Back	
Control	0.0%	74.4	5.0	2.010	4.0	245	246	122
PCC (HO)	20.0%	74.2	4.8	1.628	4.9	193	197	77
WX065	20.0%	75.0	5.2	1.747	27.7	126	146	88
WX066	20.0%	75.2	5.3	1.794	19.7	106	112	85
WX067	20.0%	75.3	5.1	1.714	25.9	171	170	107
WX069	20.0%	73.9	5.1	1.752	19.9	126	139	95
WX070	20.0%	74.3	5.0	1.721	33.9	118	131	88
WX071	20.0%	73.8	5.1	1.753	34.4	128	143	85
WX072	20.0%	75.7	5.3	1.765	27.5	118	129	88
WX073	20.0%	72.7	5.0	1.740	21.8	120	126	81
WX074	20.0%	74.1	5.2	1.792	24.1	107	115	91
WX075	20.0%	73.6	5.2	1.803	20.7	119	130	92
WX076	20.0%	73.8	5.1	1.763	22.6	113	125	84

Table 3b. Paper testing data used for the statistical modeling.

Description	Ash Level (520 C) (%)	Basis Weight (gsm)	Tensile Index (Nm/g)	Brightness (ISO)	Normalized Opacity (to 74 gsm)	Scattering Coefficient of the sheet	Scattering Coefficient of the filler
Control	0.0%	74.4	32.0	87.7	80.5	393	N/A
PCC (HO)	20.0%	74.2	16.1	90.3	88.2	678	1784
WX065	20.0%	75.0	19.0	91.2	91.6	926	2984
WX066	20.0%	75.2	16.1	91.5	92.3	999	3429
WX067	20.0%	75.3	21.7	89.1	85.3	535	1112
WX069	20.0%	73.9	18.2	91.2	91.4	924	2959
WX070	20.0%	74.3	16.9	91.4	91.4	922	3026
WX071	20.0%	73.8	16.7	91.4	90.9	888	2872
WX072	20.0%	75.7	17.5	91.8	91.2	928	3003
WX073	20.0%	72.7	19.3	91.2	90.7	876	2957
WX074	20.0%	74.1	18.0	91.5	91.7	958	3186
WX075	20.0%	73.6	19.0	91.1	91.1	884	2832
WX076	20.0%	73.8	19.9	91.6	91.4	943	3237

Statistical Analysis of Data Using Minitab:

In this analysis, the process conditions employed to manufacture nano-fibers were correlated to SNF in paper resulting in mathematical models. An example of the mathematical models correlating process condtions and normalized opacity is given in the following opacity example.

Opacity = 468.8 – 1.5 T – 0.12 R – 367.7 Ca/Si + 330 S + 0.00049 T*RPM + 1.48 T*Ca/Si – 1.35 T*S

where the independent variables are:

	Levels		
	-	0	+
T = Temperature [=] °C	230	240	250
R = Impeller Speed [=] RPM	150	250	350
Ca/Si = Ca/Si Ratio [=] Molar Ratio	1.25	1.30	1.35
S = Reaction Solids Concentration [=] Pounds/Gallon	0.25	0.325	0.40

Main Effects: The effect of each above independent variable on fibrous filler quality, which in turn, affects normalized paper opacity are shown in Figure 1.

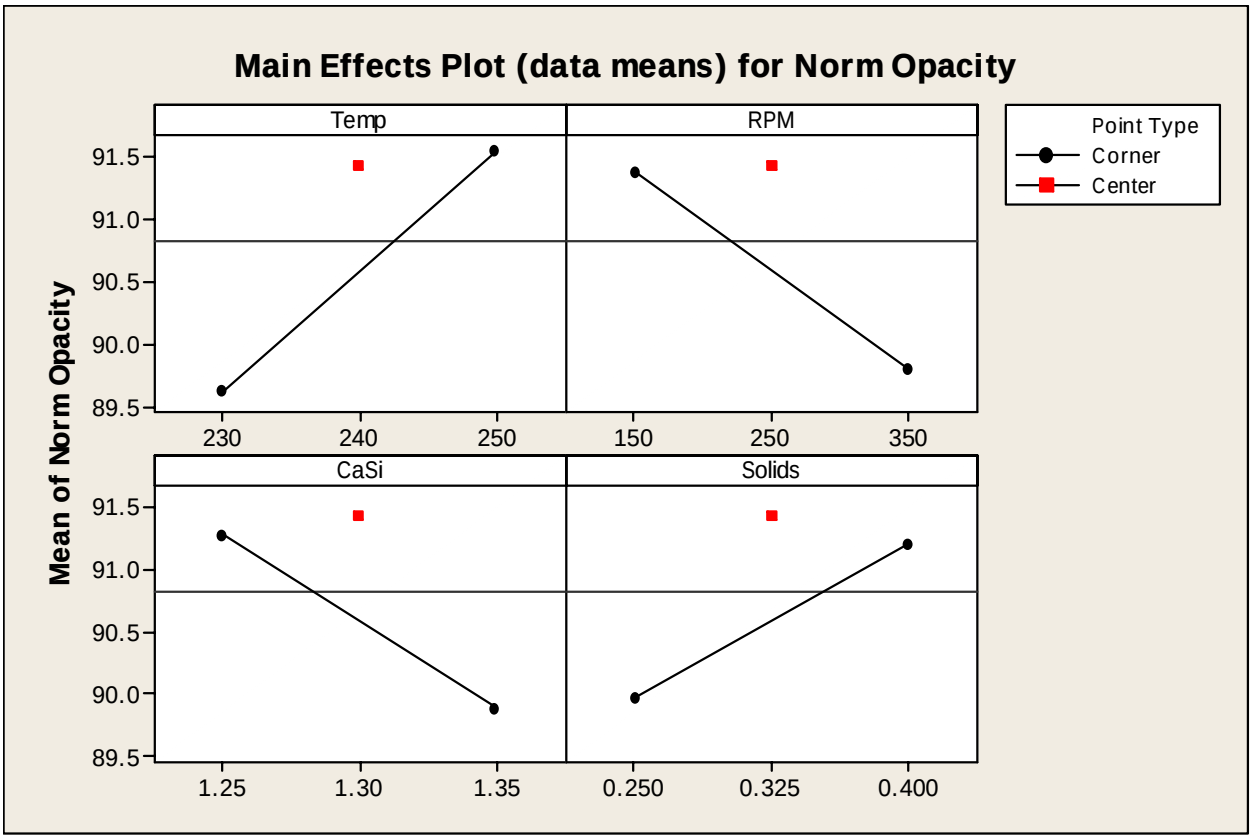

Figure 1. The main influences on normalized opacity of each process variable.

The other key findings were;

Stiffness. The results did not show significant effect of process variables on sheet stiffness.

Bulk. The range of values did not look significant.

Sheet Porosity. Only rotation per minute of the agitator produced the most significant effect on sheet porosity.

Filler Scattering Coefficient "s". According to the analysis, the process conditions which impact the sheet scattering coefficient/power of SNF are an interaction between temperature and concentration, as well as between temperature and calcium silica ratio. Concentration of slurry was found to be not significant.

Next Steps

The experimental design we carried out was only a half factorial design. We need to complete the remaining half of the design to get information about the full impact of process conditions on the quality of silicate nano-fibers and, in turn, its impact on paper properties.

TASK II: **-Lawrence Livermore National Laboratories**: To study and elucidate the mechanism of Silicate Micro-Fiber and Silicate Macro-Particle formation

LLNL has not been able to produce good quality of fibrous filler in their reactor. However, they are working with GRI to reproduce fibrous filler in their lab.

TASK III – GRI & Paper Companies: Development of Ultra-High Ash Paper (Up to 50% Calcium and Silica Based Filler)

Task III-2.1 To study the effect of high "Fibrous Filler" (25%-50%) content on paper properties and paper processes (combination of silicate nano-fibers and silicate macro-particles).

In order to produce a paper containing 40-50% filler (replacing natural fiber) an optimization study was undertaken. The three main fillers used were silicate nano-fiber (SNF), silicate macro-particle (SMP0 and precipitated calcium carbonate (PCC). The details of the experiment and the statistical design are given below.

"Mixtures" Design

Objective:

To optimize the combination of fibrous fillers (SNF in Figure 2 and SMP in Figure 3) and PCC (Figure 4) to manufacture ultra high ash papers (40%+).

Materials:

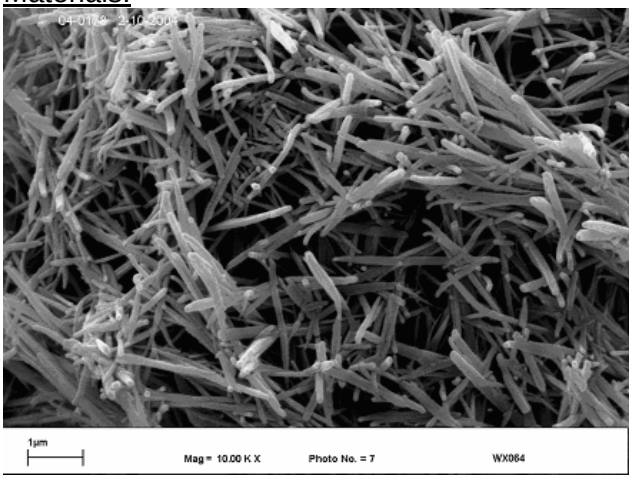

Figure 2. SEM of silicate nano-fibers (SNF) used for the mixtures design experiment.

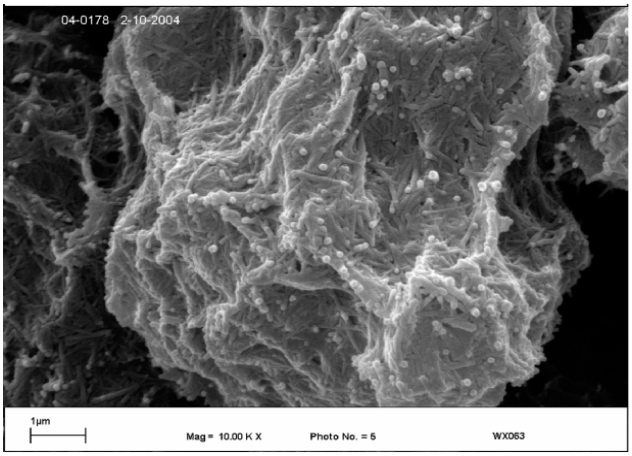

Figure 3. SEM of silicate macro-particles (SMP) used for the mixtures design experiment.

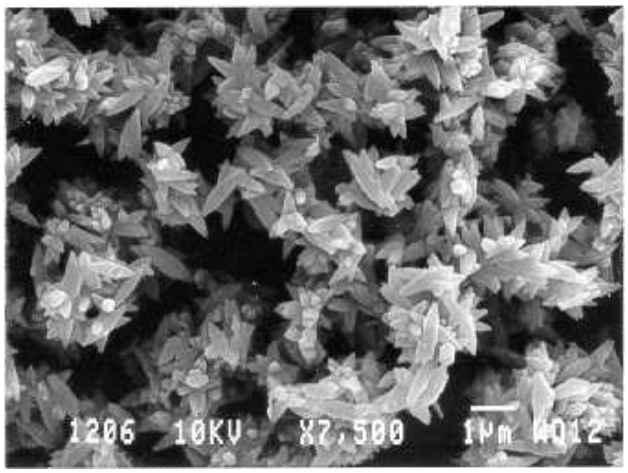

Figure 4. SEM of scalenohedral PCC used for the mixtures design experiment.

Table 4. Typical pigment properties of each of the three pigments used for this experiment which includes silicate nano-fiber (SNF), silicate macro-particle (SMP) and PCC.

Pigment	Mean Particle Size (micron)	XRD Analysis	Surface Area (m^2/g)
SMP	~15	Riversidite	200.0
SNF	~20	Foshagite	20.0
PCC	~2.0	Calcite	4.0

Design of Experiment:

A statistical design of experiment (D.O.E.) was adopted to study the effect of "mixtures" of fibrous fillers, SNF and SMP, and PCC on paper properties. A geometrical representation of the "mixture" design is given in Figure 5.

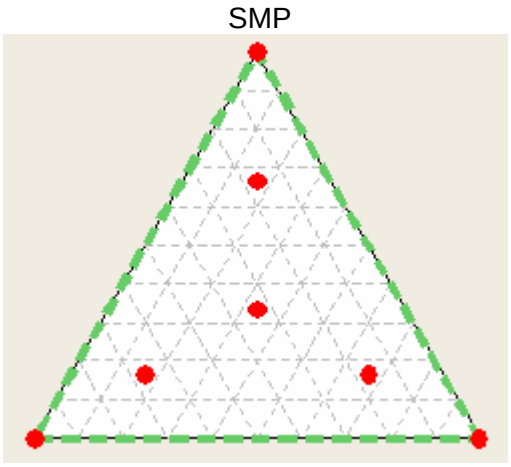

Figure 5. Mixtures used at three filler loadings, namely 15, 30 and 45%.

In addition to the above, the effect of ash level was also studied. The geometry of the complete design is further represented in Figure 6.

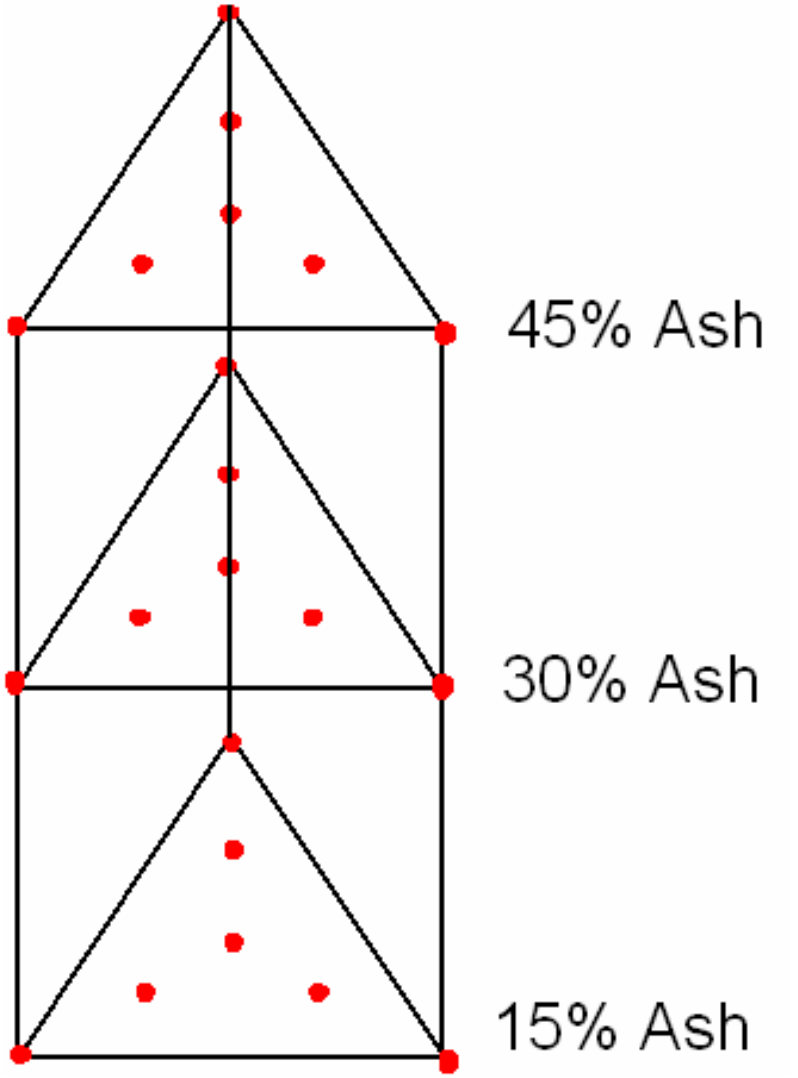

Figure 6. The overall design of the “mixtures” design of experiment.

The hand sheets were made according to the experimental conditions described above. The sheets were conditioned, calendared and tested for the following key paper properties.

- Sheet Bulk
- Smoothness
- Porosity
- Stiffness
- Brightness
- Normalized Opacity

The results are given in Table 5.

Table 5. Paper testing data used for the mixture design study.

Pigment Composition	Ash Level (%)			Basis Weight (gsm)	Bulk (cc/g)	Gurley Porosity (sec/100cc air)	Haggerty Smoothness (Front) (Sheffield Units)	Gurley Stiffness (mg)	Brightness (ISO)	Normalized Opacity (to 74 gsm)
	PCC	Ca-Si	Total							
15% PCC	14.4%	-1.0%	13.5%	72.9	1.74	3.7	212	122	89.1	86.5
15% SMP	-0.7%	13.1%	12.4%	76.4	2.06	3.4	227	190	87.9	83.3
15% SNF	1.2%	13.0%	14.2%	75.7	1.74	17.2	147	160	89.9	89.8
5% PCC, 5% SMP, 5% SNF	4.8%	8.8%	13.5%	75.9	1.83	6.5	193	153	89.1	87.1
10% PCC, 2.5% SMP, 2.5% SNF	7.4%	5.3%	12.7%	74.5	1.77	5.1	220	145	89.1	86.9
2.5% PCC, 10% SMP, 2.5% SNF	2.4%	9.8%	12.2%	76.2	1.94	4.7	220	181	88.5	85.3
2.5% PCC, 2.5% SMP, 10% SNF	2.6%	12.0%	14.6%	74.8	1.81	12.1	158	163	89.8	88.8
30% PCC	26.8%	2.3%	29.1%	74.0	1.62	5.8	167	75	90.7	90.6
30% SMP	3.2%	24.6%	27.8%	79.0	2.34	4.1	202	204	89.2	84.4
30% SNF	1.9%	27.0%	28.8%	76.1	1.84	43.5	107	142	91.7	94.0
10% PCC, 10% SMP, 10% SNF	11.9%	17.9%	29.7%	77.5	1.94	12.5	133	136	90.5	91.5
20% PCC, 5% SMP, 5% SNF	17.6%	10.3%	28.0%	76.9	1.79	8.7	160	111	90.9	91.3
5% PCC, 20% SMP, 5% SNF	6.6%	19.9%	26.6%	76.2	2.11	7.7	154	150	90.1	88.3
5% PCC, 5% SMP, 20% SNF	8.6%	24.8%	33.4%	76.2	1.91	27.7	107	163	91.6	93.6
45% PCC	43.3%	3.6%	46.9%	74.5	1.55	8.0	106	27	91.1	92.4
45% SMP	4.6%	37.4%	42.0%	76.6	2.51	4.9	155	220	89.8	85.7
45% SNF	2.4%	42.8%	45.2%	73.8	1.99	51.0	82	105	92.8	95.8
15% PCC, 15% SMP, 15% SNF	13.4%	26.3%	39.7%	78.3	1.96	17.6	118	111	91.8	93.0
30% PCC, 7.5% SMP, 7.5% SNF	25.5%	16.3%	41.8%	72.2	1.77	11.4	136	72	91.7	92.5
7.5% PCC, 30% SMP, 7.5% SNF	8.3%	32.0%	40.3%	77.1	2.24	9.4	138	140	90.9	90.1
7.5% PCC, 7.5% SMP, 30% SNF	6.2%	34.0%	40.2%	76.5	2.00	31.3	91	121	92.2	94.8

Results and Discussion:

The results of the testing were analyzed using Minitab, a statistical analysis software tool. The resulting two-dimensional graphs and three-dimensional surface plots are given in Figure 7 through Figure 30.

Key Findings:

Sheet Bulk (Figure 7 through Figure 10). The sheet bulk for the conventional filler PCC decreased with increasing ash level. However, fibrous fillers increased the bulk with increasing ash level, particularly using silicate macro-particles. The 3-D surface plots also confirm the same trend.

Sheet Smoothness (Figure 11 through Figure 14). It was interesting to note that sheet smoothness improved for silicate nano-fibers. The 3-D plots further show the effect of mixtures of SMP, SNF and PCC at 15, 30 and 45% ash levels.

Sheet Porosity (Gurley) (Figure 15 through Figure 18). The most significant result was that sheet porosity improved 7-fold (higher number is better) as silicate nano-fiber addition level increased from 15 to 45%. At 30% and 45% addition levels there was a “curvature” or synergistic effect among the three pigments.

Sheet Stiffness (Figure 19 through Figure 22). Here again the sheet stiffness of PCC-containing sheets reduced considerably as the ash level was raised from 15 to 45%. The SMP, on the other hand, increased the stiffness with increasing ash level. There is also a significant synergistic effect between the three pigments (see Figure 22).

Sheet Brightness (Figure 23 through Figure 26). Silicate nano-fibers gave higher brightness than PCC at all ash levels. The overall sheet brightness increased as nano-fibers levels were increased in the 3-component pigment mixtures.

Sheet Opacity (Figure 27 through Figure 30). Silicate nano-fibers gave 2-3 points higher opacity than PCC. There was also a significant “curvature” effect among SNF, SMP, and PCC.

In summary, it would be possible to make an ultra-high ash sheet without losing bulk and sheet stiffness using a combination of silicate macro-particles and silicate nano-fibers.

Silicate Nano-Fibers. Silicate nano-fibers can be best utilized for improving sheet optical properties, smoothness and sheet porosity.

Silicate Macro-Particles. Silicate macro-particles, on the other hand, are best suited for improving sheet bulk and stiffness.

A combination of silicate nano-fibers, silicate macro-particles and PCC can produce ultra-high ash papers.

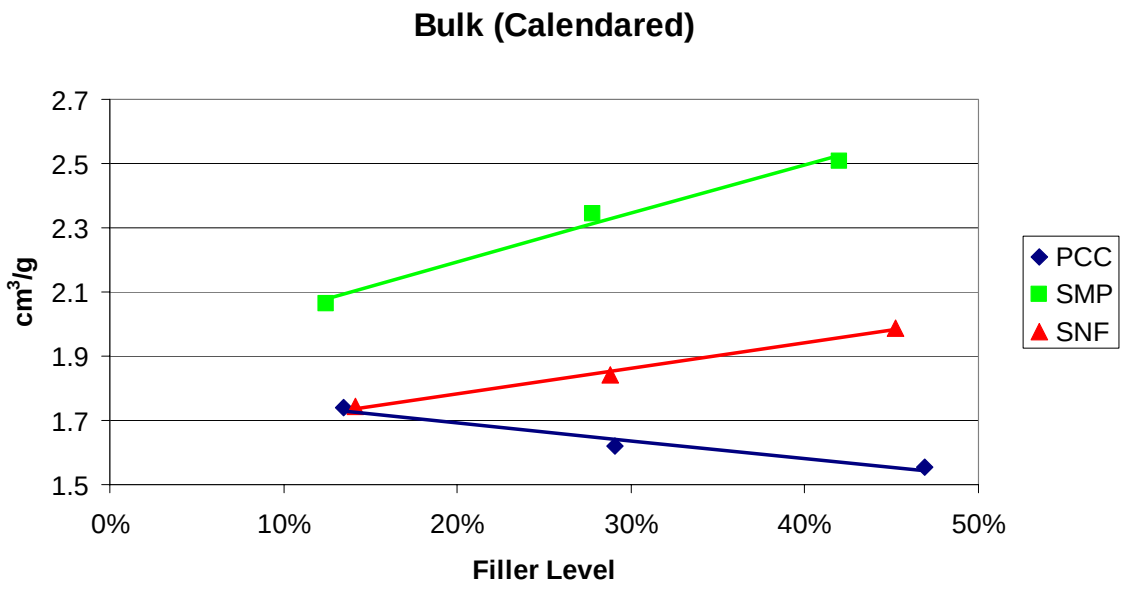

Figure 7. The effects of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on bulk..

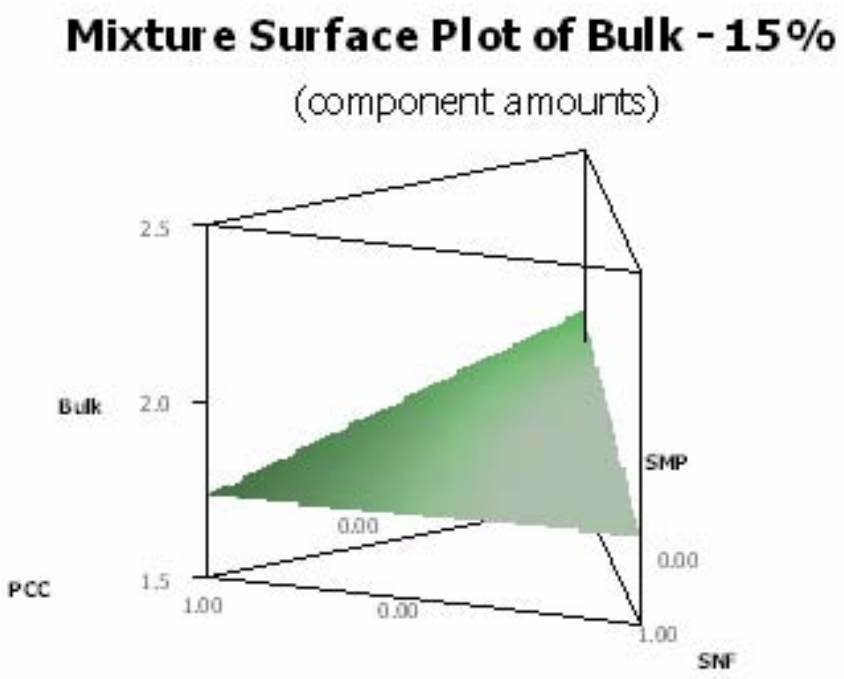

Figure 8. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on bulk at 15% ash.

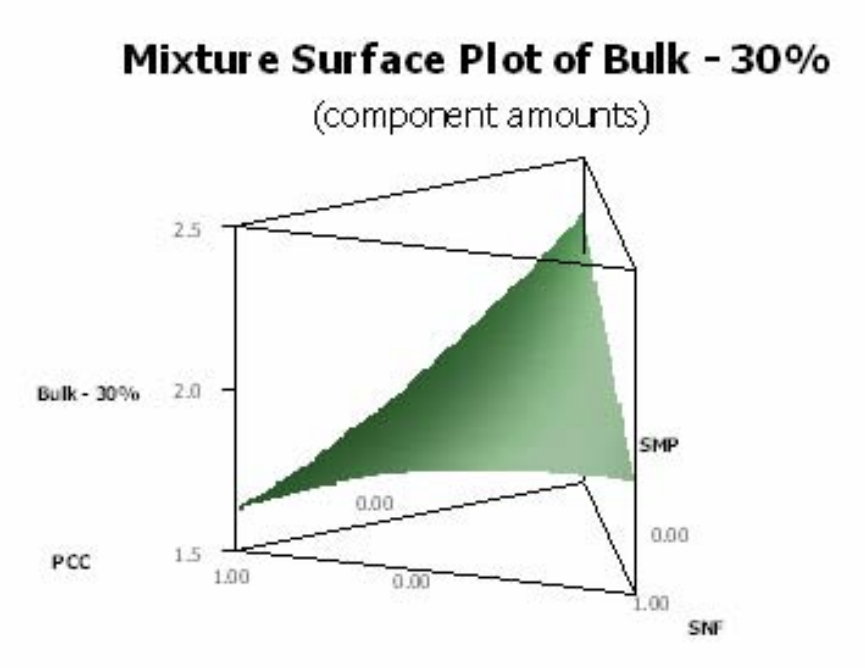

Figure 9. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on bulk at 30% ash.

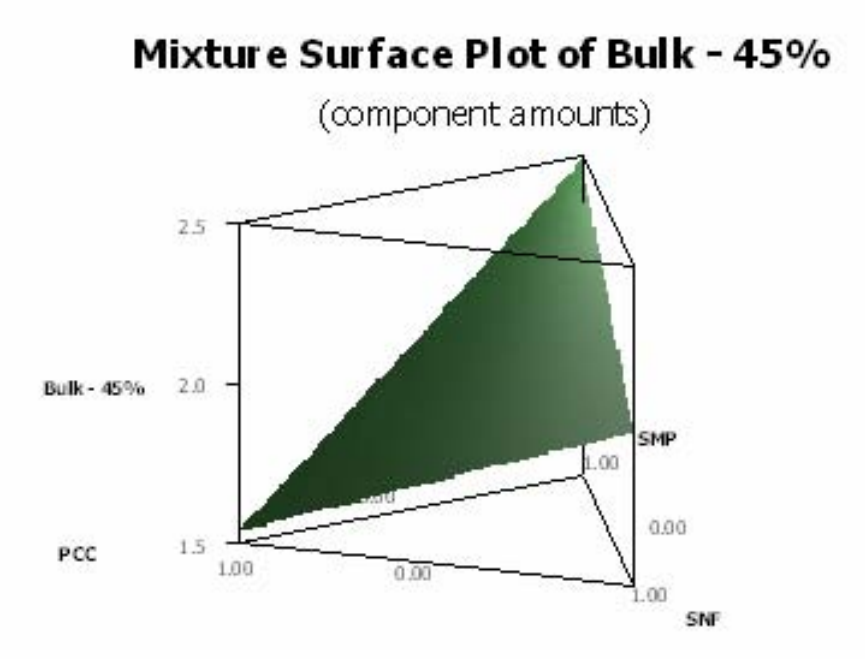

Figure 10. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on bulk at 45% ash.

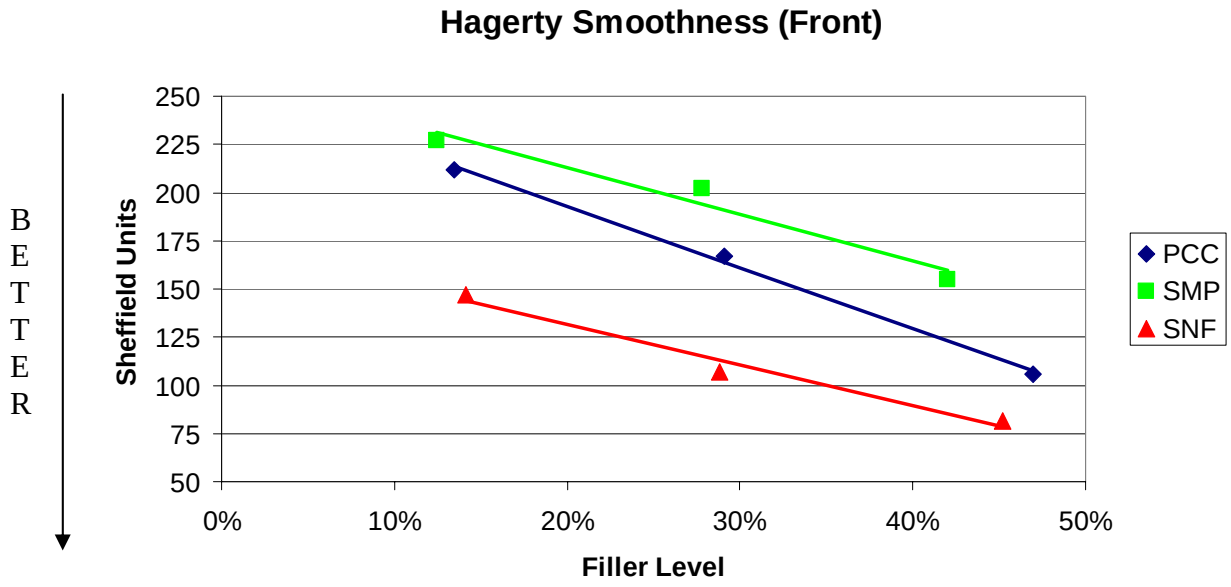

Figure 11. The effects of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on smoothness.

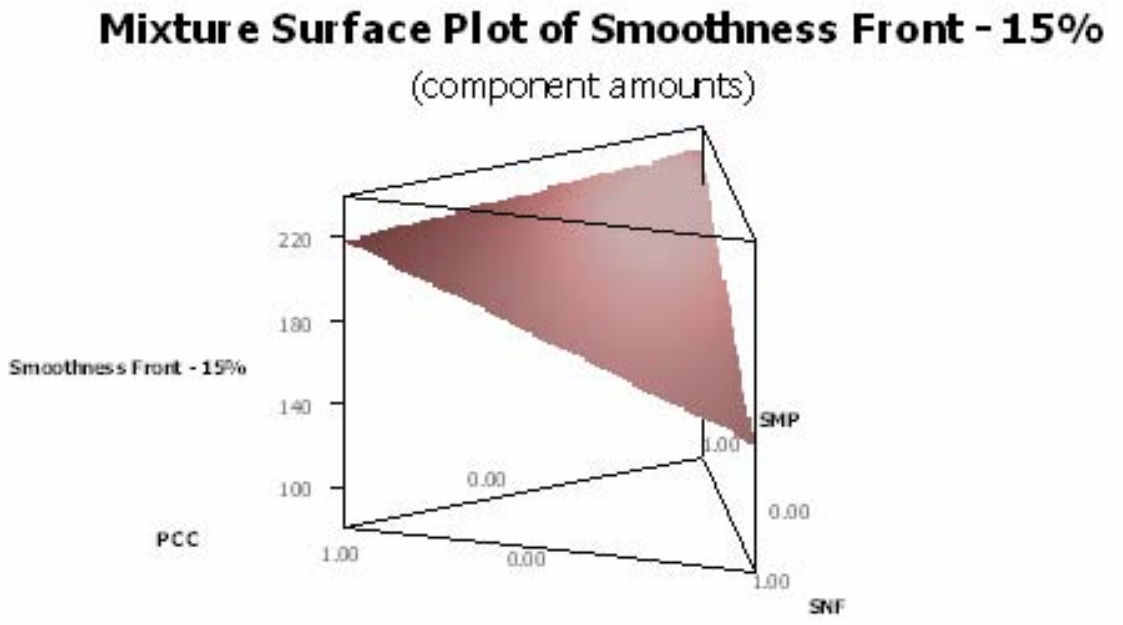

Figure 12. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on smoothness at 15% ash.

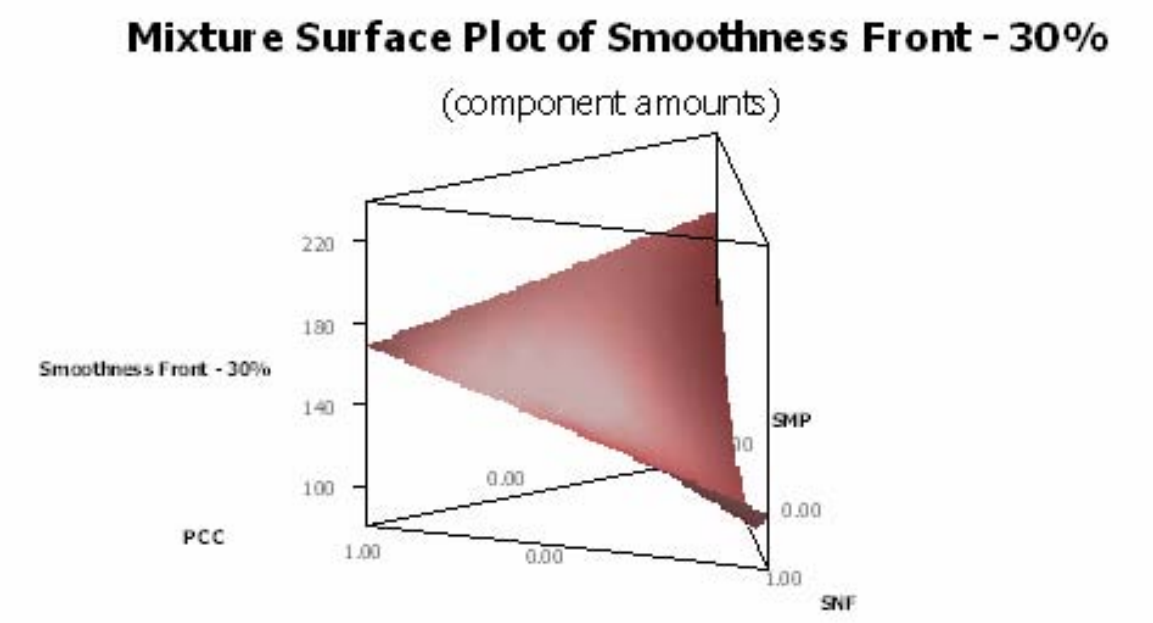

Figure 13. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on smoothness at 30% ash.

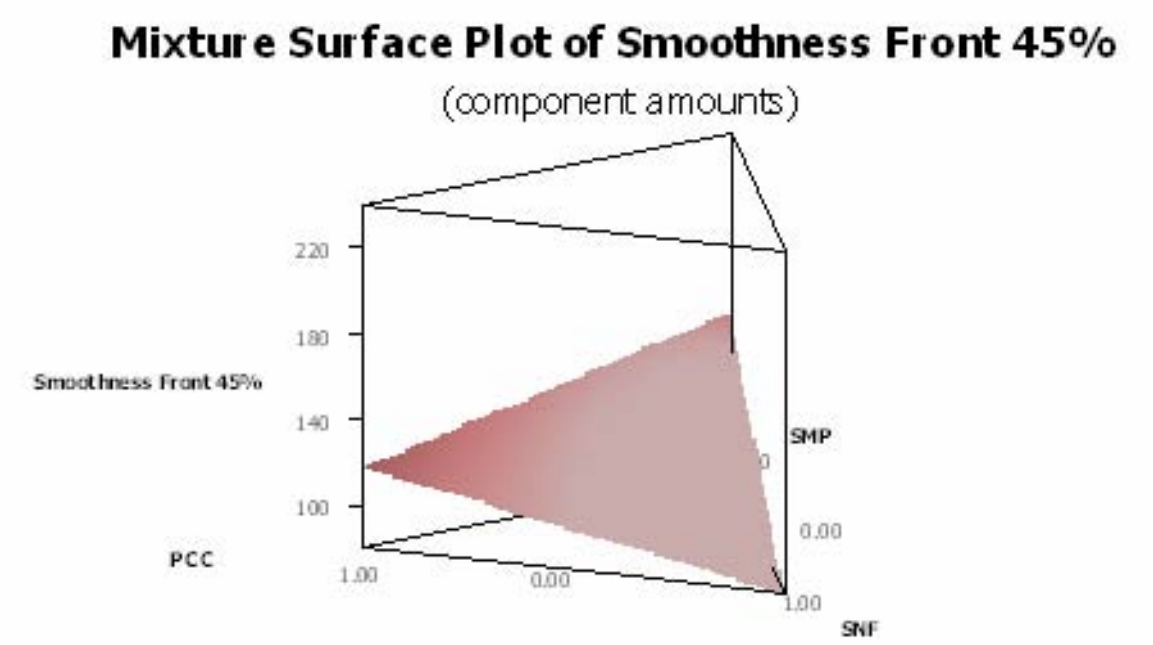

Figure 14. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on smoothness at 45% ash.

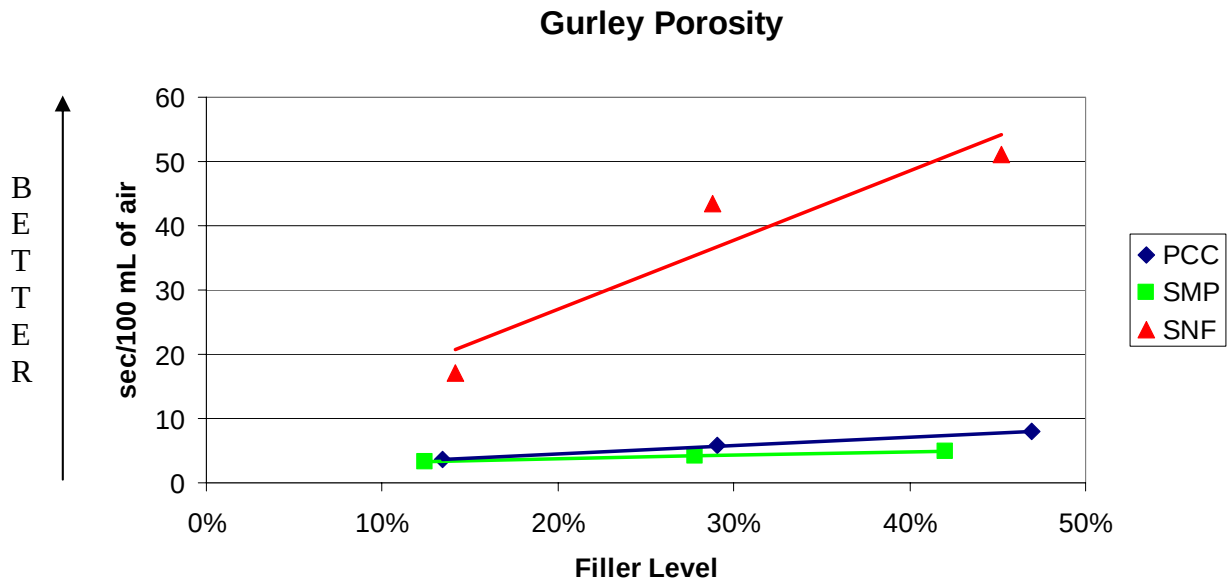

Figure 15. The effects of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on porosity.

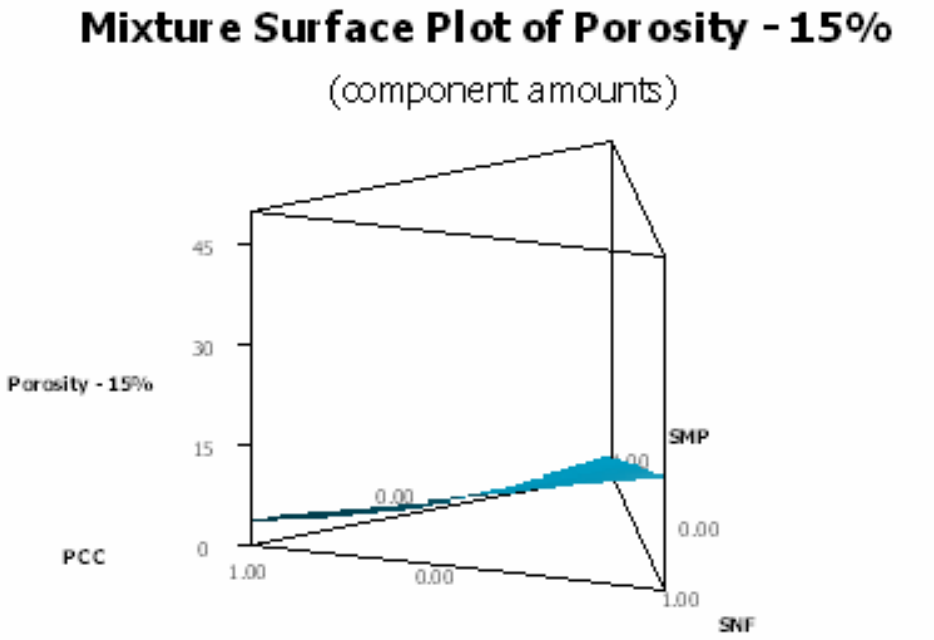

Figure 16. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on porosity at 15% ash.

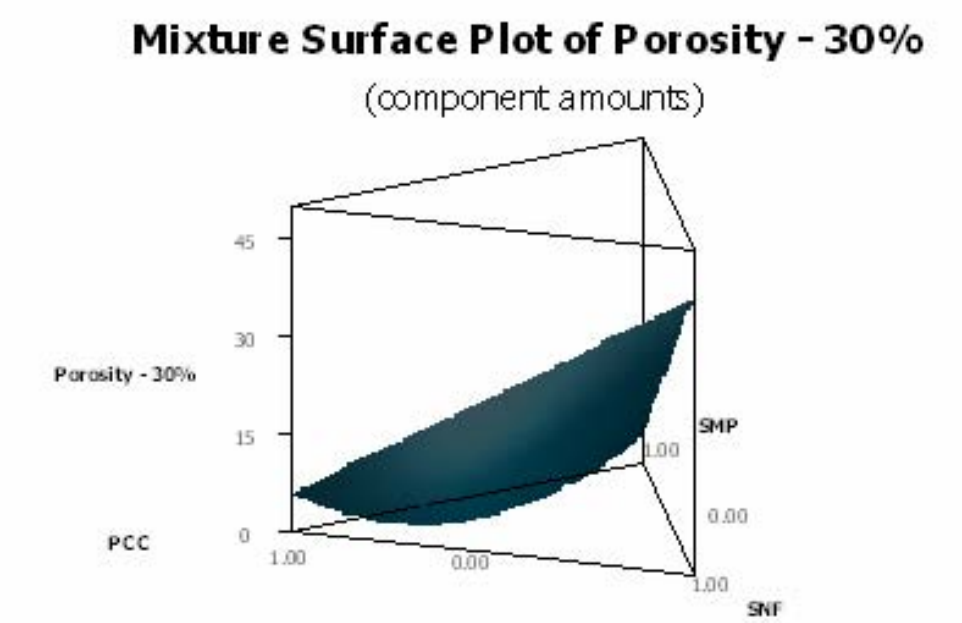

Figure 17. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on porosity at 30% ash.

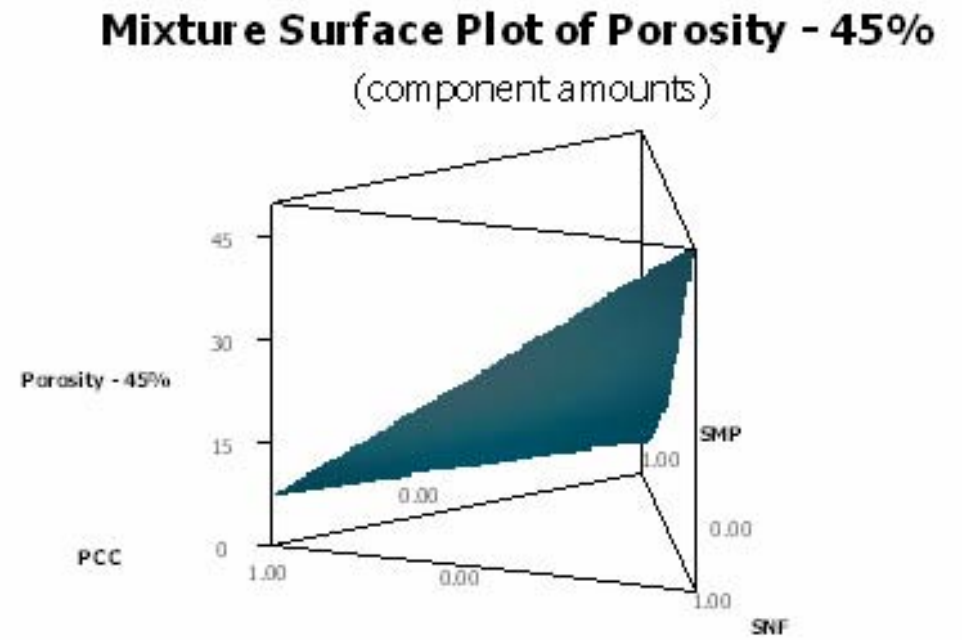

Figure 18. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on porosity at 45% ash.

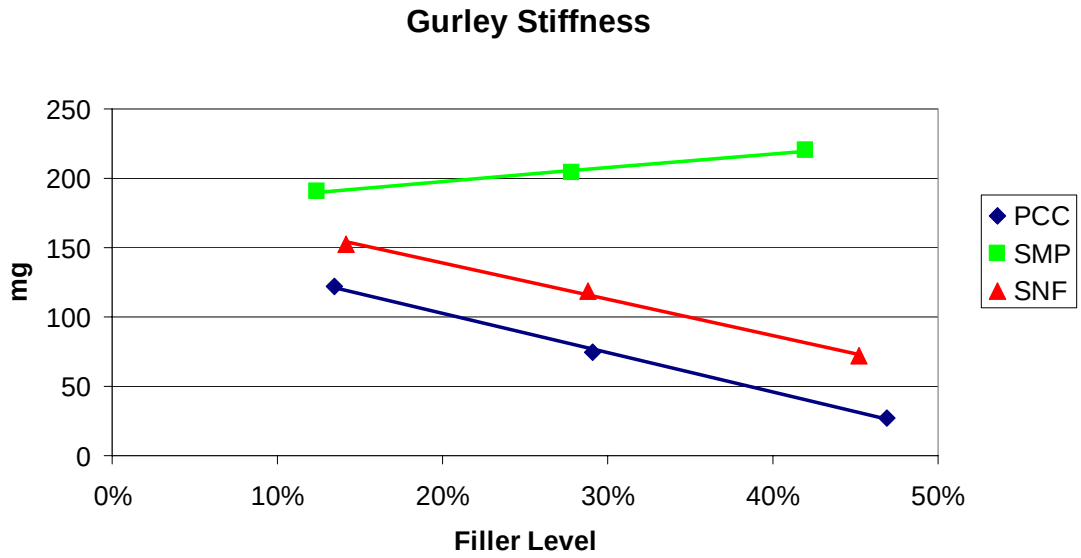

Figure 19. The effects of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on stiffness.

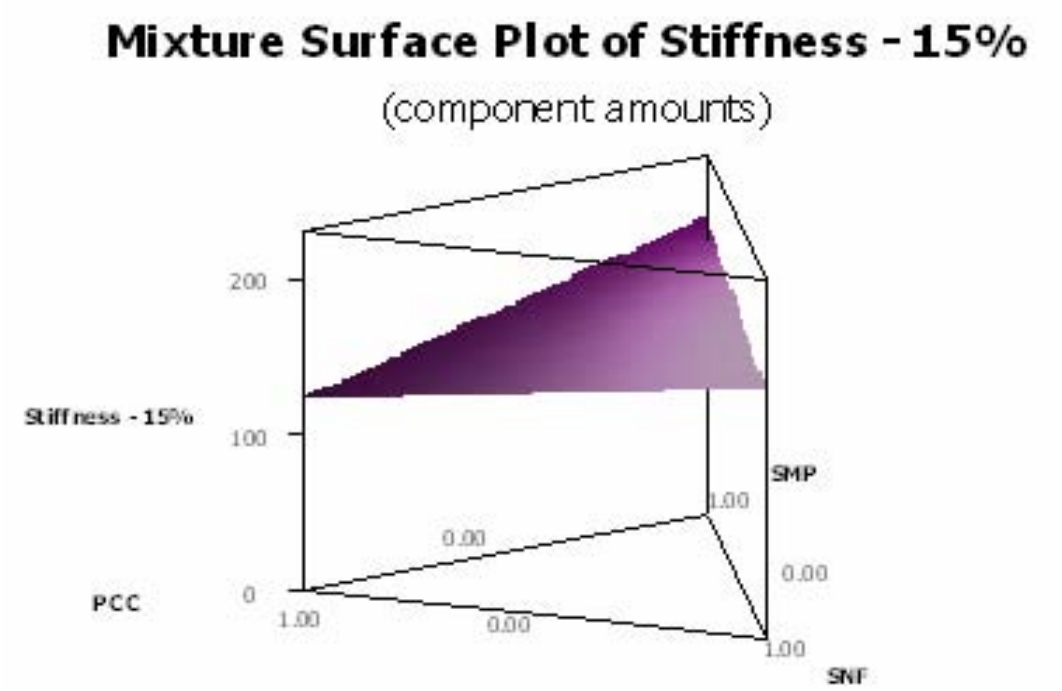

Figure 20. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on stiffness at 15% ash.

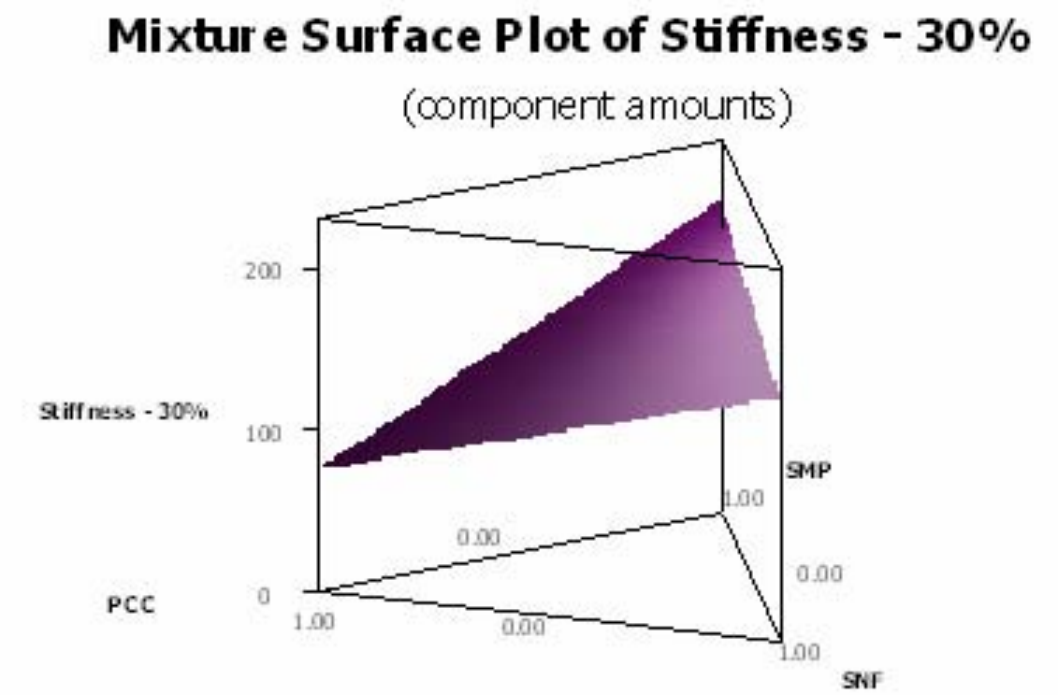

Figure 21. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on stiffness at 30% ash.

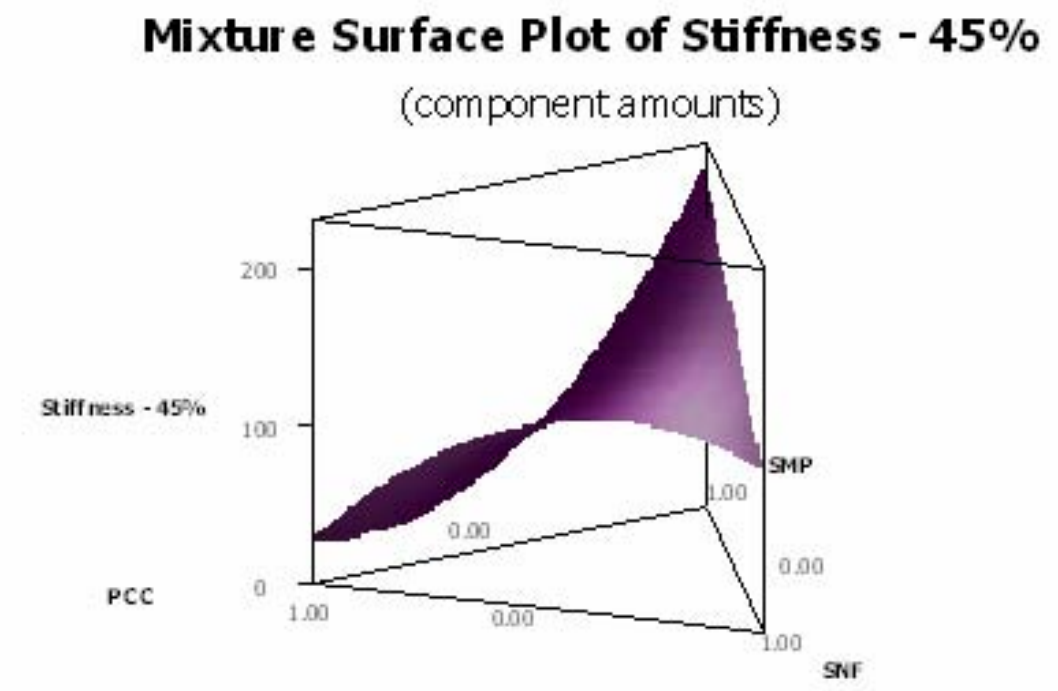

Figure 22. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on stiffness at 45% ash.

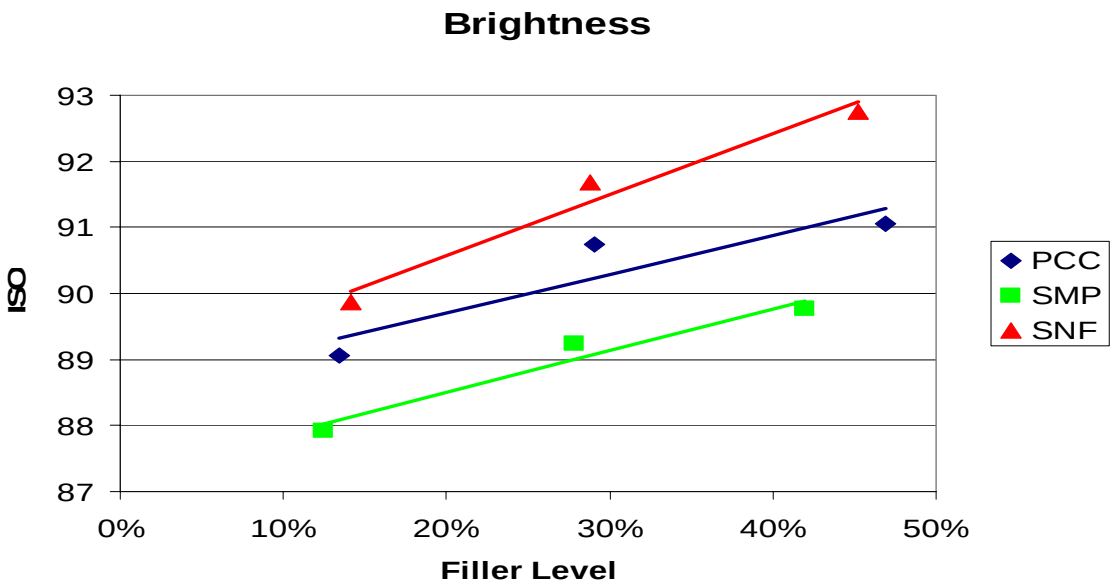

Figure 23. The effects of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on brightness.

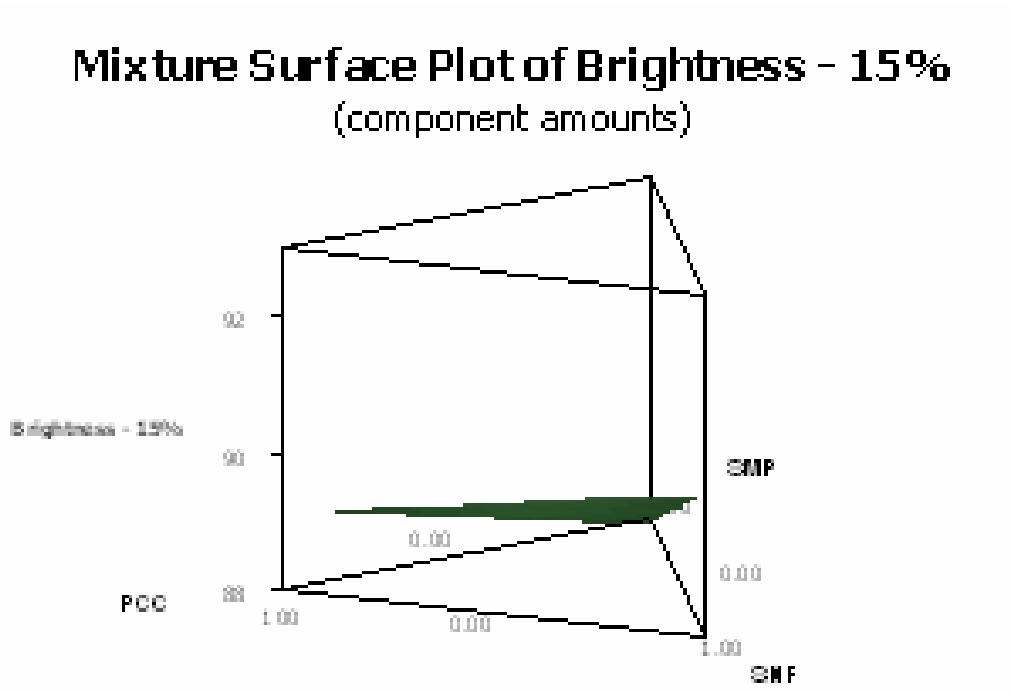

Figure 24. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on brightness at 15% ash.

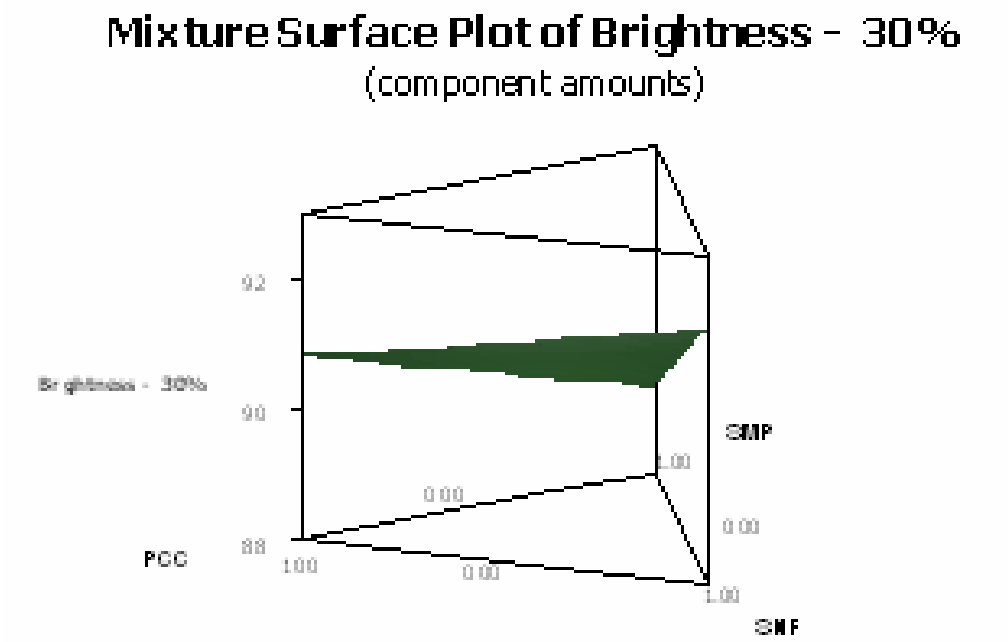

Figure 25. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on brightness at 30% ash.

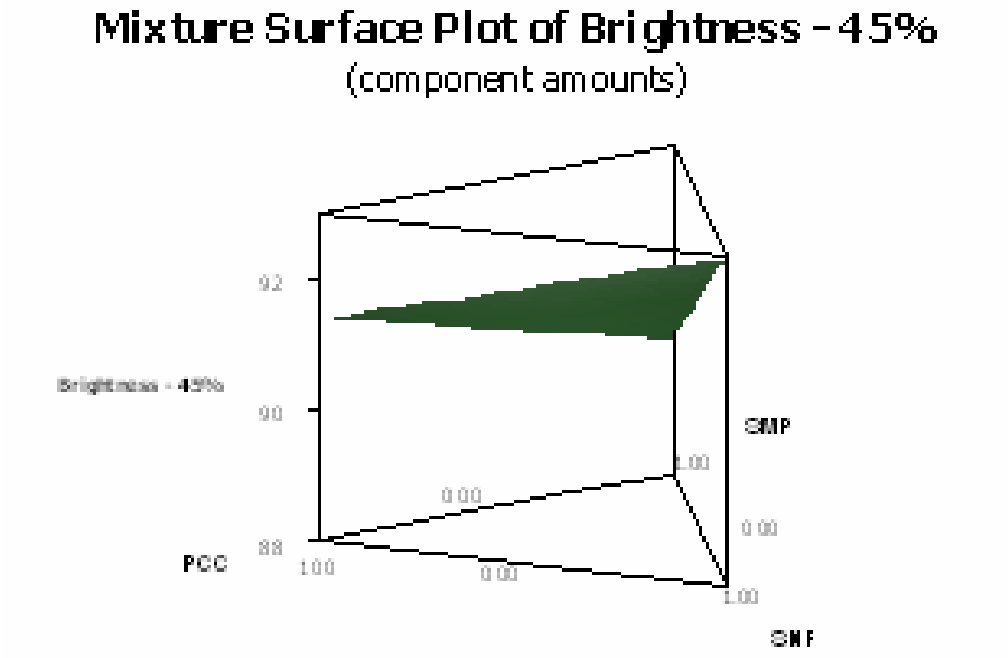

Figure 26. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on brightness at 45% ash.

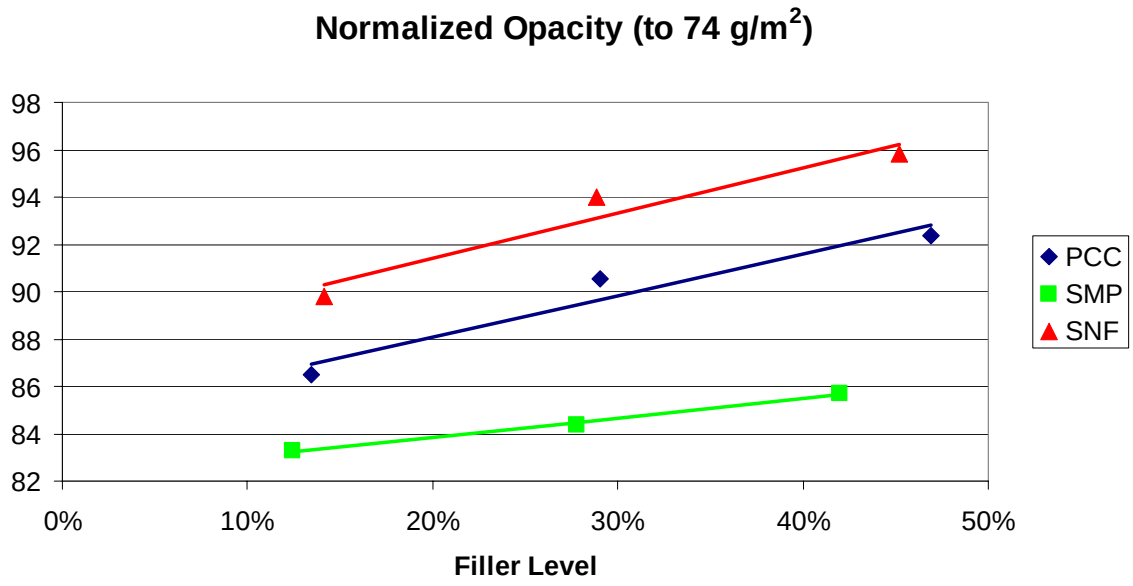

Figure 27. The effects of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on normalized opacity (to 74 gsm).

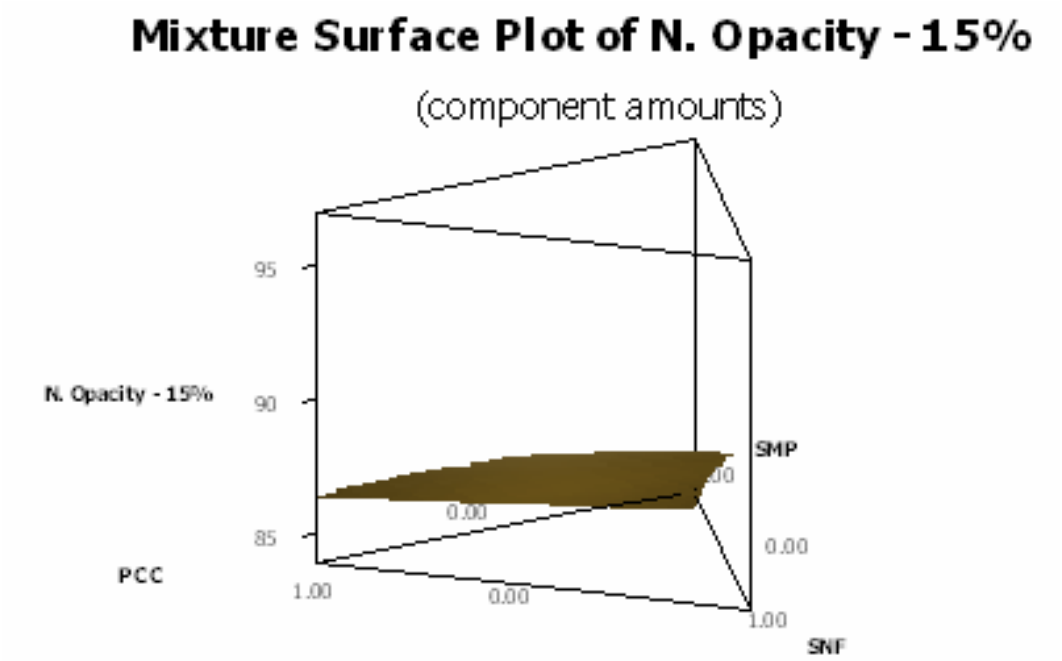

Figure 28. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on normalized opacity (to 74 gsm) at 15% ash.

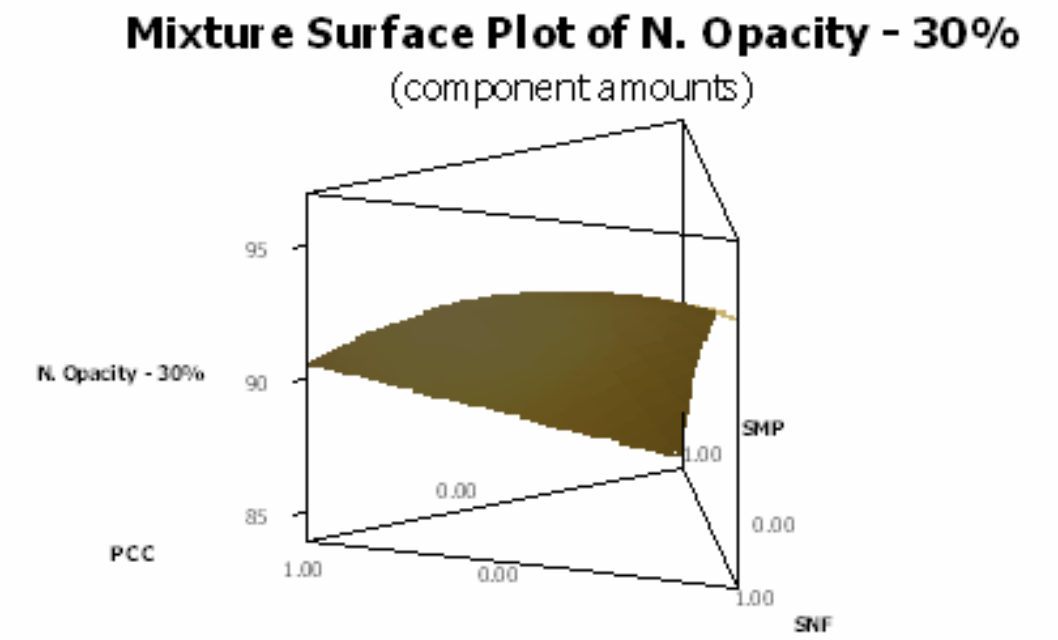

Figure 29. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on normalized opacity (to 74 gsm) at 30% ash.

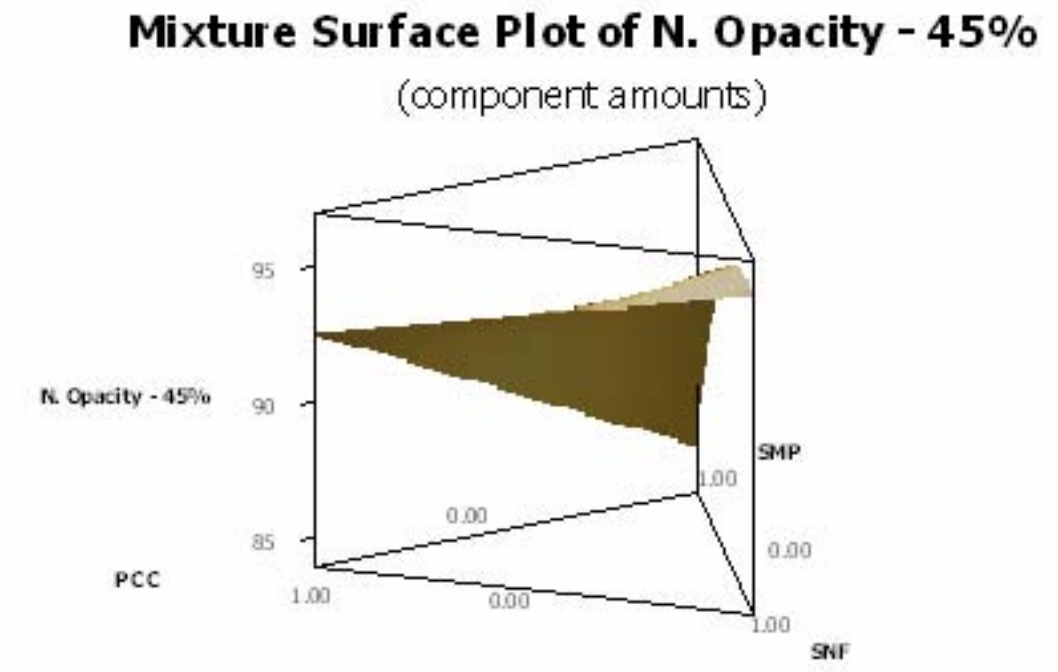

Figure 30. The effects of mixtures of silicate nano-fibers (SNF), silicate macro-particle (SMP) and PCC on normalized opacity (to 74 gsm) at 45% ash.

Task III-1.5: Preliminary system wide energy audit comparing existing pulp and paper mills vs future mills with GRI "Fibrous Filler" on site plants

Preliminary Energy Savings

Based on the data it has been demonstrated that it would be technically feasible to replace 40% pulp with 40% "fibrous fillers," thus a mill can produce 1000 tons/day paper by operating a 600 tons/day pulp mill and a 400 tons/day "fibrous filler" mill, instead of a 1000 tons/day pulp mill. The following are estimated savings in energy usage with the above-described scenario. (In the case of existing mills, the excess pulp can be sold as market pulp.)

Manufacturing of 600 tons/day pulp versus 1000 tons/day.

Material and energy balances for an integrated pulp mill, bleach plant and fine paper mill are reasonably complex. A detailed energy audit must account for numerous process technologies, equipment configurations, product mixes and a variety of local factors. However, a preliminary estimate of energy benefits has been made based on a "greenfield" mill and simplified operating assumptions. The reference mill configuration includes kraft pulping (1100 ton/day), medium consistency bleaching (1000 ton/day).

Pulp mill and bleach plant production rates would be much lower when integrated with a paper machine producing high filler loaded (40%) fine paper. As a result the total steam and power consumption of this alternative mill will be substantially lower than for the reference case. The estimated energy savings come largely from reduced fuel oil consumption in the lime kiln and combination boiler. This amounts to about 440 barrels of fuel oil per day which is equivalent to about one trillion Btu/year.

Of course, the smaller fiber line will require and produce less power than in the reference case. The quantity of purchased power in this simplified analysis will remain approximately the same for both configurations. As mentioned above, an operating mill may regularly vary purchased power; usually a reduced purchase will lead to a proportionate increase in fuel requirements and vice versa. As a result, the form of the energy savings may vary, but over a wide range of operating conditions the total will remain near one trillion Btu/year.

Steam Energy Requirement for Manufacturing of 400 tons/day "fibrous filler."

The manufacturing of "fibrous filler" involves hydrothermal reaction between calcium ion sources (usually lime, CaO) and silica sources with nominal amount of other additives. The reaction conditions for the two "fibrous filler" products are given below in Table 6. Although the initial heat requirement of the hydrothermal reaction is high, the net heat requirement is substantially reduced by heat exchangers.

Table 6. Process conditions for making silicate "fibrous fillers."

Process Conditions	Silicate Nano-Fibers	Silicate Macro-Particles
Reaction Temperature (^{o}F)	~460	~360
Pressure (psig)	~450	~160
Concentration (lb/gallon)	~0.4-0.5	~0.6-0.8

The slurry is passed through a heat exchanger to recover maximum heat, so the energy requirement for 200 tons/day each of SMP and SNF (total 400 tons/day) can be calculated on the following assumptions:

1. Slurry temperature leaving the heat exchanger = 100^{o}F
2. Steam requirement = 565,320 lb/day
3. Total Btu supplied by steam = 679,514,640 Btu/day
   Or = ~0.245 trillion Btu/year

Resulting Energy Savings:

The reduction in pulp production from 1000 tons/day to 600 tons/day saves about 1 trillion Btu/year while 400 tons/day fibrous filler production consumes about 0.25 trillion Btu/year. This implementation of 40% fibrous filler in paper production could save **0.75 trillion Btu/year** for each 1000 tons/day of paper manufactured.

TASK IV - Western Michigan University

No work carried out this quarter due to reallocation of funds.

Milestone Status Table:
Note: These milestones have been revised from the original proposal due to the current funding revisions, and in view of D.O.E. and A..F. & P.A.'s review of this project.

ID Number Scheme: Task - Year . Subtask

ID NUMBER	MILESTONE DESCRIPTION	Target Completion Date	Status
Task I	**GRI Optimization of Manufacture of Silicate Nano-Fibers (SNF, TiSil, or T-8) and Silicate Macro-Particle (SMP, or T-4)**		
Year 1			
I-1.1	Lab scale (2.0 gallon reactor) study a) Critical process parameters (temperature, reaction time, etc.) to produce Silicate Nano-Fibers b) Screening of alternate raw materials	12/31/02	Com-pleted
I-1.3	First production scale (10,000 gallon reactor) trial a) Manufacture of silicate macro-particles (SMP), employing the optimum process conditions from I-1.2 b) Lab scale characterization and testing of SMP pigment	6/30/03	Com-pleted
I-1.4	Second production scale (10,000 gallon reactor) a) Manufacture of silicate macro-particles (SMP) b) Lab scale characterization and testing of SMP pigment	8/31/03 9/30/03	Com-pleted Com-pleted
Year 2			
I-2.1	Empirical process models and response surface analysis employing the technique of designed optimization experimentation (DOE)	3/31/04	Com-pleted
I-2.2	Lab scale (2.0 gallon reactor) study a) Screening of alternate raw materials	6/30/04	Ongoing
I-2.3	Pilot scale (30 gallon reactor) study a) Scale up and verification of lab scale process models b) Characterization of pigment	6/30/04	Ongoing
I-2.4	Additional production trials using 10,000 gallon reactors (Toll Manufacturer)		Ongoing
I-2.5	Preliminary energy balance for a commercial "Fibrous Filler" plant	3/31/04	Com-pleted
I-2.6	Preliminary design for a commercial "Fibrous Filler" plant	6/30/04	Ongoing
I-2.7	Optimization of alternate lower cost raw materials, process conditions to manufacture, lower cost of silicates (less than or equal to cellulose fiber).	9/30/04	Ongoing
I-2.8	Silicate-carbonate hybrids (cost less than cellulose fiber) delivered at headbox	9/30/04	
I-2.9	Modification of "Fibrous Filler" surface employing organic molecules	12/31/04	
I-2.10	Final optimization of raw materials, process conditions to manufacture most	12/31/04	

	cost effective high performance silicate products (Nano-Fibers, Macro-Particles).		

Year 3 Goal: Commercial Validation

I-3.1	Detailed design and engineering of plant to manufacture calcium silicates	3/21/05	
I-3.2	Commercial production trials of calcium silicates and papermaking	9/30/05	

Task II	**(Lawrence Livermore National Laboratory) To study and elucidate the mechanism of Silicate Microfiber and Silicate Macro Particle formation**

Year 1

II-1.1	Characterization of GRI's Silicate Nano-Fibers (SNF)	9/30/03	Com-pleted
II-1.2	Lab preparation of GRI standard silicate products (SNF or T-8) in LLNL reactors	12/31/03	Ongoing
II-1.3	Chemical and phase analysis of the reaction products as a function of time throughout the process of synthesizing Silicate Nano-Fibers	12/31/03	
II-1.4	Special test to characterize silicate products using atomic force microscopy (AFM), Vertical scanning interferometer	12/31/03	
Year 2	***Goal: Optimization***		
II.2.1	Complete Task II-1.2, II-1.3 and II-1.4	6/30/04	Ongoing
II-2.2	Preliminary mechanism of ""Fibrous Filler" formation	6/30/04	Ongoing
II-2.3	Study the effect of impurities on formation of silicates	6/30/04	
II-2.4	Study the alternate lower cost raw materials, silica, lime source for T-8 Silicate Nano-Fibers (SNF)	9/31/04	
II-2.5	Process modeling using thermodynamic database and kinetic database available at LLNL	10/31/04	
II-2.6	Preliminary preparation of GRI's standard silicate macro-particles (SMP) in LLNL reactors and repeat task II-1.1 and II-1.2	12/31/04	
II-2.7	Improving the process of manufacturing silicate products by employing catalysts, etc.	12/30/04	
Year 3			
II-3.1	Characterization of sub-molecular structure, silol bonds	3/31/05	
II.3.2	Final kinetic and thermodynamic models to support design of commercial plant	6/30/05	

Task III	(GRI and Paper Companies) Development of Ultra-High Ash Paper (Up to 50% Calcium and Silica Based Fillers)

Year 1

III-1.1	First commercial paper machine trials	7/31/03	Com-pleted
III-1.2	Evaluate paper manufactured during production trial (both in lab and in field)	9/30/03	Com-pleted
III-1.3	To study the effect of high "Fibrous Fillert" (25%-50%) content on paper properties and paper processes (combination of silicate nano-fibers and macro-particles)	12/31/03	Ongoing
III-1.4	Second and third commercial scale paper machine trial	11/30/03	Com-pleted
III-1.5	Preliminary system wide energy audit comparing existing pulp and paper mills vs future mills with GRI "Fibrous Filler" on site plants		Ongoing

Year 2

III-2.1	Complete III-1.3	3/31/04	Com-pleted
III-2.2	Screen new wet end additives to enhance sheet strength	6/30/04	Ongoing
III-2.3	Paper machine production trials	6/30/04	Ongoing
III-2.4	To study the effect of "Fibrous Fillers" on energy saving during the following paper machine unit operations: a) Drainage b) Pressing c) Drying (pre size press) d) Drying (post size press)	9/30/04	
III.2.5	Preliminary system wide energy audit comparing existing pulp and paper mills vs future mills with GRI "Fibrous Filler" on site plants	3/31/04	Com-pleted
III-2.6	Effect of pigment on chemical additives like internal sizing, starch, dyes, etc.	5/31/04	Ongoing
III-2.7	Paper quality / performance (printing, dusting)	7/31/04	Ongoing
III-2.8	New value added product development (e.g., inkjet paper, 40% filler composite)	9/30/04	Ongoing
III-2.9	Study the mechanism of fiber to Silicate Nano-Fiber bonding at higher ash levels (20-50%)	12/31/04	Ongoing

Year 3 Goal: Validation of Technology

III-3.1	Commercial paper machine production using commercially produced silicate "Fibrous Filler" (nano-fibers, macro-particles)	3/31/05	

III-3.2	Field trial of paper produced with commercially produced T-4 and T-8	9/30/05	
III-3.3	Full life cycle analysis of existing pulp and paper mills vs future pulp and paper mills with GRI "Fibrous Filler" on site plants	12/31/05	

Task IV	**(Western Michingan University) Optimization of surface treatment formulations (S. Abubakar, M. Joyce)**

Year 1

IV-1.1	Determine the compatibility of starch, PVOH binders and silicate pigments	6/30/03	Com-pleted
IV-1.2	Maximize coating solids using five different binders	6/30/03	Com-pleted
IV-1.3	Determine minimum pigment-binder ratio for inkjet print quality	9/30/03	Com-pleted
IV-1.4	Study the effect of temperature and solids on silicate coatings	9/30/03	Com-pleted
IV-1.5	Study the dry coating structure, ink density comparison with silica gel	9/30/03	Com-pleted
IV-1.6	Study absorptivity and surface energy of Silicate Nano-Fibers and silicate macro-particles using contact angle measuring device and methods to improve print densities	12/31/03	Ongoing
IV-1.7	Analyze data and submit report	12/31/03	Com-pleted

Year 2 Goal: Size press study to characterize dry coating structure

IV-2.1	Lab scale a) Optimization of coating formulation using GRI's fibrous fillers, binders, water fasteners, etc.	6/30/04	No Other Work Done This Quarter
IV-2.2	Comparison of optimum formulation with other pigments	6/30/04	
IV-2.3	Pilot coater (cylindrical lab coater) a) Application of optimum coating formulation on a pilot CLC coater	9/30/04	
IV-2.4	Analyze the data and final reports	9/30/04	

Year 3

IV-3.1	Formulate silicate pigment coating for water-based flexographic and rotogravure grades of paper	3/31/05	
IV-3.2	Pilot coater trials (4,000 fpm)	4/30/05	
IV-3.3	Analysis of coating structure	5/31/05	
IV-3.4	Printing of coated paper on 4-color rotogravure Cerutti press	6/30/05	
IV-3.5	Printing of coated paper on 3-color Comco flexographic press	6/30/05	
IV-3.6	Test for print densities using X-Rite densitometer	6/30/05	

IV-3.7	Analyze the data and submit the final report	9/30/05	

Budget Data (as of date): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To	Approved					
Year 1	4/14/03	4/13/04	$700,000*	$300,000	$1,000,000	$537,415**	$399,000 ***	$932,790**
Year 2	4/14/04	4/13/04	$700,000*	$300,000	$1,000,000			
Year 3	4/14/05	4/13/06	$700,000*	$300,000	$1,000,000			
Year 4								
Year 5								
		Totals	$2,100,000	$900,000	$3,000,000	$537,415**	$399,000 ***	$932,790**

* Amount includes $420,000 to be paid directly to LLNL.

** Through March 31st, 2004.

*** This includes some invoices from our Industry Partners and some estimated values. In-kind support received to date includes:

1) Weyerhaeuser has given GRI a laboratory space and access to equipment and technician services; estimated value of $156,000 to date.
2) Gray's Harbor Paper (GHP) has provided: 1) space and utilities for the GRI 30 gallon reactor; and 2) direct labor to assist GRI staff in operating the reactor and paper machine trial time; invoiced at $243,000.

This represents 42.7% of the cost share.

Plans for the Next Quarter

Task I

I-2.1 Verify process models for 2.0-gallon reactor
I-2.2 Lab scale (2.0 gallon reactor) study
  a) Screening of alternate raw materials
I-2.3 Pilot scale (30 gallon reactor) study
  a) Scale up and verification of lab scale process models
  b) Characterization of pigment
I-2.4 Additional production trials using 10,000 gallon reactors
I-2.6 Preliminary design for a commercial "Fibrous Filler" plant

Task II

II-2.1 Complete Task II-1.2, II-1.3 and II-1.4

Task III

III-2.2 Screen new wet end additives to enhance sheet strength
III-2.3 Paper machine production trials

Task IV

Work temporarily suspended due to reallocation of funds.

Guided Acoustic Wave Monitoring of Corrosion and Erosion in Recovery Boiler Tubing

Chinn: Lawrence Livermore National Laboratory

CPS#01157

Quarterly Progress Report
For: Guided acoustic wave monitoring of corrosion in recovery boiler tubing

Covering Period: Apr 1, 2004 – Jun 30, 2004
Date of Report: Jul 15, 2004

Contractor: Lawrence Livermore National Laboratory
B&R Number: ED1801
Subcontractors Joseph Rose, Penn State University

Contact: Principal Investigator: Diane J. Chinn
(925)423-5134
chinn3@llnl.gov

Project Team: DOE-HQ contact: Gideon Varga
AF&PA contact: Thomas Grant
Collaborator: Margaret Gorog, Weyerhaeuser
Collaborator: Sandy Sharp, Westvaco

Project Objective: This project will research all aspects related to the use of guided acoustic waves to monitor the progression of corrosion in recovery boiler tubing. After an initial feasibility study, the project will focus on development of a practical implementation of guided acoustic wave sensors for recovery boiler tubing.

Background:

In the kraft recovery boiler, water-filled tubes constitute the structure of the furnace serving to absorb thermal energy from the furnace. Exposed to combustion on the fireside and filled with pressurized flowing feedwater, recovery boiler wall tubes must withstand large and variable thermal and mechanical stresses. Furnace gas temperatures up to 2500˚ F combined with the harsh molten salt environment can cause premature corrosion on the outer diameter of the recovery boiler wall tubes.

Extensive damage to recovery boiler tubes can result in a significant safety and environmental hazard. Considerable plant resources are expended to inspect recovery boiler tubing. Currently, visual and ultrasonic inspections are primarily used during the annual maintenance shutdown to monitor corrosion rates and cracking of tubing. If corrosion or cracking is detected, tubing must be repaired or replaced during the shutdown.

Guided acoustic waves have been developed as an inspection technique for tubular members for many years. The feature of this acoustic technique is its cost-effectiveness in inspecting long lengths of tubes from a single inspection point. Recent applications on nuclear steam generators have shown that guided acoustic waves can inspect entire cross-sections of tubes over 50 - 75 feet. This technique appears very promising for recovery boiler tube application by expediting annual inspection and providing on-line periodic monitoring of tube integrity. Development of a sensor for monitoring the integrity of recovery boiler tubes during the lifetime of the furnace would allow timely replacement of cracked or corroded tubes.

Status:

A paper was presented at the TAPPI Spring Conference in Atlanta as well as a Peer Review session. We are continuing commercialization efforts with Alstom Power and making improvements for field utilization. The EMAT sensors were modified so that the matching network can be mounted on the transmitter and the preamplifier can be mounted on the receiver. Previously, the matching network and preamplifier were separate boxes that would dangle from the sensors. The mounting of these circuits onto the sensors will make them easier to use in the field.

Plans for Next Quarter:

We will continue commercialization efforts with Alstom Power including development of both system and sensors for field use.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1.1	Feasibility Study Yr.1	9/4/00		
1.1.1	Preliminary model of guided waves	6/12/00	6/12/00	Two papers presented at QNDE at Iowa State
1.1.2	Assess transducers	3/24/00	3/24/00	
1.1.2.1	EMAT	3/24/00	3/24/00	
1.1.2.2	Comb PZT	3/24/00	3/24/00	
1.1.3	Obtain tube samples	2/25/00	7/31/00	Samples from 3 sources have been sent to LLNL
1.1.4	CT char of samples	3/17/00	3/23/01	
1.1.5	Assess guided waves	9/4/00	9/30/00	
1.2	Report Yr.1 results	9/25/00	10/24/00	Presentation at Agenda 2020 Meeting in Texas
2.1	Development work Yr.2	9/7/01		
2.1.1	Model wave-defect interaction	12/22/00	6/10/01	Circumferential planar defect modeled
2.1.2	Design sensors	2/23/01	3/1/01	Design sent to Krautkramer-Branson
2.1.3	Validate sensors on synthetic defects	4/20/01	6/1/01	
2.1.4	Design sensor system	9/7/01		ongoing
2.2	Report Yr.2 results	9/28/01	10/16/01	Presentation at Agenda 2020 Meeting
3.1	Development work Yr. 3	8/30/02		
3.1.1	Build prototype system	1/18/02		ongoing
3.1.2	Test system	3/1/02		ongoing
3.1.3	Field system	4/12/02		ongoing
3.1.4	Transfer technology	8/30/02		ongoing
3.2	Report Yr 3 and final results	9/27/02		

Budget Data (as of 9/30/01):

[$K]	Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period	DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
Year 1 (10/1/99 to 9/30/00)	$350	$70	$420	$325	$120	$445
Year 2 (10/1/00 to 9/30/01)	$400	$120	$520	$321	$118	$439
Year 3 (10/1/01 to 9/30/02)	$260	$260	$520	$194	$144	$338
Year 4 (10/1/02 to 9/30/03)	$0	$0	$0	$62	$60	$122
Year 5 (10/1/03 to 9/30/04)	$0	$0	$0	$98	$12	$110
Totals	$1010	$450	$1460	$1000	$454	$1454

Evaluation and Development of a Prototype Electrokinetic Sonic Amplitude (ESA) System for On-Line Measurement of Zeta Potential...

Good: Pacific Northwest National Laboratory

CPS#01162

National Laboratory Field Work Proposal
Quarterly Progress Report

Project Title: Evaluation and Development of a Prototype Electrokinetic Sonic Amplitude (ESA) System for On-Line Measurement of Charge in Papermaking Process Streams

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 27, 2004

Contractor: Pacific Northwest National Laboratory
Richland, WA 99352

FWP Number: 40114; ED-18-01-00-0

Subcontractors: IPST - Institute of Paper Science and Technology
MU - Miami University of Ohio

Other Partners: Colloidal Dynamics, Weyerhaeuser, Buckman Laboratories

Contact(s): Project Manager, Dr. Brian J. Tucker, (509) 375-3889, brian.tucker@pnl.gov
Principal Investigator, Dr. Morris S. Good, (509) 375-2529, ms.good@pnl.gov

Project Team: DOE-HQ contact – Dickson Ozokwelu, Dickson.ozokwelu@ee.doe.gov

Project Objective: Demonstrate a functional prototype of an ESA system for on-line measurement of charge in papermaking process streams. Benefits would include savings in paper making additives, less build up of colloidal material in white water, mill water savings and improved recyclability, less machine down time due to loss of drainage control, greater substitution of cheaper paper fillers for more expensive pulp fibers, increased production rates and energy savings from lower steam requirements. Current limitations make charge an infrequent measurement and ineffective over the wide range of paper furnishes.

Background: Particle surface charge and dissolved polymer charge affect many papermaking phenomenon. Due to measurement difficulty, most mills rely on periodic (e.g., one measurement per shift) laboratory measures for gross wet chemistry adjustments. "Forest Products – Agenda 2020," stated that research is needed to develop a new device that will work over the entire papermaking consistency range (5%--0.5%), handle a wide range of furnish compositions, enable automated monitoring of process streams, and be reliable while being low cost. ESA offers a solution to satisfy these needs.

The basis of ESA measurement is the converse of an effect discovered by Debye in 1933 where an alternating current (AC) potential was produced when suspensions of colloidal particles were subjected to ultrasonic waves. The ultrasonic waves perturbed the ionic environment around the particles in an oscillatory fashion, giving rise to the observed alternating voltage potential. This voltage potential is a function of the zeta potential of the particles. More recently, O'Brien, Cannon and Rowlands developed in 1995 a phase lag method for determining particle size and zeta potential of colloidal suspensions of spherical particles. Taggert reported in 1985 that the

ESA technique appeared to correlate well with microelectrophoresis measurements of clay particles but suspensions of wood fibers failed to produce a detectable signal. Strazdins reported in 1992 and Jaycock reported in 1995 that microelectrophoresis indicated that in a slurry of pulp and filler particles, the charge of the filler particles closely correlated to the charge of the pulp fibers. Cationic demand measurements from a 3% consistency, hardwood fiber suspension were shown at the April 2001 project review. The project team therefore, concluded that on-line measurement of charge of wood fibers is feasible whether the signal solely comes from suspended fibers or inorganics.

Progress to Date:

This project has made significant contributions in the area of paper chemistry by using advanced technologies in an effort to gain a better understanding of the paper chemistry process. This work has disproved several hypotheses that were established at the beginning of the project and led to a realization that better fundamental understanding of paper chemistry is needed to proceed and succeed. Based on the outcome of these results, we redirected the project to obtain a fundamental level of understanding of paper chemistry instead of proceeding with an ineffective mill demonstration of a non-functional measurement instrument. Therefore, it was decided that several of the remaining tasks (fabricate a flow loop, integrate system and flow loop, harden system for mill demo, and demonstrate on-line measurement at mill) would be cancelled in lieu of additional meaningful experiments. We are still collaborating with a local paper mill to obtain actual mill pulp samples for experimentation. This quarter has focused on establishing a fundamental paper chemistry baseline for future work in the area of electrokinetic sonic amplitude.

Current Quarter Status:

- Progress this quarter was largely conducted by students in an attempt to conserve the remaining financial resources.
- Fundamental studies were performed to acquire a better understanding of paper chemistry in both the new instrument (Zeta Probe) and the industry standard instrument (Mutek). A carefully controlled set of experiments were conducted to determine the validity of the electroacoustic technique on paper fibers. This set of experiments revealed results consistent with predicted theoretical values.
- Another final set of controlled experiments is being conducted to verify side-by-side results with the common industry method of determining cationic demand.
- Results from these final tests will be presented in the final report.

Plans for Next Quarter: The project will continue to utilize student staff to conserve funds and conduct additional paper chemistry studies, prepare a journal article, and close out the project. This final set of tests will result in a more comprehensive understanding of the chemical differences that are taking place in both the Zeta Probe instrument and the charge analyzer; mandatory for accurate interpretation of results. Test results from this project will be written up and submitted to an industry journal for publication. The project will be closed out by the end of this fiscal year.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Procure Cationic Demand System	10/15/01	10/15/01	Complete.
2	Train Personnel	10/19/01	10/19/01	Complete.
3	Modify System	8/1/02	12/24/02	Complete.
4	Fabricate Flow Loop	8/1/02		This task will not be performed due to lack of benefit to the overall project goal
5	Integrate System and Flow Loop	8/15/02		This task will not be performed due to lack of benefit to the overall project goal
6	Conduct Optimization Experiments for Wood Fibers	9/1/02		Comparing ESA with industry standard (Mutek) measurements
7	Conduct Experiments on Paper Furnishes	9/15/02		Experiments are underway
8	Harden System for Mill Site	1/31/03		This task will not be performed
9	Demonstrate On-Line Measurement at Mill	3/31/03		This task will not be performed
10	Establish Commercialization Plan	9/30/03		Colloidal Dynamics will begin plans to commercialize the technology if the approach proves to be technically feasible

Budget Data (As of 6/25/04):

	Approved Spending Plan ($K)			Actual Spent to Date ($K)		
Phase / Budget Period	DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
Year 1 (10/1/99 to 9/30/00)	372	128	500	126	21	147
Year 2 (10/1/00 to 9/30/01)	375	125	500	332	36	368
Year 3 (10/1/01 to 9/30/02)	200	115	315	357	41	398
Year 4 (10/1/02 to 9/30/03)*	*	*	*	115	2	117
Year 5 (10/1/03 to 9/30/04)*	*	*	*	8	0	8
Totals	947	368	1,315	938	100	1,038

*Year 4 and 5 Approved Spending Plan ($K) funding is carryover from Year 3.

Due to the changes in project scope, cost share dropped during the last portion of this project. It was anticipated that the development of a mill-hardened system and the mill demonstration would heavily involve Weyerhaeuser in-kind contributions. In addition, recent changes in research priorities at Weyerhaeuser resulted in a lack of interest in the project. These two matters led to a lower in-kind cost share amount for the last portion of this project.

Implementation of a TMP Advanced Quality Control System at a Newsprint Facility

Green: Augusta Newsprint Co.

ID14210, CPS#01704

QUARTERLY PROGRESS REPORT

Project Title: Implementation Of A TMP Advanced Quality Control System At A Newsprint Manufacturing Plant.

Covering Period: April 1, 2004 thru June 30, 2004

Date of Report: July 27, 2004

Recipient: Augusta Newsprint Company
2434 Doug Barnard Parkway
Augusta, Ga. 30906
PH.#706-798-3440

Award Number: DE-FC07-01ID14210/DE-FC36-01ID14210

Subcontractors: Pacific Simulation Invensys

Other Partners: Names

Contact(s): John Green/Project Engineer, PH.#706-798-3440 x610, Jgreen@AugustaNewsprint.com

Project Team: David Robertson/DOE, Valri Robinson/DOE, John Green/Augusta Newsprint, Bill Strand/Pacific Simulation Invensys

Project Objective: This project provides for the implementation of an advanced, model predictive multi-variant controller that works with the mill's existing distributed control system. The method provides real time and online predictive models and modifies control actions to maximize quality and minimize energy costs. Using software sensors, the system can predict difficult-to-measure quality and process variables, and make the necessary process control decisions to accurately control pulp quality while minimizing electrical usage.

Background: To optimize the TMP process, Augusta Newsprint and Invensys teamed up to implement Advanced Quality Control. As a result, the mill will see increased pulp quality, reduced Kraft Fiber Usage, and overall reduced energy needed to manufacture a ton of pulp. These savings will amount to approximately $1.12 million/year after the system is totally implemented.

Status: The Control Infrastructure portion of the project is complete. This involved designing & implementing a process control data server utilizing two interfaces, 1) DCS Interface – This is for all continuous process data, and 2) MIS Interface – Most off-line testing (pulp & paper quality) are stored in the MIS system. All testing data that is in the MIS system (PI System) must be available to the system.

An Initial Simulation was then performed to develop a steady state and dynamic simulation of the mill operation from the chip pile through the pulp mill. Next a Time Synchronization Simulation was performed to predict effects on pulp quality in real time during various points in the pulping process. This is all part of establishing a beginning baseline of the pulp process so that optimization can be achieved.

Regulatory Controls in the TMP Plant had to be trended & inspected so that any repairs or enhancements could be made to provide for optimal process control when the system is brought online in automatic control. All controls work is complete in the area of the Main Line Refiners, and Main Line Refiner Control scenarios have been implemented, and continue to be fine tuned. Specific energy and blowline consistency are being automatically controlled to achieve and maintain the desired freeness & fiber length. Reject Refiner Control is complete & on control. There were many instrument hardware upgrades that had to be implemented to facilitate auto control on all three (3) Reject Refiner Lines. Auto Dilution Control, current transmitters for screw press motor amps, and new consistency meters had to be added in order to achieve necessary performance in the Reject Refiner Lines Area.

The project team has had to modify control strategies, and update area instrumentation so that Energy goals can be met. Invensys Pacsim is involving every possible resource available to assure that the overall 1-3% Energy Reduction goal is met, while optimizing stock quality targets. The Energy Optimization portion of this project is complete, and we continue to optimize these control strategies.

Plans for Next Quarter:

The team is currently adjusting the auto process control so that minimum levels of added fiber quality can be achieved while maximizing on total electrical energy saved. The energy saving to fiber quality issue optimization is ongoing even though we are exceeding our initial goal of 1.12 million/year in energy reduction.

Patents: N/A

Publications/Presentations:

An OIT generated paper that will occur in “Energy Matters” on this project has been written and will be published.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
Task 1	Project Management	2004		Ongoing
Task 2	Initial Data Analysis	Oct. 2001	Oct. 2001	
Task 3	Control Infrastructure	Oct. 2001	Oct. 2001	
Task 4	Initial Simulation	Oct. 2001	Oct. 2001	
Task 5	Time Synchronization	Oct. 2001	Oct. 2001	
Task 6	Paper Quality Models	N/A		
Task 7	Evaluation of Regulatory Control	Feb. 2002	Feb. 2002	
Task 8	Detailed Unit Operation Modeling	Feb. 2002	Feb. 2002	
Task 9	Detailed Control	Feb. 2002	Feb. 2002	
Task 10	Paper Machine Advisory System	N/A		
Task 11	Train Personnel	Feb. 2002	Feb. 2002	
Task 12	Post Installation Optimization	2003-2004		Ongoing

Budget Data (as of June 30, 2004)

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	8/15/01	9/30/03	$450,000	$593,156	$1,043,156	$450,000	$569,434	$919,434
Year 2	9/30/03	12/30/03	$50,000	$188,880	$238,880	$0	$74,885	$74,885
Year 3	1/1/04	6/30/04	$50,000	$188,880	$238,880	$100,000	$157,527	$257,527
Year 4			$50,000	$188,880	$238,880			
Year 5								
Totals								

Contactless Real-Time Monitoring of Paper Mechanical Behavior During Papermaking (2)

Lafond: Institute of Paper Science and Technology, LBNL

ID14344, CPS#00792, CPS#00829

QUARTERLY PROGRESS REPORT

Project Title: Laser Ultrasonics Web Stiffness Sensor

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 30, 2004

Recipient: Institute of Paper Science and Technology at Georgia Tech, Atlanta, GA
And Lawrence Berkeley National Laboratory, Berkeley, CA

Award Number: DE-FC07-02ID14344

Subcontractors: none

Other Partners: ABB Industrial systems (Industrial partner)

Contact(s): Rick Russo 510-486-4258, rerusso@lbl.gov
E. Lafond 404-894-3707, emmanuel.lafond@ipst.gatech.edu

Project Team: DOE Program Managers: Charles Russomanno, Joseph Springer; Research Team: IPST@GT: Ted Jackson, Emmanuel Lafond, Xinya Zhang; LBNL: Paul Ridgway, Rick Russo

Project Objective: The objective is to provide a sensor that uses non-contact, laser ultrasonics to inspect the mechanical state of paper on-line. Tasks include optimization of ultrasound generation on moving paper, development of interferometric detection schemes for on-line operation, and construction of a prototype for single point application on a paper machine.

Background: Laser ultrasonic methods have the potential to greatly extend the utility of on-line ultrasonic telemetry. Existing on-line ultrasonic techniques using contact transducers function only on board grades. Laser ultrasonic methods could perform at higher speeds without causing damage to lightweight papers. Laser ultrasonic methods are able to determine bending stiffness. Bending stiffness is the property that determines end-product rigidity and is of great importance to a wide variety of paper grades. Laser ultrasonics could also provide single-sensor in-plane and out-of-plane characterization and give the first on-line gauge of stiffness orientation.

This project is the continuation of project DE-FC07-97ID13578. It is the combined efforts of two organizations with complementary experiences in paper physics and laser ultrasonics. LNBL is expert in the art of laser acoustic wave generation. Progress here is necessary to induce the largest possible ultrasonic disturbance without damaging the sheet. They developed a scanning-mirror, Mach-Zehnder interferometer that works well at high speeds on a web-simulator. IPST @ GeorgiaTech contributes paper physics expertise and close relations with the paper industry. They have also demonstrated laser ultrasonic capabilities by constructing unique laboratory ultrasonic systems for paper. The group continues to work together to improve these technologies for web measurements. ABB is our industrial partner and is contributing web stablization technology, sensors enclosures, sensor design advices, and softwares.

Status:

On April 6, Paul and Emmanuel traveled to the Boise-Cascade paper mill of Wallula, WA and talked about of a possible mill trial of the laser ultrasonic stiffness sensor with the mill's process engineers, product development manager, and paper machine superintendent.

Paper machine # 3 of the Wallula mill has an ABB platform similar to Escanaba, where the sensor could be installed. There was an obvious interest there but prior to forwarding to the mill manager our request for a mill trial, the process engineers asked for: a transport system of the cables between the sensor head and the auxiliary system, detection laser, that is compatible with the wider web and geometry of the platform, and a letter of intent from ABB offering a competitive advantage to the mill about the sensor, in exchange of the mill trial.

We discussed with ABB, which provided us with a smart solution that will fit the configuration of the platform on the paper machine and that was declared acceptable by the mill personnel. For the second item, the letter of intent, we also discussed with Steve Sturm from ABB, who drafted the ABB letter of intent. ABB intends to provide advantageous pricing for the beta trial of the sensor (6 months or semi-permanent installation) in exchange of the mill participating to the alpha trial (2 week demonstration). The letter was finalized and faxed to Boise at the end of June and we are awaiting their feedback.

In early May, the whole research team attended the annual review meeting for the project at PaperSummit in Atlanta, with reviewers selected by the Dept. of Energy. We first made a presentation open to the public, then participated to a closed-door discussion with the reviewers where many interesting technical comments were made. The research team also received at this occasion from TAPPI, the plaque for the outstanding research paper award.

Gary Baum, working with Paul Ridgway and Emmanuel Lafond put together a presentation about the sensor in the form of a video + slides with audio comments. This was mostly done for the purpose of educating paper mill's process control engineers and mill managers about the technical aspects, installation, and value proposition of the sensor. We think it will facilitate our work when negotiating the mill trial. As it is a good summary of the sensor capabilities, it was also sent to the Dept. of Energy.

In June, Emmanuel Lafond and Ted Jackson did more testing with the sensor on heavy basis weight grades to determine what is the maximum basis weight compatible with it. To our relative surprise, we found out we were able to measure the flexural rigidity and shear rigidity on moving paperboard with basis weight from 210 g/m^2 (brown 42-Lb) up to 319 g/m^2 (bleached 69 Lb). This only required a slight increase in the energy per pulse, which is within the safe operating range of the fiber optic for generation. In 2001, the pulse duration of the generation laser we used during our pilot coater demonstration was 5 ns. This duration has been adjusted to 15 ns with a different generation laser which is more favorable for generating the low frequencies that are mostly propagated by paperboard. Also, our signal processing software is now more sophisticated than in the past and more immune to noise. The only drawback we found so far is that the appropriate frequency range of analysis is narrower for paperboard than for light weight paper. In the case of light weight grades the analysis was routinely carried from a few tens of kHz to 600 kHz or higher. In the case of board, the high frequency cut-off is much lower, almost never exceeding 300 kHz. Nevertheless, when we compared the stiffness values obtained on-line with the off-line values from the Two-Wave mixing laboratory instrument (which works well on all paper grades) we found very similar and consistent values, that is why we deemed this frequency range acceptable for board.

This quarter, Ted Jackson also continued to improve the software of the on-line system. He worked mostly on the display of the results so that we now have a real-time display of the flexural rigidity and shear rigidity stiffnesses as function of the time on a scrolling window. This will allow the paper machine operators to observe trends in the stiffnesses and adjust parameters on the paper machine accordingly (compensate for low stiffness, adjust actuators during grade changes, etc…). Using Paul's input, he has also started to develop the log (recording) part of the software so that the recorded stiffness data can be replayed later and reanalyzed if necessary.

The new development of the sensor working for paperboard opens new opportunities and we conveyed this information to MeadWestvaco, a big producer of board and carton grades. MeadWestvaco exhibited an interest and promised to forward the information to its Evadale, TX and Covington, VA mill to look into a possible mill trial of the sensor on paperboard.

With the alpha mill trial drawing near, we feel we need to work more closely with our industrial partner, ABB in view of commercialization. In July, Emmanuel Lafond and Gary Baum will travel to ABB in Columbus, OH, to present the latest results from the sensor and discuss alpha and beta mill trials, interfacing the sensor with the ABB actuators, its integration into the ABB quality control system, and future commercialization plans.

Also in July, Paul Ridgway will present our results at the 2004 QNDE (Quantitative Non-Destructive Evaluation) conference, and do some additional experiments on static paper at LBNL. In August he will travel to Atlanta to help IPST personnel to carry more experiments on moving boards and help finalize some details of the sensor (temperature and moisture corrections). We will also continue to improve the software together.

Last but not least, on June 22, our research team was awarded the 2004 Van den Akker Prize for Paper Physics for the research work done on this project. Our 2003 JPPS paper was selected as the greatest contribution to the field of paper physics this year. The prize is distributed by IPST but the selection committee is independent from it and made of members from different research organizations and paper companies.

Plans for Next Quarter:

- Continue our efforts for signing up mills for a 2 weeks full-scale demonstration
- Work with ABB towards the alpha and beta mill trial and commercialization
- Finish static testing of various paper grades with the Mach-Zehnder interferometer system at LBNL
- Test more moving paperboard grades with the sensor; validate results with off-line testing
- Refine on-line sensor software and hardware (create “bare bones” mill operator panel, improve log file reader, incorporate and verify influence of temperature and moisture corrections)

Development of METHANE deNO$_X$ Reburning Process for Wastewood, Sludge, and Biomass Fired Stoker Boilers

Bryan: Gas Technology Institute

GO10418, CPS#00933

Quarterly Technical Progress Report
for the period ending June 30, 2004
for
Development of METHANE de-NOX® Reburning Process for Wood Waste and Biomass Fired Stoker Boilers
and
Utilization of Non-Condensable Gases as Reburn Fuel in FPI Wood Waste and Sludge-Fired Stoker Boilers
and
Advanced METHANE de-NOX for Woodwaste-Fired Stoker Boilers

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 28, 2004

Award Number: DE-FC36-99GO10418

Project Team: Joseph Springer, DOE project manager; Carrie Capps, DOE Project Monitor; David Highsmith, Georgia-Pacific Port Hudson Operations Project Manager; Tom Gilmore, Boise DeRidder mill project manager; Chad Stodola, Boise International Falls project manager; Larry Szymanski, ESA Environmental Solutions; Tom Giaier, Detroit Stoker Company project manager; Fluent Inc., Reaction Engineering Inc, University of Illinois at Chicago.

Submitting Organization:

Gas Technology Institute (GTI)
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Des Plaines, IL 60018-1804

IGT Technical Contacts:

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Subcontractors: ESA Environmental Solutions, Sargent & Lundy LLC, Fluent Engineering, Reaction Engineering and University of Illinois at Chicago

Other Partners: Gas Research Institute, IGT Sustaining Membership Program, Detroit Stoker Company, Boise Cascade and Georgia-Pacific Corporation

Project Objectives: The primary project objective is to demonstrate the effectiveness of the METHANE de-NOX® (MdN) process for promoting more efficient use of wood waste and sludge for steam generation while keeping NO_x and CO emissions in compliance biomass–fired stoker boilers in the Forest Products Industry (FPI). A second objective is to investigate the use of non-condensable gas (NCG) and stripper off gas (SOG) as reburn fuel in the MdN technology. This process extension enhances existing reburn technology benefits by further reducing natural gas consumption while providing an effective waste gas disposal option.

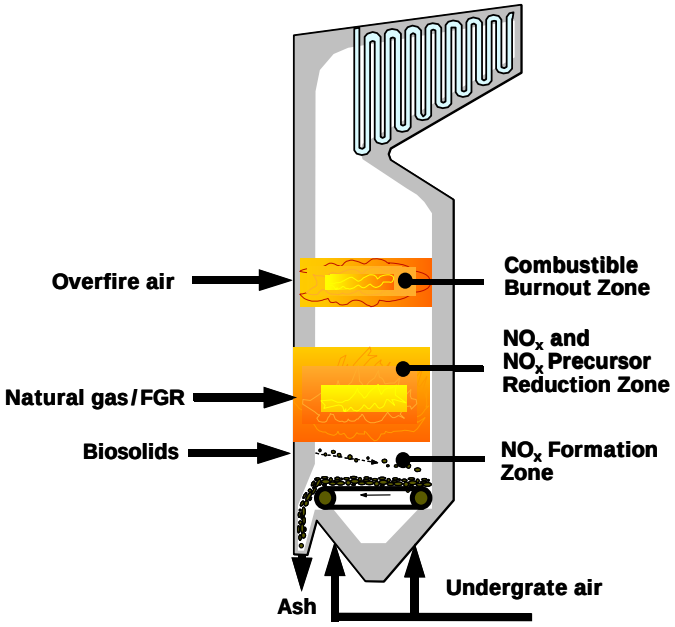

Figure 1. MdN reburn process uses fuel and air staging for combustion improvement and reduced NOx emissions

Background: The firing of biosolids can be limited by the low heating value and presence of bound nitrogen in these fuels. High moisture fuels result in inefficient combustion due to the latent heat of water vapor that is lost to the stack. High fuel moisture biosolids can also contribute to poor fuel distribution and piling, resulting in poor undergrate air distribution, uneven combustion at the grate, and increased emissions of CO and NO_x. Fuels with high nitrogen content such as secondary and tertiary treatment solids also contribute to increased NO_x emissions, limiting the ability to fire these fuels in boilers operating near their NO_x permit limit. Cofiring supplemental fuel such as natural gas through auxiliary burners helps to improve combustion effectiveness and to reduce NO_x emissions. However, these benefits are typically limited to the fractional input of the cofiring fuel.

The MdN reburn process uses both fuel- and air-staging to improve combustion and reduce boiler emissions. A small amount of natural gas and recirculated flue gas (FGR) is injected above the stoker grate to create a well-mixed, oxygen-deficient atmosphere immediately above the primary combustion zone (Figure 1). Air distribution between the undergrate and overfire air is also adjusted to reduce oxygen availability in the lower furnace and improve burnout in the upper furnace. Hotter and less-oxidizing conditions at the grate promote the decomposition of fuel-bound nitrogen compounds to reduce nitrogen oxide formation, while deeper air staging improves burnout in the upper furnace and allows operation with lower excess air. The added heat release and gas mixing at the stoker grate also improves combustion of difficult-to-burn woodwaste fuels. As a result, more high-moisture waste fuels can be burned, while reducing NO_x emissions, stabilizing combustion and improving boiler efficiency through reduced carbon losses and operation with lower excess air.

An MdN boiler retrofit consists of four primary components: 1) a natural gas supply and injection system, 2) a flue gas recirculation system, 3) air distribution adjustments that may include overfire air system modifications, and 4) control integration. Depending on many operational conditions and constraints, which vary widely for FPI woodwaste-fired boilers, the

MdN process can reduce NO_x emissions by 30 –50% and improve boiler thermal efficiency up to 2%, while stabilizing grate combustion and increasing the ability to fire difficult-to-burn fuels.

The project has resulted in the successful of the MdN technology on a bark- and sludge-fired boiler at a Boise Cascade paper mill in International Falls, MN and baseline testing and evaluation of two additional bark-fired stoker boilers at other mills. As a result of this testing, a continuation project was awarded in 2001 under Cooperative Agreement DE-FC36-99GO10418 to extend the application and benefits of the technology to include a flexible combustion-based disposal option for NCG through their use as reburn fuel in bark and hog fuel boilers. In this project, an existing NCG collection and distribution system will be incorporated into a reburn system retrofit to be developed and demonstrated on a 200,000 lb/h MCR (maximum continuous rating) bark-fired boiler at a second Boise mill in DeRidder, Louisiana.

Another MdN system installed at a Georgia- Pacific paper mill at Port Hudson, LA in 2002 achieved NO_x reduction of over 30% on a 225,000 lb/h bark and gas cofired boiler. A second continuation project awarded in May 2004 has resulted in the design and installation of a modified overfire air (OFA) and flue gas recirculation (FGR) system to further improve the boiler's energy and emissions performance.

Base Project:

Development of METHANE de-NOX® Reburning Process for Wood Waste and Biomass Fired Stoker Boilers

Status:

This development effort was divided into two phases. In Phase 1, a 300-MMBtu/h wood waste and sludge-fired stoker boiler at Boise Cascade's paper mill in International Falls, MN was retrofitted with the MdN technology. Site testing was conducted in December 1999. Results from 15 parametric tests proved the technology's effectiveness by meeting all projected performance goals as follows:

- Increased sludge firing by over 150% from the current 1.2-1.5 tph to 4 ton per hour
- Increased thermal efficiency for 40-100% load by 1 to 2%
- Reduced NO_x emissions by over 50% compared to previous cofiring mode
- Decreased natural gas input by 25% compared to the previous cofiring mode

Based on these favorable results, Boise Cascade formally accepted the MdN retrofit and the American Forest and Paper Association (AF&PA) recognized MdN's performance benefits with a 1999 Environmental and Energy Achievement Award in the Energy and Management and Innovation Category. The I. Falls system has now logged over 4 years of continuous operation without a major problem reported since being placed into full-scale operation on December 12, 1999.

Phase 2 activities in the base project consist of a series of tasks aimed at promoting the use of MdN technology within the FPI. Major tasks completed in this phase include: successful demonstration of long-term MdN performance at the I. Falls site; development of a customized computational fluid dynamic (CFD) model simulating MdN in a wood waste- and sludge-fired stoker boiler; and completion of on-site baseline testing and evaluation of two additional bark-fired stoker boilers in the FPI, one of which led to the DeRidder continuation project.

Base Project Work Summary:

Phase 1, Tasks 1 – 3

All work is complete

Phase 2, Tasks 4 – 10

All work is complete

Phase 2, Task 11 MdN Technology Database for Wood Firing

No work was performed in this task during the quarter.

Phase 2, Task 12 MdN Engineering Design

The main technical hurdle thus far encountered in design and implementation of MdN reburning technology has been the large variation in boiler and support equipment configuration and condition among the Pulp and Paper Industry's hog fuel boiler population.

A modeling study was completed during the previous quarter to develop guidelines for the key engineering design and operational choices typically encountered when retrofitting METHANE de-NOX technology on woodwaste-fired stoker boilers. During the current quarter, the model results were applied to the design and installation of a modified OFA/FGR system at the G-P Port Hudson mill under Continuation Project 2 discussed below.

Phase 2, Task 13 Commercialization and Technology Transfer

The MdN technology has been licensed to a new licensee, ESA Environmental Solutions, LLC. ESA/ES is a limited liability corporation located in Pittsburgh PA. ESA/ES is an engineering and equipment supply company that specializes in supplying system design, engineering and turnkey installation of combustion-based NOx reduction technology for utility and industrial boilers.

Baseline testing has been completed for four woodwaste-fired boilers during the project to date, resulting in full MdN system installations in two of the four with a third installation pending. ESA has submitted a proposal for baseline testing and MdN retrofit on another wood-fired boiler in the U.S. The first of two MSW-fired MdN-equipped waste-to-energy facilities in Japan has been brought online and an additional coal-fired power boiler has been retrofitted with full MdN on the East Coast. A total of 12 power boilers are now equipped with the technology with an additional two boilers (one MSW-fired and one woodwaste-fired) and one wood-fired proposal pending.

<u>Continuation Project 1:</u>

Utilization of Non-Condensable Gases as Reburn Fuel in FPI Woodwaste and Sludge-Fired Stoker Boilers (MdN with NCGs)

Status:

The continuation project seeks to use NCG and SOG to enhance the benefits already demonstrated by MdN by utilization of these gases as reburn fuel in place of natural gas in hog fuel stoker boilers.

The MdN with NCGs performance objectives are:

- utilize to the maximum extent possible all low-volume high-concentration (LVHC) NCG and SOG waste gases consistent with safe and reliable operation
- decrease reburn natural gas consumption by more than 25% compared with original MdN operation
- reduce NO_x emission by over 40% compared to baseline (uncontrolled) conditions
- improve carbon burnout and increase boiler efficiency.

The development efforts will include a system retrofit on Boise's DeRidder No 2 Power Boiler followed by on-site performance tests to demonstrate effectiveness and validate process benefits. Due to boiler outage constraints, it is expected that the MdN installation on No. 2 Power Boiler at the DeRidder mill will not occur until early 2005. As a result, no design or test work was conducted during the quarter.

Work Summary

Task 1. Baseline Testing

Baseline testing of No. 2 Power Boiler at Boise's DeRidder paper mill in Louisiana is complete. Baseline testing was conducted to characterize current boiler performance before MdN installation and to provide data to validate the CFD model developed to facilitate the MdN system design.

Task 2. LVHC and HVLC Gas System Evaluation

The waste gas system evaluation is complete.

Task 3. Modeling and Conceptual Design

The MdN modeling for the original conceptual design development is complete. As part of the recently awarded Advanced METHANE de-NOX project discussed under Continuation Project 2 below, additional modeling will be conducted in support of detailed design engineering. Baseline boiler operating data previously collected will be used as the basis for an expanded CFD modeling evaluation for the DeRidder Boiler No. 2. The modeling study and modified conceptual design will be finalized in cooperation with DeRidder Engineering to accommodate any existing layout, mechanical or operational constraints. The modified conceptual design will be the basis for detailed design, procurement and installation to be completed under Continuation Project 1.

Task 4. Detailed Engineering

There was no activity in this task during the quarter.

Task 5. Procurement and Installation

There was no activity in this task during the quarter.

Task 6. Parametric Testing

There was no activity in this task during the quarter.

Task 7. Long-Term Testing

There was no activity in this task during the quarter.

Task 8. Data Processing and Analysis

Baseline test data processing is complete. The Baseline Test Report has been completed and submitted to Boise.

Task 9. Model Validation

There was no activity in this task during the quarter.

Task 10. Project Management

Due to boiler outage constraints, it is expected that the MdN installation on No. 2 Power Boiler at the DeRidder mill will not occur until early 2005. No design or test work was conducted during the quarter.

A paper on the development and demonstration of the MdN technology for woodwaste-fired boilers was presented at the 2004 TAPPI (Technical Association of the Pulp and Paper Industry) Spring Technical Conference on May 5 in Atlanta.

GTI completed the PI Questionnaire and participated in a Project Review Meeting with the DOE Peer Review team following the TAPPI presentation in Atlanta.

A proposal for supplemental funding was prepared and submitted to DOE/ITP in the previous quarter to apply the CFD modeling methods and optimization strategies to two boilers, Power Boiler No. 1 at Georgia-Pacific's mill at Port Hudson, LA and No. 2 Power Boiler in the Boise mill at DeRidder, LA. GTI received authorization to proceed at risk with this work in April 2004 and the final contract modification was received in June 2004. Additional work conducted on this project is discussed under Continuation Project 2 below.

A paper on the MdN technology was written and presented at the U.S.-China Workshop for Advanced Technology of Industrial Boilers in Beijing China in June. The conference was jointly sponsored by Chinese boiler companies, U.S. EPA, U.S. DOE NREL and DOE/NETL.

Continuation Project 2:

Advanced METHANE de-NOX for Woodwaste-Fired Stoker Boilers

The project to apply CFD modeling methods and optimization strategies to the existing MdN system on the No. 1 Power Boiler at Georgia-Pacific's mill at Port Hudson, LA was started during the current quarter. The R&D objectives of the Port Hudson project are to further optimize the MdN system to reduce NOx and improve CO burnout, allowing operation at lower excess air levels and higher boiler efficiency and reducing cofiring gas usage. The project is being conducted as a quick turnaround project, with commissioning, performance testing, optimization and reporting to be completed by September 2004.

Task 1. Port Hudson Modeling and Conceptual Design

The modeling study and conceptual design for modifications to the boiler's OFA and FGR systems were finalized in cooperation with Port Hudson Engineering during the quarter. Modifications to the original MdN system included:

- Elimination of the undergrate FGR supply duct and controls
- Addition of a new FGR supply duct and manual damper to the OFA duct ahead of the OFA flow meter
- Addition of OFA supply ducts and manual dampers to the old 5" dia. mid-level OFA nozzles (4 each) in the North and South walls of the boiler
- Addition of 1" dia flow restrictors in the original MdN nozzles in the North and South walls just above the grate
- Plugging of selected nozzles in the upper level OFA banks (4 each side) in the East and West walls of the boiler

A P&ID, Control Diagram, and updated Arrangement drawing for the modified system were prepared and forwarded to Port Hudson Engineering to be used to solicit contractor bids for detailed engineering and installation. The technical approach for performance improvement was to improve the distribution of FGR and OFA. Eight of the original fourteen mid-level OFA nozzles were reactivated for improved mixing of CO-rich gases from the rear of the grate with O_2-rich gases from the front of the grate. Eight of the twenty-two upper-level OFA nozzles were plugged to allow operation of the OFA header at higher pressures for improved penetration and mixing in the upper furnace without significantly increasing air flow there. In the original system, most of the FGR was introduced through the MdN nozzles just above the grate and a small amount was blended with sweep air to the bark feeders. In the modified system, most of the FGR is blended with OFA to the mid- and upper-level OFA nozzles and a smaller amount flows to the MdN nozzles and sweep header. The benefits of blending FGR with OFA are increased mass flow and reduced oxygen concentration in the OFA, resulting in improved OFA penetration and mixing in the furnace for better CO burnout without increased NOx formation.

Task 2. Port Hudson Detailed Engineering and Installation.

GTI reviewed detailed engineering design drawings for the modifications developed by G-P's selected design and installation contractor. Comments were provided on the OFA and FGR ductwork designs, including sizing, routing, and location of manual dampers, flowmeters, static pressure taps and Pitot ports. GTI also provided comments for flow restrictors in the MdN gas and FGR injection nozzles.

Fabrication and installation of the new OFA and FGR ductwork runs was begun around No. 1 Power Boiler during the first week of May in preparation for a boiler outage for final ductwork tie-ins during the week of May 10th. All modified components were installed during this outage with the exception of three flow meters, one for FGR flow to the OFA system and two that measure FGR/OFA flow to the reactivated mid-level OFA nozzles at the front and rear of the boiler. These flowmeters require twelve weeks for delivery and will therefore have to be installed at a later date.

GTI began mobilizing for boiler testing at Port Hudson in late April when authorization to proceed at risk was received. GTI arrived on site on May 12 to begin setup of equipment for boiler testing and to review and assist in the boiler modifications. A continuous CO sampling

system, analyzer and data logger was set up in an air-conditioned trailer by the scrubber to allow longer term monitoring of stack CO. Installation and tie-ins were completed by May 15 and GTI provided the initial settings for the modified OFA, FGR and MdN dampers and injectors for commissioning and startup.

Task 3. Port Hudson Boiler Performance Testing

GTI tested the modified MdN system from 5/16 through 5/20/04 to evaluate performance and determine appropriate operating settings for the manual dampers and header pressures. Since the flow meters intended to measure the flow of FGR to OFA and OFA/FGR mix to the north and south mid-level OFA nozzles had not been installed, Pitot measurements were made to confirm that these flows were in the desired ranges. The FGR/OFA mix was checked with GTI's gas analyzers to determine the FGR concentration in the OFA.

The manual FGR dampers to the newly restricted MdN gas/FGR injection nozzles near the grate were adjusted to significantly reduce FGR through the nozzles. Operation with the reduced flow was found to reduce the quantity and particle size of fly ash carried over from the boiler to the mechanical collection tank. It will also eliminate the occasional occurrences of "blowback" of unburned bark off the front of the grate.

The FGR to OFA system was tested from 10% to 25% FGR concentration in the OFA. It was found that in the closed position with the OFA header at 20" wc, the FGR to OFA damper leaks enough to maintain about 10% FGR in the OFA. The FGR concentration will rise somewhat if the OFA pressure is reduced due to increased differential pressure across the FGR damper. In order to increase the FGR concentration in the OFA without reducing the OFA pressure, the FGR damper was opened to get 20-22% FGR concentration. By reducing the oxygen concentration in the OFA with FGR, it was found that the OFA header pressure could be increased to the upper-level nozzles for improved mixing and CO burnout without significantly increasing NOx formation in the upper furnace.

The reactivated mid-level OFA headers to the north and south walls of the boiler were tested over a range of OFA pressures and nozzle patterns, including all eight wide open, two center nozzles in each side open, four open in the south wall only, four open in the north wall only, and a staggered or interlaced arrangement with two open in the north and south wall. The best CO performance was found with the interlaced arrangement, and the mid-level nozzles were left in this arrangement.

The minimum-fire setting on the gas cofiring burners was reduced from about 50 MMBtu/h to about 33 MMBtu/h. This will reduce overall gas usage and increase the boiler's capacity for bark burning. The bark was extremely wet at the beginning of the visit, but improved toward the end. Based on the initial testing, bark burning rates of 32-34 tph are expected to be sustainable with average bark moistures. Total air, undergrate air and OFA readings were all higher with the modified system. The OFA reading now includes about 20% FGR and excludes flow to the north mid-level OFA nozzles due to the way the ductwork was routed. The total air reading (plus the unmetered HVLC to the grate) was consistent with the amount of bark and gas being burned. ID fan loading varied with steam load, bark usage/moisture and FGR usage and was running 90 – 93% during the visit. This was consistent with the 190-200 Kpph steam load, high

bark moisture and increased FGR usage. Toward the end of the visit, the ID fan was in the 88-90% range as the bark appeared to be drier.

At the end of the visit, arrangements were made with Port Hudson Process and Lab personnel to monitor and calibrate the CO sampling system, analyzer and data logger and retrieve CO data, which will be evaluated for the next several months together with PI data for No. 1 Power boiler to characterize the boiler and modified MdN system performance and potential adjustments for further improvement prior to compliance testing.

Task 4. Port Hudson Data Processing and Evaluation

In the initial testing it was found that the boiler's emissions performance has been improved. Prior to the modifications, NOx could be reduced to about 0.20-0.22 lb/MMBtu with CO levels of about 1000 – 2000 ppm. Reducing furnace exit oxygen could reduce NOx to well below 0.20 lb/MMBtu, but CO would rise to as high as 3000-5000 ppm. With the modified system, CO levels below 1000 ppm were achieved with NOx below 0.20 lb/MMBtu at a wet boiler exit O_2 concentration of 3 – 5 %.

Task 5. DeRidder Modeling and Conceptual Design

This work will be performed under Task 3 of the DeRidder NCG project.

Plans for Next Quarter:

1. Complete optimization of the modified MdN system at Port Hudson and long-term testing of the optimized system.
2. Initiate the additional modeling study for No. 2 Power Boiler at DeRidder.

Milestone Status Table

ID Number	Task / Milestone Description	Original Completion	Actual Completion	Current Negotiated Completion
MdN at International Falls				
Phase 1 Tasks				
1	Engineering Design for IF Unit #2	09/98	09/98	
2	Procurement/Installation at IF Unit #2	11/98	11/99[1]	
3	Field Parametric Testing of IF Unit #2	12/98	12/99[1]	
Phase 2 Tasks				
4	Long-term Performance Testing at IF Unit #2	07/00	08/00	
5	Pilot-Scale Testing at EPA	10/00	Task suspended	
6	Furnace Computer Modeling	01/01	02/01	
7	Boiler Baseline Testing	08/00	04/01	
8	Boiler Baseline Testing	08/00	11/01	
9	IF Unit #2 Simulation	12/00	10/01	
10	Data Processing and Analysis	02/01	12/01	
11	MdN Technology Database for Wood Firing	02/01		12/04[2]
12	MdN Engineering Design	02/01		12/04[2]
13	Commercialization and Technology Transfer	03/01	12/02	
14	Project Management and Reporting	04/01		12/04[2]

MdN with NCGs at DeRidder				
Tasks				
1	Baseline Testing	04/02	06/02	
2	LVHC and HVLC Gas System Evaluation	05/02	03/03	
3	Modeling and Conceptual Design	08/02	06/03	
4	Detailed Engineering	12/02		06/04[3]
5	Procurement and Installation	04/03		09/04[3]
6	Parametric Testing	06/03		09/04[3]
7	Long-Term Testing	09/03		12/04[3]
8	Data Processing and Analysis	09/03		12/04[3]
9	Model Validation	11/03		12/04[3]
10	Project Management	09/03		12/04[3]
Advanced MdN at Port Hudson & DeRidder				
Tasks				
1	Port Hudson Modeling and Conceptual Design	05/04	05/04	
2	Port Hudson Detailed Engineering and Installation	05/04	05/04	
3	Port Hudson Boiler Performance Testing	08/04		
4	Port Hudson Data Processing and Evaluation	08/04		
5	DeRidder Modeling and Conceptual Design Review	09/04		
6	Project Management	09/04		

[1] Host site environmental permit delay

[2] Tasks are being held open to capture results from DeRidder and Port Hudson projects.

[3] Further delay expected since boiler outage for final tie-ins cannot be scheduled before the first quarter of 2005. Will complete Port Hudson retrofit in the interim, and then apply results to DeRidder design.

Methane de-NOX Budget Data: Costs are in $(000)

			Approved Spending Plan			Actual Spent to Date		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	10/1/1998	9/30/1999	200	530	730	120	420	540
Year 2	10/1/1999	9/30/2000	300	180	480	364	702	1,066
Year 3	10/1/2000	9/30/2001	250	210	460	257	269	526
Year 4	10/1/2001	12/31/2001		130	130	-7	174	167
		Totals	750	1,050	1,800	734	1,565	2,299

Utilization of NCGs Budget Data: Costs are in $(000)

			Approved Spending Plan			Actual Spent to Date		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	1/1/2002	12/31/2002	377	141	518	241	361	602
Year 2	1/1/2003	12/31/2003	223	568	791	47	33	79
Year 3	1/1/2004	3/31/2004				7	0	7
		Totals	600	709	1,309	287	394	689

The above budget data covers project work through the first quarter of 2004. GTI has recently implemented a new accounting software system: Deltek Costpoint. Due to this major company-wide transition process, our Accounting Department will be delayed in completing the month-

end closing for June 2004. In order to provide accurate and complete data for the above budget tables and the Financial Status Report, we must wait until the books are closed in June to obtain the data for the second quarter. For additional information please contact:

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Use of Borate Autocausticizing to Supplement Lime Kiln and Causticizing Capacities

Cameron: Western Michigan University

GO10623, CPS#01486

1st Quarterly Progress Report – Year 1

For: Use of Borate Autocausticizing to Supplement Lime Kiln and Causticizing Capacities

Covering Period: (April 1, 2004 to June 30, 2004)
Date of Report: (July 23, 2004)

Recipient: Western Michigan University
Award Number: DE-FC36-01GO10623
Subcontractors: None

Other Partners: US Borax – Cash and In-kind
International Paper Company Cash and In-kind
Babcock and Wilcox Company In-kind

Contact: John Cameron 269-376-3508

Project Team: Administered for DOE by Margo A. Gorin

Project Objective: Provide the necessary knowledge to commercialize borate-based partial autocausticizing. This project will determine the effects of borate autocausticizing on causticizing efficiency, kraft pulping, resulting black liquor properties, and the relationships between mill and laboratory data.

Background: Boron autocausticizing refers to a non-conventional causticizing process that uses boron oxides to release carbon dioxide (CO_2) directly from sodium carbonate (Na_2CO_3) in the kraft furnace. Sodium hydroxide (NaOH) is then generated directly in the green-liquor dissolving tank. In boron autocausticizing, sodium metaborate and sodium carbonate react in the furnace to form trisodium borate (Na_3BO_3), and carbon dioxide [reaction (1)]. On dissolving, the trisodium borate reacts with water to form sodium hydroxide and regenerate the metaborate, [reaction (2)].

$$NaBO_2 + Na_2CO_3 \Leftrightarrow Na_3BO_3 + CO_2 \qquad Furnace \qquad (1)$$

$$Na_3BO_3 + H_2O \Leftrightarrow 2\,NaOH + NaBO_2 \qquad Dissolving\ Tank \qquad (2)$$

Laboratory results and on-going mill trials have confirmed the above reactions. Among the observations of the on-going mill trials are: (1) the furnace decarbonizing reactions occur as predicted from the above equations, (2) the causticizing efficiency appears to increase, (3) borate may increase the efficiency of the pulping reaction, (4) as expected, less energy was required for calcining and causticizing, and (5) lime limited mills have been able to reduce lime purchases. For partial autocausticizing to achieve acceptance, the mechanisms and controlling parameters must be identified, understood and optimized.

Quarter Highlights: The project was reviewed at the Tappi Technology Summit March 28 to 31 and at the 2004 Tappi Summit to be held May 3 to May 5. At the Technology Summit, full borate autocausticizing was chosen as a future technology. This is different from the current project where only part of the caustic demand was supplied by borate autocausticizing. An industrial consortium has been to determine the economic feasibility of pursuing full borate autocausticizing.

Work during the second quarter 2004 quarter focused on confirming and quantifying the effect of borate on kraft pulping described in Task II.

***Task I*: Quantify the effect of partial autocausticizing on increased causticizing efficiency.** The work on the causticizing reactions is complete. The increased efficiencies observed in the mill trials and the mechanisms responsible for these increases have been confirmed. The increase in the lime-mud settling rate is currently being studied. It is believed that the increase in lime mud settling rate is due to the reduced number of calcium carbonate particles in the lime mud. Since partial autocausticizing reduces the need for burnt lime, fewer lime particles are present after causticizing which will increase the lime mud settling rates.

Task II: **Determine the effect of partial autocausticizing on kraft pulping**. Other laboratories have confirmed the increase in pulp yield, first identified at Western Michigan University. US Borax has contracted and independent testing lab to study the effect of borate on yield of Southern pine (loblolly pine). In pulping to a kappa number of 30 or lower, the increase in yield with southern pine was about 0.25%. This is lower than that see for black spruce or commercial western chips, confirms that borate can increase pulp yield, but the behavior depends on pulping conditions and species.

***Task III*, Determine the effect of borate on the resulting black liquor properties**. This work is complete. A major concern with borate autocausticizing is the effect on the resulting black liquor properties. Work in this area is complete and shows only minor effects of the additional inorganic load on the black liquor properties.

Mill Trials: The trials run to date and a summary of the major results are shown below. As shown in this table several trials have been conducted in North America. Most of these trials run well, but have been discontinued. The primarily reason for discontinuing these trials is due to the difficulty of documenting the process economics. The international trials have been more successful in economic documentation and some of these trials are continuing as long term processes. It is expected that once the economics are proved through these international trials, there will be more interest in North America.

Borate Autocausticizing Trial Summary

Mill	Status	AC Level	Recaust. Control Issues	Reaction Efficiency	Fouling Concerns	Increased SO2 Emission	Corrosion Concerns
1 Canada	Discontinued	100%	No	Excellent	No	No	No
2 Canada	Discontinued	25-30%	Yes	Good	No	Spikes	No
3 US	Discontinued	5-20%	No	Fair	No	Yes? Spikes	No
4 US	Discontinued	-	-	Good	No	No	No
5 – No 2 Repeat	Discontinued	10%?	Yes	Good	No	Spikes	No
6 US	Discontinued	10%	Yes	Good	No	No	No
7 US	Discontinued	10-15%	Yes	Poor	Yes?	No?	No
8 US	Discontinued	10-15%	No	Good	Yes	No?	No
9 US	Discontinued	10%	Yes?	Good	No	No?	Yes
10 Sweden	On-going	10-15%	No	Fair	Yes	No	No
11 US	Resuming'04	12%	No	Fair	No	Yes	No
12 Canada	Discontinued	15%	Yes	Excellent	No	No	No
13 New Zealand	On -going	10-12%	No	Fair	Yes?	Yes ?	No

Plans for Next Quarter: The major plans for the next quarter are:

1. Continue pulping studies to determine the optimum operating conditions.

2. Prepare final Report and Project Budget

Milestone Status:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
	Project Start	10/01/01	12/04/01	
1	Causticizing Efficiency Determination			
1.2	Obtain Kinetic Data on Molten Salt Reactions	4/30/01	4/30/01	
1.3	Install Automatic titrator	4/30/01	4/30/01	Initial tests confirm system
1.4	Design Causticizing Reactor	5/15//01	5/30/01	
1.4.1	Place Order with Vendor	6/01/01	7/01/01	
1.4.2	Modify and Install Reactor	8/01/01	12/01/01	Reactor has been installed and initial tests are in progress. This is not expected to delay the project.
1.5.1	Conduct Initial Causticizing Experiments	9/01/01	9/01/01	On existing laboratory equipment, this is keeping this item on tack
1.5.2	Obtain Causticizing Rate and Kinetic data	12/01/01	9/01/01	More data required, will not delay project
1.5.3	Develop Model for Causticizing Reaction	12/01/01	9/01/02	The data appears more complex than originally anticipated and more data is required. This will not affect the overall completion of the project.
1.6	Thermodynamic Model	8/01/02	12/01/02	Much of model is complete, Plan to complete work on thermodynamics and reaction chemistry by 12/01/02. This will not affect the overall completion of the project.
1.6.1	Correlate Model to Laboratory and Mill Data	4/01/03	6/01/3	This is on-going, but the effect on yield seen in the mills is encouraging
2	Pulping Reactions			
2.2	Develop Plan for Pulping Experiments	3/30/01	3/30/01	Pulping experiments are going well
2.3	Obtain Wood Chips	5/01/01	5/01/01	Three species were obtained
2.4	Preliminary Pulping Experiments	8/01/01	8/01/01	**Significant Increase in Yield found**
2.4.1	Pulping Experiments with Borate	2/01/02	2/01/02	Increase in pulping selectivity with borate
2.4.2	Analyze Pulping Experiments	8/01/02	8/01/02	Results published at Pulping Conference as noted above.
2.5	Develop Pulping Model	12/30/03	12/30/03	Pulping Model is complete with a yield increase of 2% for Softwood, but no yield increase for hardwoods.
2.6	Compare to Mill Data	3//01/04	3/01/04	This process is on-going and well continue as new mill data are received.
2.6	Pulping Report	8/30/04		New Project Closure due to analysis of on-going trials and delay in 2003 funding
3	Black Liquor Properties			
3.1.1	Conduct Initial Study on Boiling Pt Rise	3/01/01	3/01/01	
3.1.2	Conduct Initial Study on Viscosity	3/01/01	3/01/01	
3.1.3	Analyze Black Liquor from Pulping Experiments	3/01/02	6/01/02	Analyze is continuing and should not delay project
3.2	Property Report	3/01/03	3/01/4	Reports in publication
4	Final Report	12/04/03		An extension in the final report has been requested to 11//04. The DOE funding has been delayed and this extension will help to better manage the project'

Table 2, Project Budget

TYPE OF EXPENSE	**FEDERAL**	**THIRD PARTY COST SHARE**					**RECIPIENT COST SHARE**	
SPONSOR	DOE	International Paper	US Borax	US Borax	US Borax	Babcock & Wilcox	WMU	
WMU CONTROL #	25-2214870	29-2214790	29-2214770	29-7000790	NA	NA	NA	
	Direct Expense	Direct Expense	Direct Expense	Direct Expense	In-kind Expense	In-kind Expense	Direct Expense	TOTAL EXPENSE
BUDGET PERIOD								
1. 12/04/00 - 09/30/01	28,406.52	0.00	0.00	0.00	30,836.00	0.00	57,638.73	116,881.25
2. 10/01/01 - 09/30/02	140,525.88	843.19	1,458.06	0.00	0.00	1,153.28	71,718.13	215,698.54
3. 10/01/02 - 09/30/03	(327.44)	4,029.48	41,608.26	3,975.59	0.00	0.00	29,835.07	79,120.96
4. 10/01/03 - 06/30/04	17,850.75	0.00	6,671.96	10,737.29	0.00	0.00	17,025.16	52,285.16
TOTAL EXPENSE	186,455.71	4,872.67	49,738.28	14,712.88	30,836.00	1,153.28	176,217.09	463,985.91

Improved Recovery Boiler Performance Through Control of Combustion, Sulfur, and Alkali Chemistry

Baxter: Brigham Young University, INEEL

ID14276, CPS#01697

QUARTERLY PROGRESS REPORT

Project Title: Improved Recovery Boiler Performance through Control of Combustion, Sulfur, and Alkali Chemistry

Covering Period: April 1, 2004 through June 30, 2004

Date of Report: July 29, 2004

Laboratory: Brigham Young University
350 CB
Provo, UT 84602

FWP/OTIS Number: DOE F 241.2, Notice of Energy R&D

Subcontractors: University of Maine; McDermott Technologies, Inc.; University of Utah; Chalmer's University, IPST

Other Partners: Idaho National Energy and Environmental Laboratory; University of Toronto; Åbo Akademi University; Weyerhaeuser Inc.; Ahlstrom Power

Contact: Larry Baxter, (801) 422-8616, larry_baxter@byu.edu

Project Team: Joe Springer, Beth Dwyer

Project Objective: The objectives of this project are

1. Determine black liquor drying and devolatilization elemental and total mass release rates and yields.
2. Develop a public domain physical/chemical kinetic model of black liquor drop combustion, including new information on drying and devolatilization.
3. Determine mechanisms and rates of sulfur scavenging in recover boilers.
4. Develop non-ideal, public-domain thermochemistry models for alkali salts appropriate for recovery boilers
5. Develop data and a one-dimensional model of a char bed in a recovery boiler.
6. Implement all of the above in comprehensive combustion code and validate effects on boiler performance.

Background: Black liquor recovery boiler energy and environmental performance depends strongly on the combustion characteristics of entrained black liquor solids. The combustion processes that currently lack sufficient characterization and strongly impact recovery boiler operation include:

droplet/particle formation, drying, devolatilization, and elemental release rates; sulfur scavenging in the upper furnace; and sodium and sulfur dominated condensed-phase thermochemistry. The energy performance and capacity of kraft recovery boilers are highly sensitive to these processes, as they strongly impact throughput, stability, carbon removal and sulfate reduction reactions in the char bed, heat distribution in the furnace, and deposit properties.

Previous research programs have advanced the understanding of black liquor combustion and sulfur chemistry. Yet, the intrinsic kinetics of black liquor devolatilization have not been measured and the effect of black liquor drop size on fundamental burning processes has not been experimentally verified. In addition, sulfur scavenging mechanisms and rates in the upper furnace are interpreted differently by different experts. Finally, the thermochemistry of alkali salts relevant to black liquor combustion is in principle known (through phase diagrams) but in practice not readily accessible. This information is needed to improve the design and operation of kraft recovery boilers, to improve energy efficiency, and to maximize throughput and availability of recovery boilers.

The principal investigators on this project intend to collaborate to establish these issues using combinations of experimental measurements and model development. The proposed research program makes use of facilities and advanced numerical models at each of the institutes indicated. The principal investigators are uniquely qualified to undertake the experimental and modeling tasks in this project. Moreover, the identified forest products industrial involvement and sponsorship will ensure that the work remains relevant and timely. Results collected thus far are encouraging for the project, and all parties are working together to improve what needs to be done to further more accurate testing.

Status: During this quarter, a formal program review was held in conjunction with the International Chemical Recovery Conference (ICRC) in Charleston, SC. Attending this meeting were all subcontractors except INEEL and representatives from most of the forest products industry (Weyerhaeuser, International Paper, Georgia Pacific, Tom Grace, vendors and equipment suppliers, etc.). Several papers were presented during the conference that summarized progress in most of the technical areas. Short summaries of the remaining technical areas were provided together with programmatic information (deadlines, budgets, schedules, etc.). Feedback from both the industrial and academic attendees was positive with a formal Go decision for the Go/No Go decision point in the Gantt chart. Citations for the eight papers fully or partially supported by this project and presented at the ICRC are included near the end of this report.

In addition to the papers, the posters and PowerPoint presentation material, much of which includes more recent information than is in the papers, are included at our website (www.acerc-byu.edu).
In addition to the eight ICRC papers, seven separate papers on work related to this project were accepted for the STCBC meeting to be presented next quarter in Victoria, B.C. These papers and this conference are less directly related to black liquor than is the ICRC. However, all of the papers cited have some overlap with the work under this project. These citations are also included near the end of this report.
Separate technical areas are summarized below, in many cases with reference to the papers.
With the formall Go/No Go decision made at the project review meeting, the final subcontracts from BYU are being written. These should be completed in the next quarter for the last year of the project.

Aerosol formation

A complete first version of a model and comparisons to literature values of aerosol composition and size is now complete. The model still needs to be interfaced with a comprehensive computer code. See the ICRC paper for full details of the model.

Bed Model and Char Bed Experiments

A theoretical model of a char bed is nearly complete but includes only qualitative comparison to experimental data. Data are being gathered separately but they suggest that the kinetics used in the model are not appropriate for the bed. BYU and the University of Maine currently are trying to develop appropriate kinetics. Three separate ICRC papers summarize this work as cited below.

Advanced Devolatilization Modeling

Preliminary parameters for a chemical-structure-based devolatilization model appropriate for black liquor are now published (see ICRC paper). There remain some discrepancies in the time-resolved data for Iisa and the predictions, but it appears the issue may primarily be in the time calculation of the data. Chalmers/IPST and BYU currently are resolving this issue.

Fume Deposition

Rates and mechanisms of fume deposit formation have been fully explored and empirical correlations for deposit formation rate appear in the ICRC paper and an improved version in the PowerPoint presentation indicated below.

Intermediate-Sized Particle Formation

Definitive indications of the amount, size, and mechanisms of ISP formation from suspended black liquor droplets are included in the paper on ISP formation below. This portion of the project is now essentially complete..

Effects of Particle Shape and Size on Conversion Rates

Experimental and theoretical results discussing the impacts of particle shape and size on combustion are included in the ICRC and STCBC papers below. These have been largely reconciled with data clearly showing that particle shape profoundly impacts combustion rate in ways that are predicted by the model. There remain small discrepancies between the model and the data, but the major trends are clear.

Non-ideal thermochemistry

No formal paper summary exists that discusses the non-ideal thermochemistry of condensed-phase alkali salts. This work is currently behind schedule by about two months but will hopefully be caught up in the next quarter. A fully functional code with partial validation exists, but the non-ideal portions of it have not been completely properly implemented or tested.

Sulfur species diagnostic development

The development of a diagnostic to measure sulfur species in a recovery boiler is at least 12 months behind schedule. The University of Utah investigators indicate they will need at least a 12-month, no-cost extension to complete this work. Solid theoretical analyses and equipment procurement are complete and the instrument is under construction.

Plans for Next Quarter:

- Remaining discrepancies between models and data outlined above will be resolved.
- More time-resolved liquor particle combustion data will be collected.
- Interfaces between the various submodels discussed above and a comprehensive model will be developed.
- Submodel development and parameterization will continue and hopefully be finalized for several submodels.

Patents: One patent was transferred (donated) to BYU during this quarter.

Publications/Presentations:

The following papers were either presented and appeared in print or were submitted during the last quarter. All relate in whole or in part to issues under investigation in this project.

1. Baxter, L. (2004). Biomass-coal co-combustion: Opportunity for affordable renewable energy. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004
2. Baxter, L. L., G. Hatch, S. A. Sinquefield and W. J. Frederick (2004). An experimental study of the mechanisms of fine particle deposition in kraft recovery boilers. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 1**:** 393

3. Connolly, T. S. and A. R. P. v. Heiningen (2004). Measurement of carbon dioxide gasification of kraft black liquor char in a laboratory char bed reactor. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004
4. Connolly, T. S. and A. R. P. v. Heiningen (2004). Measurement of gas composition inside a recovery boiler char bed. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004
5. Dunaway, D., S. Lokare, M. Anderson, L. Baxter, D. Tree and H. Junker (2004). Ash deposition rates for a suite of biomass fuels and fuel blends. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004
6. Fletcher, T. H., H. R. Pond, J. Webster, J. Wooters and L. L. Baxter (2004). Prediction of tar and light gas during pyrolysis of black liquor and biomass. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 1**:** 91
7. Halpenny, E. and L. L. Baxter (2004). Computer simulated multi-component aerosol formation and chemistry. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 2**:** 825
8. Hunsaker, M., E. Barlow, R. Johnson, D. Griffin, D. Briggs and L. Baxter (2004). Renewable transportation fuels from biomass and black liquor. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004
9. Lisa, K. (2004). A comparison of the sulfation rates of different fume species in recovery boilers. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 2**:** 1043
10. Lisa, K. and A. D. Mahvelat (2004). A model for black liquor devolatilization kinetics. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 2**:** 833
11. Ip, L.-T., D. Ripa, A. Thiriot, W. Roberts, D. Tree and L. L. Baxter (2004). Intermediate-sized particle (isp) formation during black liquor droplet combustion. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 2**:** 1059
12. Lokare, S., J. D. Dunaway, D. Rogers, M. Anderson, L. Baxter and D. Tree (2004). Effects of fuel ash composition on corrosion deposits. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004
13. Lu, H., J. Scott, K. Echols, P. Foster, B. Ripa, R. Farr and L. L. Baxter (2004). Effects of particle shape and size on black liquor and biomass reactivity. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004

14. Lu, H., J. Scott, B. Ripa, R. Farr and L. L. Baxter (2004). Effects of particle shape and size on black liquor and biomass reactivity. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 2**:** 871

15. Ohran, B. J., M. M. Choi, S. Kær and L. L. Baxter (2004). Comprehensive, three-dimensional cfd model of a reacting char bed. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 2**:** 931

16. Wang, S., F. Fonseca, A. Miller, E. Llamazos and L. Baxter (2004). Biomass fly ash in concrete. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004

17. Wessel, R., L. L. Baxter, C. Shaddix, C. Verrill, J. W. James Frederick, S. Lien and H. Tran (2004). Particle formation and deposition in recovery boilers. 2004 International Chemical Recovery Conference, Charleston, South Carolina. June 6-10, 2004**,** 1**:** 363

18. Wu, C., B. Damstedt, S. Burt, D. Tree and L. Baxter (2004). Fuel-nitrogen chemistry during combustion of low-grade fuels in a low-no_x burner. Science in Thermal and Chemical Biomass Conversion, Victoria, British Columbia, Canada. Aug. 30 - Sept. 2, 2004

Milestone Status Table: The following table summarizes the milestones, planned and actual completion. The planned completion milestone dates submitted with the second quarterly report are shown below.

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Combustion Characterization			
1.1	Complete initial parameterization of drying and devolatilization code, include kinetics and composition.	12/15/03	100	
1.2	Complete first new single-droplet experiments.	6/16/03	5/30/2003	
1.3	Complete first spray imaging experiments.	6/16/03	0	
1.4	Make Go/No Go decision regarding drying and devolatilization work based on literature review and initial results.	6/16/03	5/19/2003	Unanimous Go Decision
1.5	Complete characterization of droplet size distributions from splatter plate and initial model of size.	11/15/04		

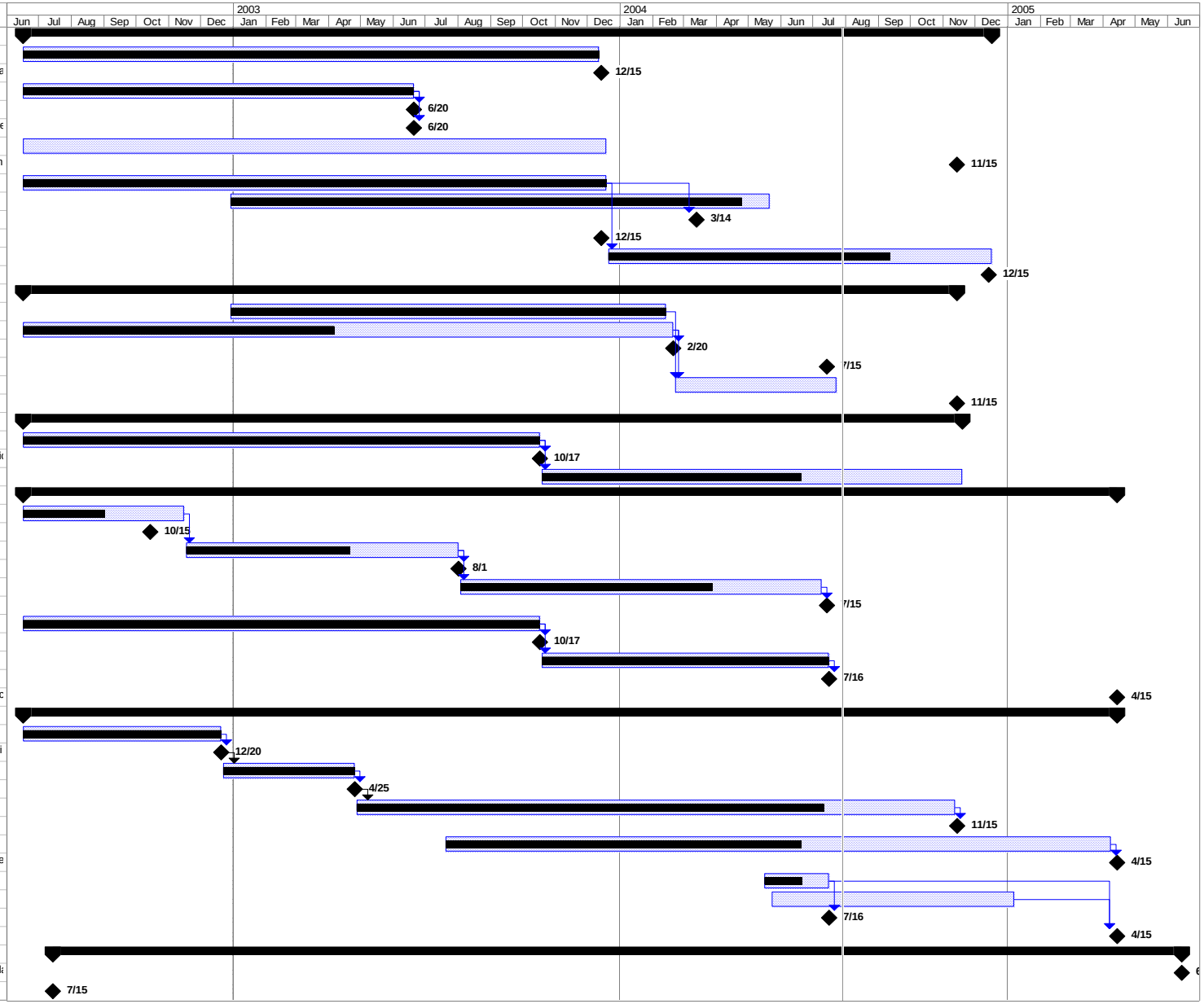
1.6	Complete devolatilization experiments in LEFR with one liquor	12/15/03	50
1.7	Complete devolatilization experiments in LEFR with additional two liquors	12/15/04	50
2	Sulfur Chemistry		
2.1	Complete experiments and first predictions of sulfur scavenging.	2/16/04	15
2.2	Make Go/No Go decision regarding sulfur modeling based on scavenging results.	7/15/04	
2.3	Complete sulfur scavenging model with comparisons to data.	11/15/04	50
3	Alkali Chemistry		15
3.1	Complete validation of initial (no lattice model) version of public-domain thermochemical code.	10/15/03	70
4	Char Bed Combustion		
4.1	Laboratory Testing of Char Bed Burning	6/17/02	6/17/2003
4.2	Complete construction and commissioning of U Maine char bed test facility	10/15/02	6/30/2003
4.3	Complete investigation of the effect of temperature in the U. of Maine char bed test facility	7/31/03	95
4.4	Complete investigations of experimental variables at U. of Maine char bed facility	7/15/04	70
4.5	Char Bed Modeling	6/17/02	
4.6	Complete initial modeling of existing IPST devolatilization data.	12/16/02	12/16/02
4.7	Complete detailed model formulation of laboratory char bed combustion	10/15/03	6/30/2003
4.8	Complete computational code for laboratory char bed combustion	2/16/04	90
4.9	Complete modeling of laboratory char bed and deliver final algorithms of the rates of char bed combustion, alkali vaporization, and sulfur	4/15/05	70

	conversion reactions.		
5	Reconcile Results with Commercial Operation		
5.1	Validation of Char Bed Model	6/17/02	
5.2	Complete construction and commissioning of probes and setups for char bed sampling at IP mill in Jay, Maine	12/16/02	95
5.3	Complete initial char bed and gas sampling at IP mill in Jay, Maine	4/15/03	100
5.4	Complete char bed sampling at IP mill in Jay, Maine	11/15/04	15
5.5	Complete simulation of char bed measurement results at IP, Jay, Maine mill using the char bed combustion model.	4/15/05	0
5.6	Prediction of Commercial Operation	4/15/05	
5.7	Complete incorporation of particle model into comprehensive model.	7/15/04	0
5.8	Comparison to Commercial Observations	4/15/05	0
6	Project Administration		
6.1	Issue final report documenting experimental and numerical results, and model formulation.	6/15/05	
6.2	Complete detailed project plan, Gantt chart, and internal reporting schedule.	7/15/02	7/30/2003

Budget Data (as of 06/30/04):

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	06/02	06/03	683,048	339,295	1,022,973	249,512	296,529	546,041
Year 2	06/03	06/04	615,280	359,741	975,021	654,616	152,747	807,363
Year 3	06/04	06/05	560,716	350,942	911,658			
Year 4								
Year 5								
Totals			1,859,044	1,050,608	2,909,652	904,128	449,276	1,353,404

ID	Task Name
1	**Combustion Characterization**
2	Paramaterize drying and devolatilization code (BYU)
3	Complete initial parameterization of drying and devolatilization code, include kinetics a
4	Perform first single-particle experiments (BYU)
5	Complete first new single-droplet experiments and first spay imaging experiments.
6	Make Go/No Go decision regarding drying and devolatilization work based on literature
7	Characterize droplet size distribution from splatter plate
8	Complete characterization of droplet size distributions from splatter plate and initial m
9	First experiments in LEFR (one liquor) (Chalmers)
10	Model devolatilization data
11	Complete initial modeling of existing IPST devolatilization data.
12	Complete devolatilization experiments in LEFR (one liquor)
13	Final experiments in LEFR (Chalmers)
14	Complete devolatilization experiments in LEFR (three liquors)
15	**Sulfur Chemistry**
16	Sulfur scavenging predictions (BYU)
17	Sulfur scavenging measurements (UoU)
18	Complete experiments and first predictions of sulfur scavenging.
19	Make Go/No Go decision regarding sulfur modeling based on scavenging results.
20	Compare sulfur scavenging measurements with data
21	Complete sulfur scavenging model with comparisons to data.
22	**Alkali Chemistry**
23	Develop equilibrium model with capacity for non-ideal chemistry (BYU)
24	Complete validation of initial (no lattice model) version of public-domain thermochemic
25	Include lattice model for nonidealities (BYU)
26	**Char Bed Combustion**
27	Laboratory Testing of Char Bed Burning
28	Complete construction and commissioning of U Maine char bed test facility
29	Temperature effect on char bed reactivity (UoM)
30	Complete bed temperature investigation
31	Bed experiments (UoM)
32	Complete all experimental investigations
33	Char Bed Modeling (UoM/BYU)
34	Complete detailed model formulation of laboratory char bed combustion
35	Char bed code development (UoM/BYU)
36	Complete computational code for laboratory char bed combustion
37	Complete modeling of laboratory char bed and deliver final algorithms of the rates of c
38	**Reconcile Results with Commercial Operation**
39	Validation of Char Bed Model (UoM, BYU)
40	Complete construction and commissioning of probes and setups for char bed sampli
41	Prepare for field test (UoM)
42	Complete initial char bed and gas sampling at IP mill in Jay, Maine (UoM)
43	Additional field tests (UoM)
44	Complete char bed sampling at IP mill in Jay, Maine
45	Develop CFD model (B&W)
46	Complete simulation of char bed measurement results at IP, Jay, Maine mill using the
47	Develop submodels in CFD code
48	Prediction of Commercial Operation
49	Complete incorporation of particle model into comprehensive model.
50	Comparison to Commercial Observations
51	**Project Administration**
52	Issue final report documenting experimental and numerical results, and model formula
53	Complete detailed project plan, Gantt chart, and internal reporting schedule.



Demonstration of Black Liquor Gasification at Big Island

DeCarrera: Georgia-Pacific Corporation

NT40850, CPS#01630

Report 40850R14

Quarterly Technical Progress Report 14
Demonstration of Black Liquor Gasification at Big Island

Reporting Period Start Date: **April 03, 2004**
Reporting Period End Date: **July 03, 2004**

Principal Author: **Robert DeCarrera**

Reporting Date: **July 26, 2004**

DOE Award Number: **DE-FC22-01NT40850**

Submitted By: **Georgia-Pacific Corporation**
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ABSTRACT

This Technical Progress Report provides an account of the status of the project for the demonstration of Black Liquor Gasification at Georgia-Pacific Corporation's Big Island, VA facility. The report also includes budget information and a milestone schedule.

Additional information may also be found on the project web site listed below:
http://www.gp.com/containerboard/mills/big/steam.html

TABLE OF CONTENTS

Note: Any section marked by an asterisk is required (by DOE) in all technical reports.

SUBCONTRACTORS

Fluor Daniel Greenville, SC	StoneChem Baltimore, MD	CB&I Constructors The Woodlands, TX
Rentech Boiler Systems Abilene, TX	CSE Madison Heights, VA	W.C. English Lynchburg, VA
IMCO Monroe, VA	Danser Parkersburg, WV	Mohawk Construction and Supply McMurray, PA
Teton Industrial Group Alpharetta, GA	ABB Norcross, GA	Emlex Moneta, VA
VOS Electric Green Bay, WI	ThyssenKrupp Elevator Corporation Roanoke, VA	
Bay Mechanical, Inc. Virginia Beach, VA	Superior Tracing Systems, Inc Houston, TX	C.E. Thurston & Sons, Inc Columbia, SC
LaFramboise Group Massena, NY	Byers, Inc. Big Island, VA	Holley Insulation, Inc. Vinton, VA

PROJECT DESCRIPTION

The project to be conducted by G-P is a comprehensive, complete commercial-scale demonstration that is divided into two phases. Phase I was the validation of the project scope and cost estimate. Phase II is project execution, data acquisition and reporting, and consists of procurement of major equipment, construction and start-up of the new system. Phase II also includes operation of the system for a period of time to demonstrate the safe operation and full integration of the energy and chemical recovery systems in a commercial environment.

The objective of Phase I was to validate the process design and to engineer viable solutions to any technology gaps. This phase included engineering and planning for the integration of the full-scale MTCI/StoneChem PulseEnhanced™ black liquor steam-reformer chemical recovery system into G-P's operating pulp and paper mill at Big Island, Virginia. During this phase, the scope and cost estimate was finalized to confirm the cost of the project including integration into the existing system at the mill.

The objective of Phase II of the project is the successful and safe completion of the engineering, construction and functional operation of the fully integrated full-scale steam reformer process system. This phase includes installation of all associated support systems and equipment required for the enhanced recovery of both energy and chemicals from all of the black liquor generated from the pulping process at the Big Island Mill. The objective also includes operation of the steam reformer system to demonstrate the ability of the system to operate reliably and achieve designed levels of energy and chemical recovery while maintaining environmental emissions at or below the limits set by the environmental permits.

SUMMARY

The project continued Phase II commissioning and liquor trials during this reporting period. Two liquor trials were conducted on April 17 through April 25 and on May 11 through May 12. As a result of the second liquor trial, two Pulse Heaters sustained overheat damage. The Pulse Heaters were removed from the unit and shipped off site for repair. The root cause of the overheat failure has been identified as poor fluidization in the center of the Pulse Heaters. In order to redesign the fluidization system for the reformers, a cold flow modeling study was initiated. GP, StoneChem and Norampac cost shared the study. As of the end of this reporting period, final results of the modeling study were not complete.

Estimated total cost of the project is forecast at $101 million. The current spending through June is $ 83.2 million, which is approximately $1.3 million more than estimated in the spending curve presented to DOE in August 2002. GP continues to work with DOE and Congress to secure matching funds to cover the changes in scope. On August 8, 2003, G-P submitted a formal request to DOE asking for a one year extension in the duration of the contract and an additional $7.6 million in matching funds. As part of the process of revising the contract, DOE has authorized the Defense Contract Audit Agency (DCAA) to audit the last three years of project spending. The project team continues to work with DCAA to provide the necessary information to complete that process.

The project team participated in conference calls with the NETL BLG Modeling Task Group on April 13. Members of the project team visited the Norampac mill in Trenton, Ontario during the period from June 10, 2004 through June 17, 2004. The GP personnel participated in the start-up and operation of the Norampac steam reformer, which had been down for maintenance. The purpose of the trip was to exchange lessons learned and discuss future changes.

SAFETY and ENVIRONMENTAL

There were no recordable incidents during this reporting period. We currently stand at five OSHA recordables on the project:

- 4/24/01 - see Quarterly Technical Progress Report 02
- 9/18/02 - see Quarterly Technical Progress Report 07
- 01/09/04 - see Quarterly Technical Progress Report 13
- 02/13/04 - see Quarterly Technical Progress Report 13
- 03/25/04 - see Quarterly Technical Progress Report 13

The OSHA incident rate for the project is currently 2.03. GP Corporate and Mill safety departments continue to have active participation in the project, performing periodic safety audits to augment the efforts of the project team.

There were no environmental incidents during the reporting period. We currently stand at 2 environmental incidents (see Quarterly Technical Progress Report 04) thus far on the project.

All of the project environmental reporting and permits are current. During June 2004, the first phase of the environmental testing was completed for the Reformer Boiler. The final phase of testing will be completed once product gas from the reformers is available as fuel.

On June 9, 2004, GP met with representative from EPA and Virginia Department of Environmental Quality to discuss the possibility of changing the technology acceptance date. Due to the problems encountered in the

initial liquor trials and the time required to implement the necessary modifications, GP will require additional operating time to gain the experience required to accept the technology. As of the end of the reporting period, the discussions are continuing.

ACCOMPLISHMENTS

Engineering / Project Management / Procurement / Construction

The engineering effort is supporting commissioning activities by designing changes to the process and equipment as required by the experiences from the liquor trials.

Training

- Realigned operators from 3-shift, 6-person alignment to 4-shift, 5-person alignment, which includes Smelter operations
- Concentrating training efforts on individual needs to support operating with 5-person shift
- Using simulator based training
    - Structured 8-hour classes (1/wk) to review process changes made to date
    - On-shift training (operators utilizing to meet individual need)

Commissioning

During this reporting period, the project operated Reformer 1. The experience from Reformer 1 will be used to implement necessary changes prior to operating Reformer 2.
The following systems or major areas have not been commissioned:

- Reformer 2 systems
- Firing of product gas in the Pulse Heaters.
- Firing of product gas in the Reformer Boiler.
- Green Liquor Filter

Pulse Heaters 1-1 and 1-2 were shipped to the OEM for repair. These will be repaired and returned during the next reporting period

The modifications that were proven successful on Reformer 1 were implemented on Reformer 2. This included modification to the liquor injectors to reduce their internal diameter. During the next liquor trial, injectors of 2 smaller diameters will be evaluated. GP also plans to evaluate a new injector design with a steam-atomized tip.

Modifications of HRSG steam piping were implemented to control the fluctuations of steam drum level caused by swings in the 600 psig steam header. Additional modifications were made to move the location where the steam enters the header to eliminate the cooling of the fluidization steam supply to the fluidization grids.

The bottom bed solids drain from the vessel has been modified into a manual bed removal system to be used during operation. This system will be used to remove oversized bed material that segregates in the bottom of the vessel. During the next liquor trials, this system will be used to evaluate the need for an automated bottom bed removal system.

Modifications were made to the supports for the piping and ductwork attached to the Reformer vessels. These modifications were necessary due to the extent of the vessel movement during operations.

ACTIVITIES NEXT QUARTER

- Installation of the fluidizing air heater.
- Design and modification of fluidizing system for Reformer 2.
- Commission all systems associated with Reformer 2.
- Install additional instrumentation on Pulse Heater 2-1.
- Continue liquor trials.
- Modification of fluidizing system for Reformer 1.
- Installation of Pulse Heaters 1-1 and 1-2 after repairs are completed.
- Commission Green Liquor Filter.
- Evaluation of various liquor injectors.
- Evaluation of bed solids attrition system.

PROJECT ISSUES AND CONCERNS

During the liquor trials a number of issues and concerns have developed. Some of these issues are specific only to this project, while others apply to the technology.

Technology Issues

- Fluidization System Design – Experience from liquor trials 3 and 4 indicated the lower Pulse Heaters were not adequately fluidized. This led to stagnant areas of bed material within the heater, which sintered and formed a plugged area. The tubes within this area overheated and failed. Preliminary results from the cold flow modeling study confirmed the fluidization problem. The model will be used to design and test improvements.
- Aerovalve Design – StoneChem informed the project that Norampac experienced failures of the aerovalves on their Pulse Heaters. The aerovalves are operating at temperatures more than twice the design and above the maximum for the material. Additional operating time will be required to collect data and determine engineering options. GP is evaluating a metal spray coating to determine if this will reduce the rate of corrosion. Modeling and engineering will be required to resolve this issue.
- Pulse Heater Thermocouples – Pulse Heater firing is controlled by measurement of the tube temperatures. The thermowells for the thermocouples have experienced several failures due to the action of the bed. In addition, there is a concern the attachment method of the thermowells to the Pulse Heater tubes can cause cracking of the tubes. Additional operating time will be required to collect data and determine engineering options. The thermowell support attachments have been redesigned and modified. Additional instrumentation will be evaluated during future trials.
- Bed Particle Size – The technology is very sensitive to bed particle size. Size has a significant effect on carbon conversion, heat transfer from the Pulse Heater and on the motion of the bed due to bubble size. The effectiveness of attrition of the bed material by steam injection or by variation of the liquor injection will require additional operational experience to evaluate. Attrition tests will also be conducted on a pilot scale unit to aid in design.

Project Issues

- Limestone Bed – The start-up bed for the Reformer is limestone. Until the bed is converted to sodium carbonate, significant operating problems will be encountered. Nozzle plugging was an operational problem on the level/density taps, liquor injectors, and bed sample nozzles. Several modifications and changes to the operating procedures have been implemented to resolve this problem. For the next liquor trial, sodium carbonate bed solids from Norampac will be used for the bulk of the bed.
- Equipment Manufacturing – Several pieces of equipment have failed in operation due to manufacturing errors. The curing of the refractory in the Pulse Heaters of Reformer 1 was interrupted by the failure of the Pulse Heater Circulation Pump. The internal clearances in the pump were incorrect for the operating temperature. The pump was sent to the manufacturer's shop where the problem was corrected. The first liquor trial was terminated when the flue gas isolation valves failed to operate after a Pulse Heater trip. The stem clearance in the valves was incorrect causing the valves to bind in the open position. The valve shafts were machined by the manufacturer and the valves operated properly for the second liquor trial.
- Start-up Sequence – Experience from the first two liquor trials has shown that the Reformer vessel and HRSG must be brought to a temperature above the steam saturation prior to introducing the bed to the vessel. In order to be able to accomplish this, warm-up steam has been added to the HRSG water circuit and a heater has been purchased for the fluidization air. The heater will be installed prior to the next liquor trials.

PROJECT COSTS

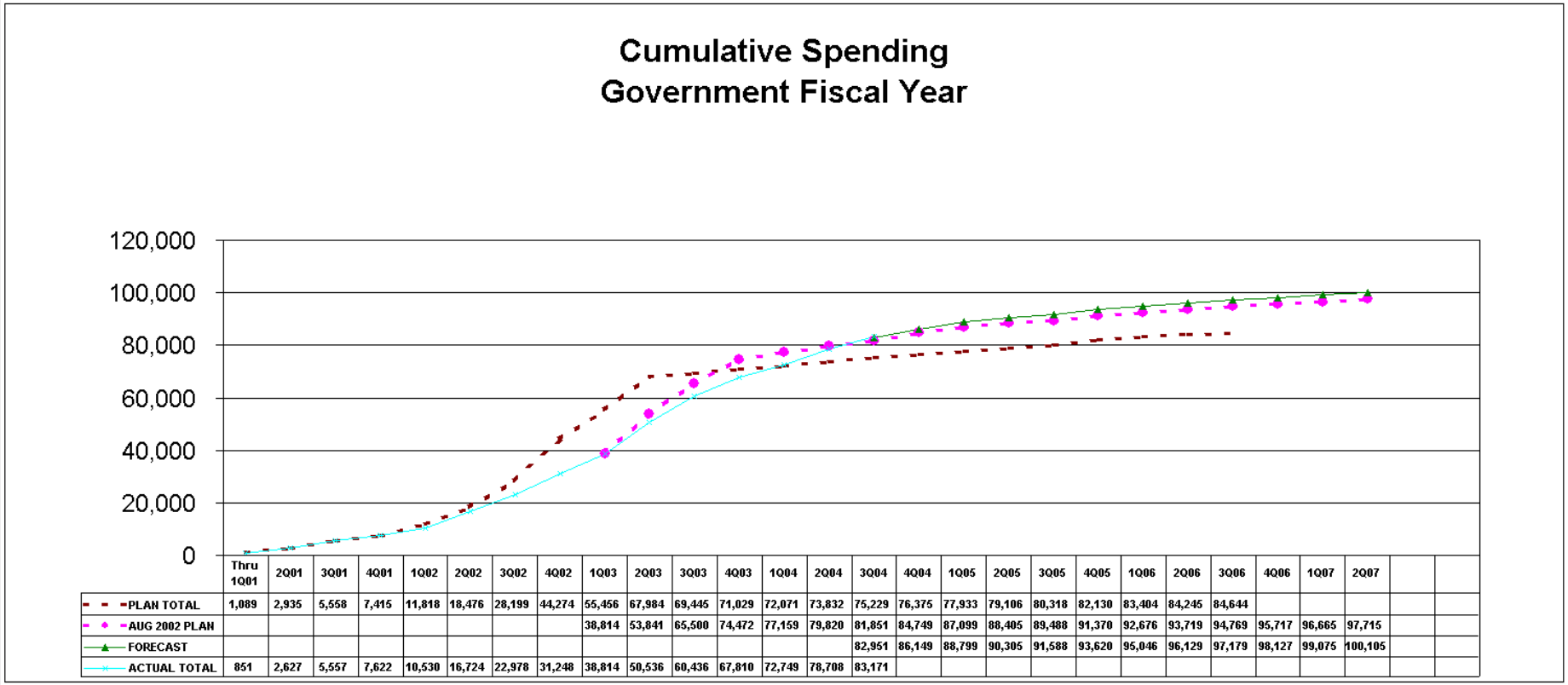
Budget Data

Project Budget Period	Period			Cumulative		
From - To	DOE	G-P	Total	DOE	G-P	Total
04/04/04-07/03/04	$2,704,465	$1,758,664	$4,463,129	$43,527,446	$39,643,456	$83,170,902
Previous Total	$40,822,981	$37,884,792	$78,707,773	52.3%	47.7%	100.0%

*** $200,000 of GP Spending offsets the DOE Retainage**

DOE Obligated Funds			
Amendment	Amount	Total	Date
000	$4,537,776	$4,537,776	2/13/2001
001	$0	$4,537,776	4/25/2001
002	$0	$4,537,776	5/3/2001
003	$0	$4,537,776	8/13/2001
004	$0	$4,537,776	8/17/2001
005	$4,671,000	$9,208,776	9/10/2001
006	$13,130,000	$22,338,776	9/17/2001
007	$162,665	$22,501,441	9/26/2001
008	$0	$22,501,441	10/31/2001
009	$0	$22,501,441	11/6/2001
010	$6,385,000	$28,886,441	2/1/2002
011	$3,684,000	$32,570,441	9/16/2002
012	$44,540	$32,614,981	9/30/2002
013	$4,000,000	$36,614,981	3/24/2003
014	$4,408,000	$41,022,981	5/7/2003
015	$3,000,000	$44,022,981	4/5/2004
016	$416,141	$44,439,122	5/11/2004
017	$0	$44,439,122	5/27/2004

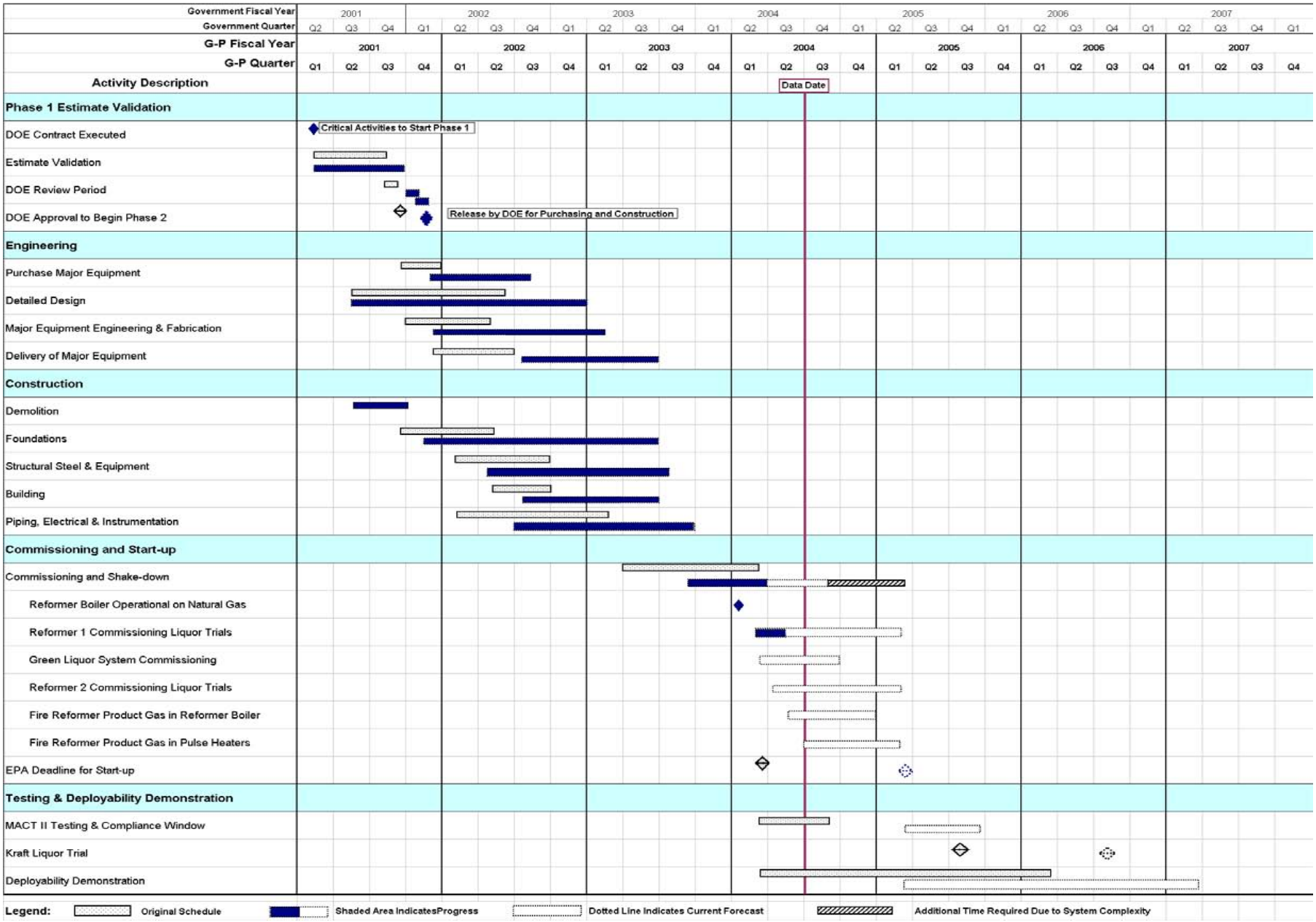
Spending Curve



	Thru 1Q01	2Q01	3Q01	4Q01	1Q02	2Q02	3Q02	4Q02	1Q03	2Q03	3Q03	4Q03	1Q04	2Q04	3Q04	4Q04	1Q05	2Q05	3Q05	4Q05	1Q06	2Q06	3Q06	4Q06	1Q07	2Q07		
PLAN TOTAL	1,089	2,935	5,558	7,415	11,818	18,476	28,199	44,274	55,456	67,984	69,445	71,029	72,071	73,832	75,229	76,375	77,933	79,106	80,318	82,130	83,404	84,245	84,644					
AUG 2002 PLAN									38,814	53,841	65,500	74,472	77,159	79,820	81,851	84,749	87,099	88,405	89,488	91,370	92,676	93,719	94,769	95,717	96,665	97,715		
FORECAST															82,951	86,149	88,799	90,305	91,588	93,620	95,046	96,129	97,179	98,127	99,075	100,105		
ACTUAL TOTAL	851	2,627	5,557	7,622	10,530	16,724	22,978	31,248	38,814	50,536	60,436	67,810	72,749	78,708	83,171													

SCHEDULE

Project Milestone Summary



EXPERIMENTAL

This report is for a demonstration project that has begun liquor trials. A cold flow model to study the fluidization within the reformer vessel was constructed and approximately 70 trials were conducted. As of the end of this reporting period, the results were not finalized. Observations during the trial correlated well with operating experience of the full scale unit. Poor areas of fluidization were identified and various changes were modeled to resolve the problem. During the next reporting period, the data will be analyzed and modifications proposed for the unit will be tested. Members of the DOE Modeling Working Group were invited to participate in the modeling.

Tube samples have been submitted to ORNL for evaluation. Analysis of the preliminary samples indicated extensive chromium carbide precipitate in the tube material in the areas of failure. This suggested overheat as a probable cause of failure. Additional testing will be conducted next quarter to better evaluate the metallurgy of the tubes.

Samples of bed solids from the liquor trials were submitted to IPST for analysis. Samples of the material plugging the Pulse Heaters were also submitted. The results of the analysis concluded that that bed solids were plugging the lower Pulse Heaters due to loss of fluidization. Per the IPST report, “poor circulation in a given region of the bed leads to a stagnation zone. The bed solids begin to sinter and form a solid matrix too strong to be completely broken up by random turbulence fluctuations.” This in turn insulated the tubes from the cooling effect of bed solids and allowed them to overheat and fail.

The project team is providing support to various DOE supported R&D projects. Some of this support is through this project and some is provided outside of this project. Projects supported include:

- DE-FC26-02NT41490 - University of Utah project "Investigation of Fuel Chemistry and Bed Performance in Fluidized Bed Black Liquor Steam Reformer"
- ORNL Materials Evaluation for Black Liquor Gasifiers – Keiser
- DOE Modeling Working Group - Keairns

RESULTS and DISCUSSION

This report is for a demonstration project that has begun liquor trials. The project has not accumulated any significant performance or test data. The project has determined the fluidization system used in the vessels is not adequate. The system will be modified during the next reporting period.

CONCLUSION

This report is for a demonstration project that has not yet operational. As such, no conclusions can be reached during this reporting period.

REFERENCES

All of the reference reports used in the preparation of this report are in a preliminary form. Once the reports are finalized the information will be included.

Mechatronic Design and Control of a Waste Paper Sorting System for Efficient Recycling

Venditti: North Carolina State University

ID13880, CPS#01199

QUARTERLY PROGRESS REPORT

Project Title: Mechatronic Design and Control of a Waste Paper Sorting System For Efficient Recycling

Covering Period: April 1, 2004 through June 30, 2004

Date of Report: July 30, 2004

Recipient: N. C. State University
Dept. of Wood and Paper Science
Raleigh NC 27695-8005

Award Number: DE-FC36-00ID13880 (switched from DE-FC07-00ID13880)

Subcontractors: None

Other Partners:
Advanced Sorting Technology, LLC, 3738 Keystone Ave., Nashville, TN 37211
Weyerhaeuser Co., WTC 2E19, PO Box 9777, Federal Way, WA 98063-9777

Contact(s): Dr. Richard A. Venditti (919) 515-6185, richard_venditti@ncsu.edu
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Project Objective

The objective of this research is to develop new sensors that will provide information on the composition of fibers, coatings and other materials found in wastepaper as inputs to a neural network algorithm in order to correctly detect specific types of wastepaper. The information will be used by an automated waste paper sorting system that is efficient, fast, accurate and completely autonomous.

Background

A literature review has pointed out an absence of published reports on the development/characterization of sensors for the detection of paper. It is considered that the correct detection of paper grades at high speed is a critical issue in improving the technology to improve automated paper sorting processes.

Research at NCSU to develop new sensors for automated wastepaper sorting was started in the year 2000 by the authors as a part of the Agenda 2020 DOE Program. Our research involved initially visiting one of the two automated sorting facilities in the United States operated by the Advanced Sorting Technologies, a partner in the current renewal proposal. This state of the art facility utilizes a fast moving conveyor (1000 ft/min, 25 tons/day) to present separated sheets of wastepaper past sensors that detect the fluorescence of bright white papers. A positive sort of the bright white papers achieved by triggering air eject streams produces a sorted white ledger stream of high brightness and a lower grade mixed office waste. Although this is a tremendous technical achievement, there still remains aspects of the sorting process that need to be improved. For example, sorting of newsprint from white ledger is problematic. Further, complications arise in the sorting process from coatings, printing and other materials from converting operations such as adhesive labels on the papers.

We then set out to solve the problem of recognizing newsprint from white ledger at high speed, a need identified by the paper recycling industry. Our approach was to develop a lignin sensor based on the fluorescence of lignin when excited by a 532 nm green laser. We have successfully established the measurement system to distinguish grades of paper by detecting relative lignin contents at speeds needed for automated sorting at high accuracy. Trials run at speeds of up to 700 ft/min in our facility on samples of newsprint and white ledger paper have confirmed the ability of the sensor to distinguish between the two. In order to address the

complications involved in coatings, printing and the like we have also been developing a high-speed vision system that tracks objects based on color. The combined information from the color object tracking, the lignin sensor, and additional sensors proposed for gloss and IR imaging as inputs to a neural network are expected to result in a system that can distinguish several complicated classes of waste paper (such as coated or waxed board) that are of special concern in recycling.

This project will involve the continuation of the development of a comprehensive robust intelligent production worthy sensing/decision making system for automated waste paper sorting.

STATUS

Work performed in this quarter was focused on:

- Studying the effect of printed color on lignin sensor response

1. Effect of color

1.1. Theory

This section discusses the effect of color on the lignin sensor response. Particularly, the effect of color printed on the paper is considered, rather than color of the paper itself. All the experiments in this section were done using a green laser. There are three key factors that affect the sensor response (apart from lignin content). They are:

1. The transmittance of the printed color at the excitation wavelength (532 nm)
2. The ransmittance of the printed color in the fluorescence bandwidth (650 +/- 10 nm)
3. Printed color dye fluorescence

The transmittance of a layer is defined as the ratio of the transmitted intensity to the incident intensity of light. Hence, if a layer has high transmittance, it transmits most of the energy incident upon it.

The intensity of fluorescence depends upon the transmittance of the printed color at the excitation wavelength. If the color has high transmittance at 532 nm (excitation wavelength) then most of the energy will be transmitted to the lignin molecules underneath it, thus resulting in a potentially higher fluorescence. Figure 1.1.1 illustrates this concept.

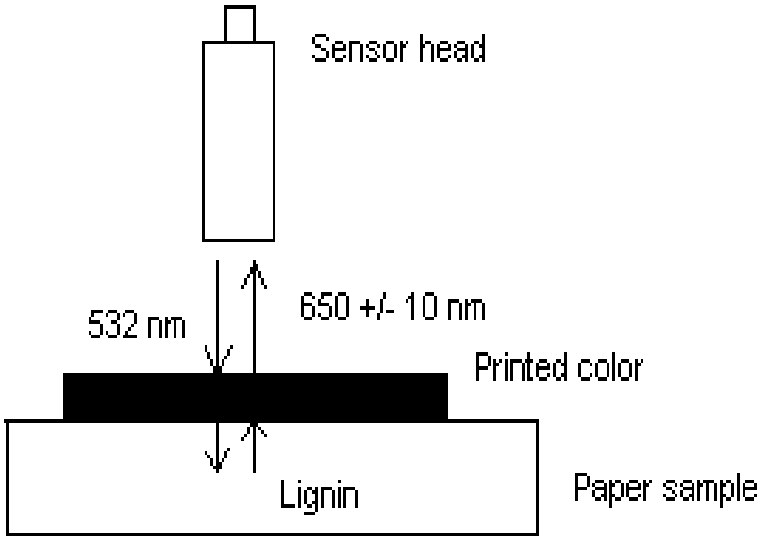


Figure 1.1.1. Effect of color

Similarly, the intensity of fluorescence detected by the sensor depends on the transmittance of the printed color in the fluorescence bandwidth (650 +/- 10 nm). If the printed color layer has high transmittance in this bandwidth then most of the fluorescence will be detected by the sensor, thus resulting in high sensor response. If the printed color layer has low transmittance in this bandwidth, then even though there is high lignin content in the paper, the fluorescent light cannot pass through the color to the sensor.

Some of the dyes used for color printing use fluorescing agents to make the color look brighter/more vivid. So, if the printed color uses such fluorescent dyes then the sensor response will be confounded and not uniquely related lignin content in paper.

1.2. Experiments and results

Different colors were printed on copy paper (CP) using a HP Desk jet 820 Cse color printer. The color samples are shown in the Appendix. These samples were placed under the lignin sensor and the response was noted (Table 1.2.1). Copy paper does not contain any fluorescence, so a high sensor response indicates the presence of fluorescing agents in the color.

Table 1.2.1 Color data

Color on CP	Normalized sensor
11A	0.48
11B	0.9
11C	0.81
11D	0.5
12A	0.07
12B	0.08
12C	0.09
12D	0.11
13A	0.12
13B	0.09
13C	0.08
13D	0.1
14A	0.8
14B	0.24
14C	0.2
14D	0.2
15A	0.04
15B	0.07
15C	0.11
15D	0.14
16A	0.38
16B	0.26
16C	1
16D	0.28
17A	0.29
17B	0.32
17C	0.46
17D	0.21
18A	0.24
18B	0.1
18C	0.12
19A	0.04
19B	0.07
19C	0.05
20A	0.14
20B	0.17
20C	0.15

It can be seen from Table 1.2.1 that colors 11A, 11B, 11C, 11D, 14A, 16A, 16C, 17B and 17C show a sensor response greater than 0.3. Copy paper alone without any color gives a sensor response less than 0.1. Hence, it can be concluded that these colors have fluorescent dyes. To further confirm this result the following experiment was performed.

The fluorescing samples 11A, 11C, 14A and 16C were printed on HP premium inkjet transparency film (HP C3834A). Figure 1.2.1 shows the experimental setup.

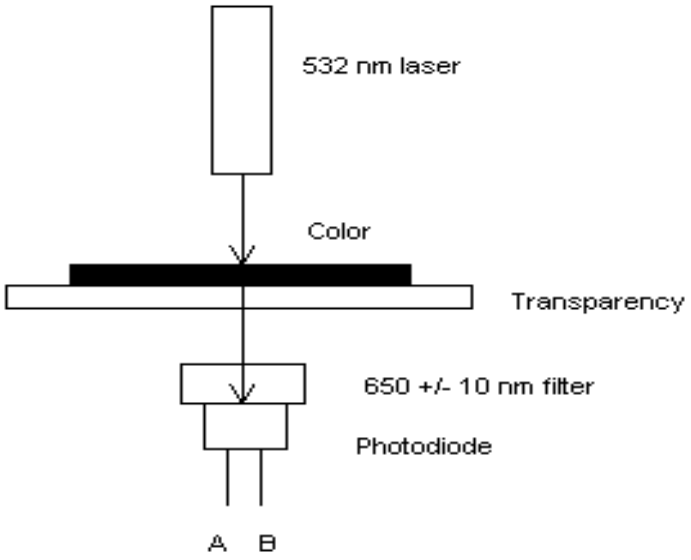


Figure 1.2.1. Dye fluorescence

Laser light is focused on the color sample printed on a transparency. The fluorescence, if any, is detected by the photodiode (Hamamatsu, S2386-45K) after passing through the filter. The filter does not transmit 532 nm, hence the photodiode picks up only fluorescence. The experiment is done in darkness to make sure that the photodiode responds only to fluorescence and not to stray light. The output is measured as a short circuit current across terminals A and B of the photodiode. Table 1.2.2 shows the results obtained.

Table 1.2.2. Dye fluorescence data

Test condition	Diode output
Laser with 650 nm narrow filter	0.06 micro amps
Clear transparency	0.05 micro amps
Sample 11C	0.11 micro amps
Sample 11A	0.09 micro amps
Sample 14A	0.15 micro amps
Sample 16C	0.17 micro amps

From Table 1.2.2 it is observed that the output for the color samples is two or three times greater than the output for a clear transparency. This result confirms the hypothesis that the dyes in these color samples are indeed fluorescent.

The following experiment was performed to determine the effect of the transmittance of the printed color on the sensor response. Color samples, which did not show any fluorescence, were printed on a transparency and the transmittance of these samples was determined using the set up shown in Figures 1.2.2 and 1.2.3.

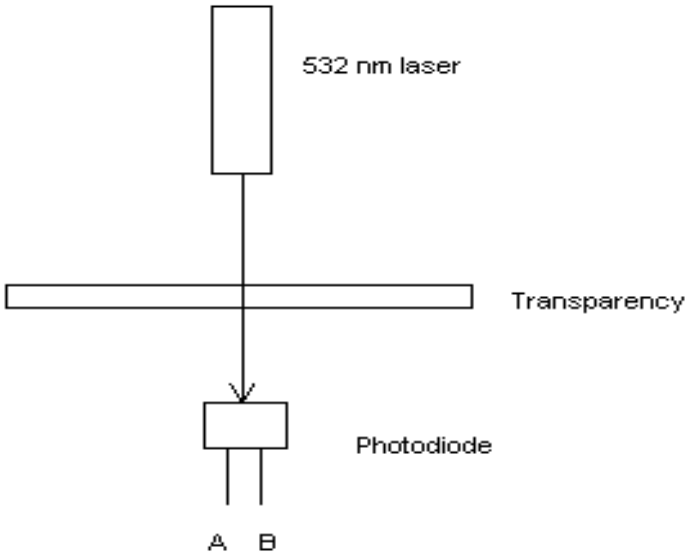


Figure 1.2.2. Incident intensity measurement

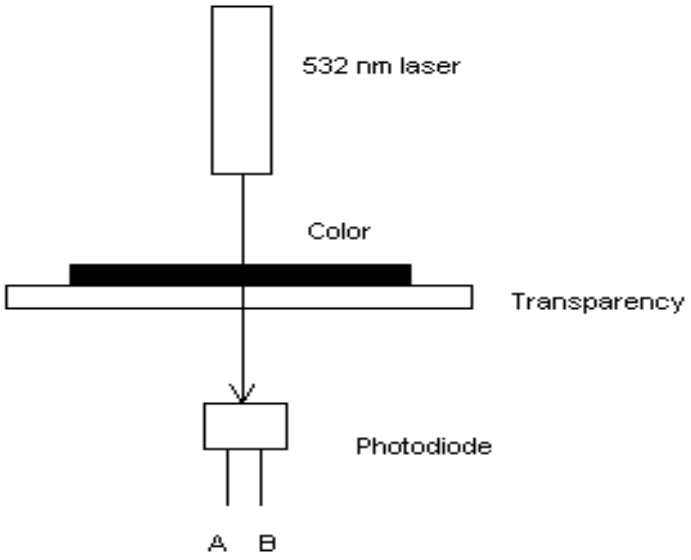


Figure 1.2.3. Transmitted intensity measurement

Figures 1.2.2 and 1.2.3 show the set ups used for measuring the incident intensity and transmitted intensity of light, respectively. The ratio of transmitted to incident intensity gives the transmittance of the color sample. The color samples used for this experiment were 12A, 12B, 12C, 12D, 13A, 13B, 13C, 13D, 15A, 15B, 15C, 17A, 17B, 17D, 18A, 18B, 18C, 19A, 19B and 19C. These samples were printed on newsprint and the sensor response was acquired. Figure 10.2.4 gives the plot of sensor response vs. transmittance of 532 nm.

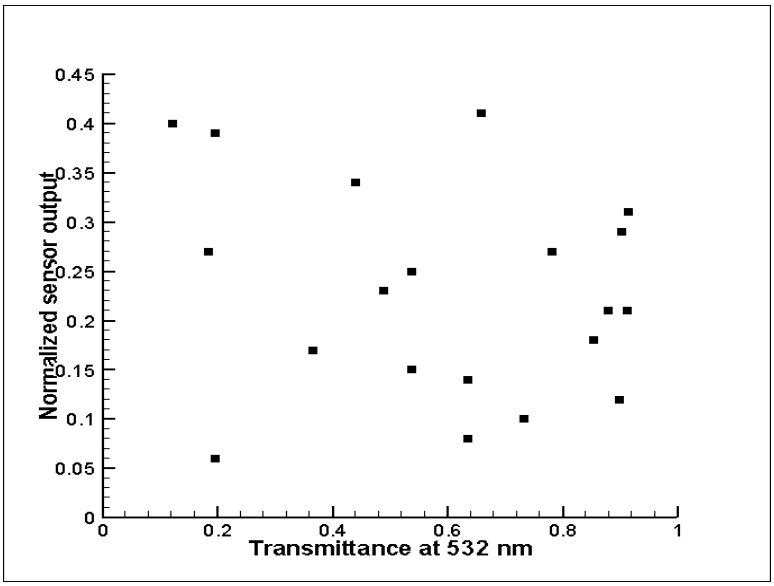


Figure 1.2.4. Normalized sensor output for newsprint with different color printing versus the transmittance of the color printing at 532 nm

From Figure 1.2.4 it can be observed that there is no clear dependence of sensor output on the transmittance of the printed color at the excitation wavelength. Newsprint without any color gives a normalized sensor output between 0.4 and 0.5. Even at relatively low transmittances, there are colors for which the sensor shows true lignin content. This indicates that even at low transmittances, there is enough energy available for the lignin molecules to fluoresce. This shows that the transmittance of the laser is not a critical factor affecting the sensor response. We can also observe from Figure 1.2.4 that even at relatively high transmittance values, some samples

show less sensor response. This also indicates that the transmittance or printed colors at 532 nm is not a crucial factor affecting the sensor response. It is hypothesized that the transmittance at 650 nm is the critical factor affect the sensor response with samples with printed color.

To test this hypothesis, the transmittance of the color samples at 635 nm was determined using the set up shown in Figures 1.2.2 and 1.2.3. Ideally, transmittance at 650 nm would have to be determined, but due to the absence of a 650 nm laser and the availability of a 635 nm laser, this experiment was done. It is assumed that the transmittances at 650 and 635 nm would be approximately equal. Figure 1.2.5 shows the plot of sensor response vs. transmittance at 635 nm.

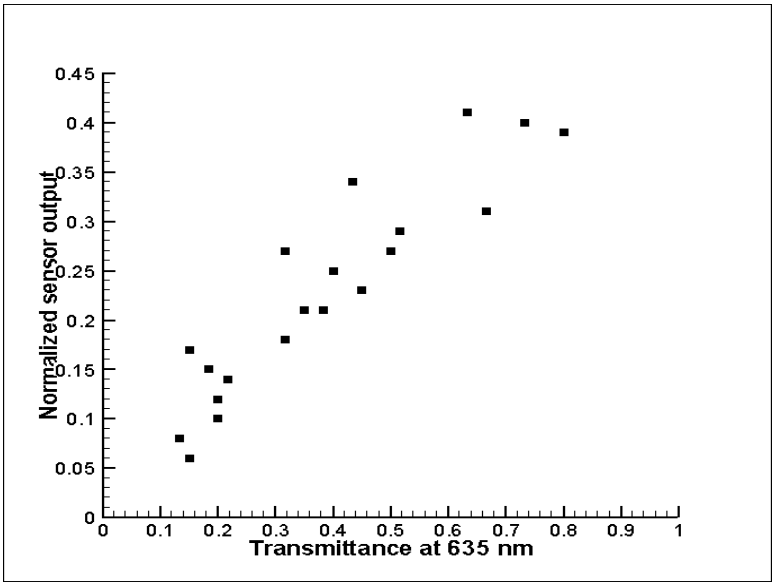


Figure 1.2.5. Normalized sensor output for newsprint with different color printing versus the transmittance of the color printing at 635 nm.

From Figure 1.2.5 it can be observed that the transmittance in the fluorescence bandwidth (around 650 nm, in this case 635 nm) has a strong affect on the sensor output. The graph shows a linear response with some scatter. As transmittance increases, more fluorescence goes through the color layer and is picked up the sensor.

1.3. Photon calculation

It is postulated that the dependence of the sensor to fluorescence and not incident intensity is due to the fluorescence intensity being much less than the incident intensity. The following shows the calculation of the ratio of excitation photons to fluorescence photons.

Calculation for number of photons emitted by laser (635 nm) in one second:

Energy of one photon = (h*c)/Lda
= (6.63*10^(-34)*3*10^(8))/(635*10^(-9))
= 3.13*10^(-19) Joules

Power of laser = 15 mW

Energy delivered in one second = 15*10^(-3) Joules

Number of photons emitted = (15*10^(-3))/(3.13*10^(-19))
= 4.79*10^(16)

Calculation for number of photons emitted due to fluorescence in one second:

Current to voltage conversion factor for photon counting module = 1 Volt / 100 nA

Hence a voltage output of 10 Volts means that there is an anode current of 1000 nA.

Current amplification = 10^(5) at a gain control voltage of 1.4 Volts

Hence cathode current = 1000 nA / 10^(5)
= 10^(-11) A

Number of electrons emitted by cathode per second = 6.24*10^(18)*10^(-11)
= 6.24*10^(7)

Quantum efficiency (QE) of a photo multiplier tube is defined as the ratio between the number of electrons emitted by the photo cathode to the number of incident photons. QE for MD 962 module is 4%.

Hence number of photons incident on the cathode = (6.24*10^(7))/0.04
= 156*10^(7)

Peak transmittance of optical filter is 75%.

Hence number of photons emitted due to fluorescence = 208*10^(7)

Therefore, ratio of excitation photons to fluorescence photons = 2.3*10^(7)

1.4. Results

From the photon calculation, we can observe that the number of excitation photons is far greater than the number of photons emitted due to fluorescence. Hence the printed color transmittance of light at the fluorescence wavelength is a far more critical factor than the transmittance at the excitation wavelength. From the data obtained, we can conclude that sensor is not capable of predicting lignin content accurately for color printed samples. Dye fluorescence and transmittance of the color are two key factors affecting sensor response.

For high speed sorting applications, the lignin sensor will not be able to detect lignin in papers printed completely with color. However, for paper with partial coverage, if the lignin sensor is capable of making several measurements on a single paper, an algorithm that chooses the maximum (or other suitable statistical descriptor) signal reading for the paper could be used to detect lignin.

Appendix: Color samples

Figure 4.1. Color 11A

Figure 4.2. Color 11B

Figure 4.3. Color 11C

Figure 4.4. Color 11D

Figure 4.5. Color 12A

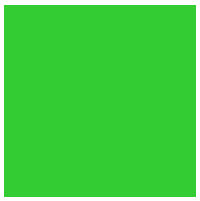


Figure 4.6. Color 12B

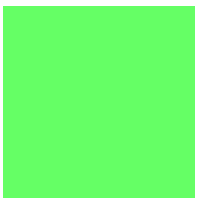


Figure 4.7. Color 12C

Figure 4.8. Color 12D

Figure 4.9. Color 13A

Figure 4.10. Color 13B

Figure 4.11. Color 13C

Figure 4.12. Color 13D

Figure 4.13. Color 14A

Figure 4.14. Color 14B

Figure 4.16. Color 14C

Figure 4.16. Color 14D

Figure 4.17. Color 15A

Figure 4.18. Color 15B

Figure 4.19. Color 15C

Figure 4.20. Color 15D

Figure 4.21. Color 16A

Figure 4.22. Color 16B

Figure 4.23. Color 16C

Figure 4.24. Color 16D

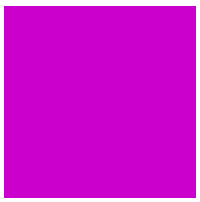


Figure 4.25. Color 17A

Figure 4.26. Color 17B

Figure 4.27. Color 17C

Figure 4.28. Color 17D

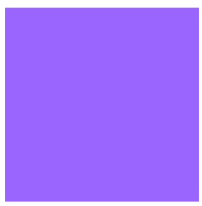


Figure 4.29. Color 18A

Figure 4.30. Color 18B

Figure 4.31. Color 18C

Figure 4.32. Color 19A

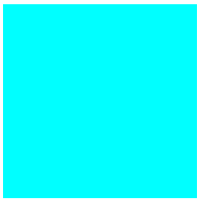


Figure 4.33. Color 19B

Figure 4.34. Color 19C

Figure 4.35. Color 20A

Figure 4.36. Color 20B

Figure 4.37. Color 20C

PLANS FOR NEXT QUARTER

- Build a solenoid system for sensor head movement
- Interface the sensor to a micro controller
- Development of an image analysis / color tracking system and planning to incorporate with the lignin sensor into a decision making algorithm

REFERENCES

Patents: None

Publications/Presentations: None

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Design robust industrially worthy lignin sensor	12/03		In progress.
2	Develop color tracking system	12/03		In progress.
3	Develop a decision making algorithm	12/05		In progress.
4	Evaluate sensing techniques for food pkg, waxed OCC, coated OCC, high adhesive paper	12/05		In progress.
5	Incorporate and test array of lignin/gloss/color sensors and decision-making algorithm.	12/06		

Budget Data (as of 6/30/04): Estimates listed below.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	1/03	12/03	80,000	20,000	100,000	80,000	20,000	100,000
Year 2	1/04	12/04	80,000	20,000	100,000	26,000	5,000	31,000
Year 3	1/05	12/05	80,000	20,000	100,000			
Year 4	1/06	12/06	80,000	20,000	100,000			
		Totals	320,000	80,000	400,000	126,000	25,000	131,000

Decontamination of Process Streams Through Electrohydraulic Discharge

Banerjee: Institute of Paper Science and Technology

ID14260, CPS#01713

QUARTERLY PROGRESS REPORT

Project Title: Decontamination of Process Streams Through Electrohydraulic Discharge

Authors: Stephen Makris, Tuan Le, Sujit Banerjee

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 16, 2004

Recipient: Institute of Paper Science and Technology at Georgia Tech

Award Number: DE-FC07-021D14260

Other Partners: Ed Fouche (EPRI), Jim Bradbury (Stora Enso).

Contact: Sujit Banerjee (404) 894-9709; s.banerjee@ipst.edu

Project Objective: The objective of this project is to explore potential applications of underwater pulsed power technology to the decontamination of process streams in recycle mills, and to enable commercialization through several mill trials.

Background: A spark discharged underwater gives rise to an acoustic wave that can inexpensively detackify stickies and pitch in mill process streams. Ink redeposition is also hindered in newsprint mills leading to lower bleach use. However, sparking can also cause unexpected aggregation which can be of benefit if controlled, but can otherwise be detrimental. The mechanism of formation of these aggregates is not understood. This project seeks to develop a fundamental understanding of how the sparker influences the behavior and interactions of various components present in process streams, so that the effect of sparking can be predicted in a mill situation. These predictions will be mill-tested so that process streams can be decontaminated in a controlled and predictable manner.

Status:

- A trial for a stickies reduction and water clarification application at Jackson Paper, Silva, NC was completed.

Table 1: Potential application points for the sparker.			
	Hydrocal	**Cloudy Water Chest**	**Primary Screen Rejects**
Volume, ft^3	800	4,500 (run volume)	2,500 (run volume)
Volume, gallons	6,240	35,000 (run volume)	20,000 (run volume)
Flow, gpm	280	1,500	725
Residence time, min	22.3	23.3	27.6
Spark rate, #/min	15	15	15
Sparks/turn	334	350	414
Sparks/ft^3	0.42	0.003	0.006
Solids In, ppm	920	350	4,200
Solids Out, ppm	260	--	--

The objective of the four-week sparker trial at Jackson Paper was to increase the removal of microstickies from the water system. The ultimate goal was to improve machine runnability by purging the system of microstickies. The mill indicated that a 10-point gain in hydrocal (clarifier) efficiency would indicate that the sparker had a very significant effect on water clarification. Definitions of improved paper machine runnability included reducing deposition of stickies and fiber in the press section and reducing the number of breaks per day. Currently, enough stickie/fiber deposits are doctored from the press section to fill about one-half of a 55-gallon barrel each shift. Jackson experiences about 3 breaks per day when producing their 23# grade. The mill indicated that reducing the number of breaks per day from three to two would be highly desirable.

Key results included an increase in hydrocal efficiency of 8+ points, a 20% reduction in sludge press filtrate microstickies, a reduction in 1st press section deposits, and an initial indication of reduced breaks during lightweight grade runs.

Our previous work indicates that the sparker can remove stickies from flotation units and reverse cleaners under certain conditions. Specifically, the application point should be of low consistency and have high enough residence time so that the volume is exposed to at least 20 sparks. Three potential sparker application points were analyzed: hydrocal dispersed air clarifier; the cloudy water chest; and the primary screen rejects chest. Table 1 summarizes the operating parameters for the three application points.

The hydrocal was the best-suited application point based on unit operational stability and low solids consistency. Also, microstickies change across the hydrocal, accessibility to service the unit, and access to historic and microstickies baseline data. The point of application was agreed upon to be just after the stock introduction to the unit and centered, roughly 3.5 feet from the head wall. This was in the area of highest mixing and should improve the spark exposure rate and uniformity of the treatment.

The major expected trial outcome was the demonstration of a statistically quantifiable improvement in operating efficiency and microstickies reduction across the hydrocal. IPST performed microstickies analysis on the inlet and outlet of the hydrocal for the duration of the trial. Aside from deposits and stickies in the final product, the single purge point for microstickies was

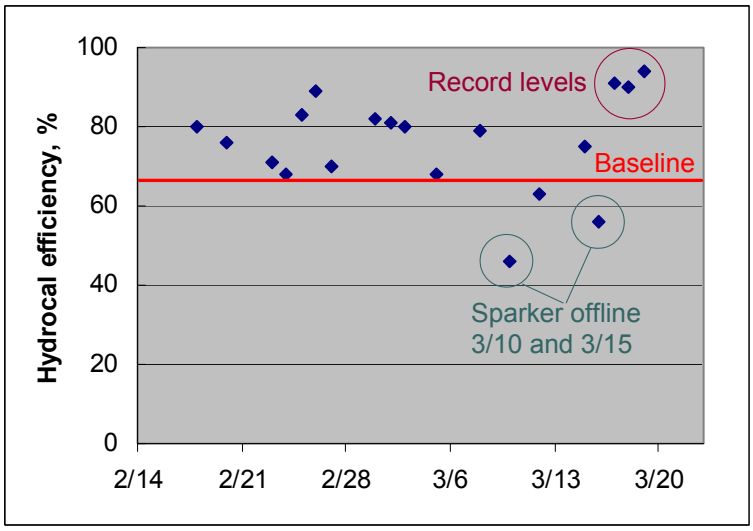


Figure 1. Hydrocal clarifier efficiency during sparker trial.

with the sludge sent to an incinerator. Therefore, microstickies analyses were also performed on the sludge belt feed and filtrate.

The chemistry and dosage to the hydrocal was kept constant during the trial. However, it should be noted that a felt-life optimization trial evaluating vacuum, shower temperature and water, was running concurrently with the sparker trial. The trial began on February 18, 2004 at 7:30 a.m. and concluded March 19 at 1:45 p.m. The sparker was set to discharge at 4,5 kv. The mill tracked the discharge range between three and five times per day, beginning one week into the trial. Voltage variation was on the order of ± 10%.

The hydrocal removal efficiency demonstrated an increase of at least eight points over the course of the trial. Measurements below the historical baseline of 66% only occurred on days of or following sparker shutdowns. Record efficiencies (greater than 92%) were consistently observed during final week of trial. Figure 1 illustrates the effect of sparking on clarifier efficiency. The sparker demonstrated a statistical improvement in clarifier efficiency (raw data presented in Appendix 1). Prior research at IPST has shown that increased solids removal correlates with stickies removal from water loop. Less stickies in water loop leads to fewer deposits and ultimately fewer machine breaks.

In contrast to the improved hydrocal efficiency, microstickies were observed to *increase* during the course of the trial, as shown in Table 2. This is an artifact and has been observed in other studies, usually reflecting the polymer load being added to the clarifier. It should be noted that the microstickies measure is based on molecular weight. Therefore, high molecular weight polymers, such as agglomeration aids, will be measured as microstickies. Microstickies at the sludge press were reduced by roughly 20%, as shown in Table 3. This represents the largest process water purge point for microstickies in the system. Post-trial baseline data is being collected to determine whether the sparker improved microstickies removal from the sludge filtrate.

Table 2: Microstickies levels across the hydrocal.				
Date	**Time**	**Hydrocal In**	**Hydrocal Out**	**% Change**
2/19	8:30 AM	680	835	+23%
2/20	3:00 PM	675	880	+30%
2/23	7:30 AM	720	775	+8%
2/23	4:00 PM	720	660	-8%
2/24	10:40 AM	720	920	+28%
2/25	7:30 AM	750	860	+15%
2/25	10:00AM	475	430	-9%
2/26	10:00AM	630	880	+40%
3/3	6:10AM	660	860	+30%
3/5	7:00AM	625	850	+36%

Table 3: Microstickies levels across the belt press.				
Date	**Time**	**Sludge Feed**	**Belt Press Filtrate**	**% Change**
2/19	8:30 AM	530	405	-24%
2/20	3:00 PM	515	470	-9%
2/23	7:30 AM	500	405	-19%
2/23	4:00 PM	525	470	-10%
2/24	10:40 AM	580	385	-34%
2/25	7:30 AM	530	385	-27%

It should be noted that no removal is observed during operations before 7:30 a.m. This is due to the transience associated with the sludge press process. Sludge is dewatered only during the first shift. The sludge accumulated overnight in the feed tank separates, with solids rising to the top. As sludge feeds from the bottom of the tank, poor dewatering performance is observed during initial operations in the morning. This may cause the noted poor microstickies removal prior to 7:30 a.m.

The mill was also concerned about deposits in the first press section. This is a key run-nability parameter, as increased sticky deposits generally lead to increased sheet breaks. Jackson has a qualitative metric to assess press section deposits, which we made more quantitative. Deposits are doctored off the press roll and accumulate in a 55-gallon garbage can. Though previously unmeasured, the mill felt that about 12 inches accumulated each shift in the bucket. The bucket is emptied once each shift. We asked the mill to measure the depth of the stickies in the bucket with a yard stick once per shift. The results are summarized in Figure 2. It is clear that the weekly average for stickies was well below 12 inches. In fact, if the mill estimate for their baseline is accurate, then by the end of the trial Jackson was realizing a 75% reduction in press section deposits.

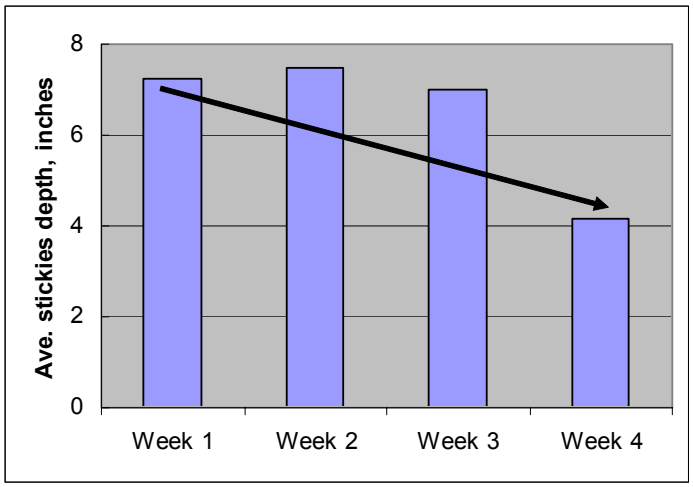


Figure 2: Stickies deposits on first press section during trial.

Table 4: Effect of sparking on sheet breaks.		
	Baseline	**Sparker Trial**
Breaks per 100 tons production	2.7	1.5
Production tons with zero breaks*	4	189
* Based on 6,400 baseline tons and 4,800 sparker tons for 23# basis weight		

The data for paper machine breaks are more difficult to analyze. The mill switches grades on the machine normally once a day on average. During this trial, however, grade changes were made much more frequently, averaging more than three per day. Due to their transient nature, increasing grade changes typically leads to increasing breaks. The mill was also shifting their product mix to more lighter-weight grades. These grades are more challenging to run and are associated with higher breaks. For example, a typical day running 34-pound encounters two breaks, while a day on 23-pound experiences three breaks.

During the month preceding the trial, 23# represented 47% of production. This increased to 61% during the sparker trial. The result was that overall differences in sheet breaks between the trial and preceding month were not statistically different. However, there were some observations that should be followed-up during any upcoming trials.

The following considers only 23# production, which is the mill's most important and difficult to produce grade. The raw data can be found in Appendix 2. This product is expected to represent more and more of the mill's production as demand for lightweight medium increases. One metric that exhibit a quantitative improvement was breaks per 100 tons of production, as shown in the following table. This was computed by dividing the total number of breaks during 23# runs by the total tons of 23# produced. The other metric was total tons of 23# without a break. This indicates the total tons made during runs without a break between grade changes. Both metrics were markedly improved during the sparker trial. These results potentially indicate that machine runnability improved during the sparker trial.

The mill experienced two instances of equipment breakdown. One was during the trial and one occurrence was during operation following the trial. The first breakdown was due to some connections becoming loose during operation. The unit was sparking poorly and was pulled out to examine the submersible components. There was noticeable coning on the electrodes and "erosion" on the insulator blocks protecting the high voltage wires located in the vicinity of the electrode gap. There was also evidence of arcing about 1/3 of the way from bottom of the submersible on the middle support where electrodes go through the frame. Photos taken by the mill may be found in Appendix 3. IPST had supplied a second submersible, which the mill installed and continued the trial. The mill was also able to rebuild the original submersible completely with a few basic and readily available parts. The mill turned the sparker back on after the initial trial. However, one of the electrical connections had come loose and the wire was pulsating in the hydrocal. The voltage level rose to 9 kV before the system was shutoff.

In summary, the results from the month-long, full-scale sparker trial at Jackson Paper are extremely promising. The mill realized a significant, 8-point improvement in clarifier efficiency. This has previously been observed at Stora Enso's Duluth Recycle Pulp Mill in Duluth, Minnesota. The sparker clearly produced superior results and provided much cleaner process water. The mill is currently considering the economic impact of cleaner process water. Initial findings also indicate the sparker may increase microstickies removal by 20% from the sludge press filtrate. Additional data is required to confirm these results. Paper machine runnability improved, as measured by a reduction in 1st press section deposits, and an initial indication of reduced breaks during lightweight grade runs.

The mill appears to be convinced that sparking improves the efficiency of the hydrocal. However, the mill has concerns about the reliability of the sparker unit, and has an interest in moving forward once this is improved.

Appendix 1. Hydrocal clarifier daily influent and effluent solids concentration and removal efficiency. The trial data were collected during Feb 18 and Mar 19.

Date	Hydrocal In	Hydrocal Out	Efficiency
2-Jan	1507	580	62%
5-Jan	1393	327	77%
6-Jan	1407	433	69%
7-Jan	850	290	66%
8-Jan	860	347	60%
9-Jan	927	327	65%
12-Jan	1167	360	69%
13-Jan	1300	367	72%
14-Jan	1000	333	67%
15-Jan	1420	340	76%
16-Jan	1190	493	59%
19-Jan	900	340	62%
20-Jan	660	510	23%
21-Jan	710	270	62%
22-Jan	680	400	41%
23-Jan	720	460	36%
26-Jan	830	260	69%
27-Jan	1210	270	78%
28-Jan	920	140	85%
29-Jan	1020	180	82%
30-Jan	1000	340	66%
1-Feb	950	270	72%
3-Feb	1120	330	71%
5-Feb	950	230	76%
9-Feb	1460	320	78%
10-Feb	1180	340	71%
11-Feb	670	230	66%
12-Feb	880	280	68%
13-Feb	1260	300	76%
16-Feb	930	290	69%
17-Feb	920	260	72%
18-Feb	1160	230	80%
19-Feb	850	320	62%
20-Feb	620	150	76%
23-Feb	1073	307	71%
24-Feb	653	207	68%
25-Feb	927	307	67%
26-Feb	1280	140	89%
27-Feb	1340	400	70%
1-Mar	980	180	82%
2-Mar	1120	210	81%
3-Mar	1046	213	80%
4-Mar	730	210	71%
5-Mar	1020	330	68%
8-Mar	1250	260	79%
10-Mar	540	290	46%
12-Mar	1030	380	63%
15-Mar	790	200	75%
16-Mar	970	430	56%
17-Mar	790	70	91%
18-Mar	1020	100	90%
19-Mar			94%

Appendix 2. Number of breaks during production runs for 23# grade before and during the sparker trial.

Baseline – Month prior to trial				30-day sparker trial			
Basis Wt	**Breaks**	**Tons**	**Breaks/100 tons**	**Basis Wt**	**Breaks**	**Tons**	**Breaks/100 tons**
23.63	7	263.16	2.7	23.45	9	199.55	4.5
23.68	6	272.4	2.2	23.54	3	271.62	1.1
23.82	4	276.01	1.4	23.54	4	278.84	1.4
23.89	3	7.58	39.6	23.58	8	262.65	3.0
23.91	2	233.55	0.9	23.59	2	270.83	0.7
23.94	5	264.13	1.9	23.61	2	127.22	1.6
23.95	2	209.89	1.0	23.61	3	268.39	1.1
23.98	3	269.77	1.1	23.62	3	264.22	1.1
23.99	1	259.97	0.4	23.62	2	282.43	0.7
23.99	4	278.1	1.4	23.63	5	261.67	1.9
23.99	7	264.01	2.7	23.64	2	274.19	0.7
24	1	160.28	0.6	23.64	1	275.14	0.4
24	3	284.05	1.1	23.64	2	276.79	0.7
24.01	3	262	1.1	23.64	2	277.26	0.7
24.03	4	287.66	1.4	23.66	5	262.24	1.9
24.03	0	3.9	0.0	23.72	1	146.89	0.7
24.05	3	286.41	1.0	23.72	3	281.45	1.1
24.05	4	279.66	1.4	23.72	5	271.22	1.8
24.07	10	221.82	4.5	23.73	0	7.97	0.0
24.07	4	231.89	1.7	23.73	0	55.46	0.0
24.07	2	282.73	0.7	23.77	2	35.02	5.7
24.08	2	97.34	2.1	23.81	0	12.02	0.0
24.09	1	237.49	0.4	23.82	0	105.9	0.0
24.09	6	269.73	2.2	23.9	0	7.43	0.0
24.1	1	164.95	0.6	23.96	1	15.45	6.5
24.12	3	212.78	1.4				
24.13	4	230.67	1.7				
24.15	2	169.4	1.2				
24.28	1	105.92	0.9				
Total	**98**	**6387.25**	**Ave = 2.74**	**Total**	**65**	**4791.85**	**Ave = 1.50**

Appendix 3. Photos of the damage to the submersible encountered during the sparker trial.

Pitting wear around the black insulators protecting the high voltage wire from the discharge

Electrode coning

Appendix 4. Raw data taken during the trial.

Date	Trial day	Basis Weight	Breaks	Tons	Stickies bucket
2/19/2004	1	23.66	5	262.24	4
2/20/2004	2	23.62	3	264.22	17
2/21/2004	3	23.73	0	7.97	
2/21/2004		26	3	281.68	
2/22/2004	4	26.08	2	295.47	
2/23/2004	5	26.2	2	68.16	4
2/23/2004		32.7	1	232.36	
2/24/2004	6	32.6	5	300.23	4
2/25/2004	7	32.46	1	97.59	
2/25/2004		26.33	0	43	
2/25/2004		23.72	1	146.89	
2/26/2004	8	23.64	2	274.19	
2/27/2004	9	23.59	2	270.83	7
2/28/2004	10	23.64	1	275.14	
2/29/2004	11	23.64	2	276.79	
3/1/2004	12	23.54	3	271.62	8
3/2/2004	13	23.61	2	127.22	
3/2/2004		25.94	2	132.73	
3/3/2004	14	23.77	2	35.02	
3/3/2004		25.93	1	253.84	
3/4/2004	15	32.57	3	164.14	12
3/4/2004		37.87	0	4.73	
3/4/2004		26.36	1	11.65	
3/4/2004		23.82	0	105.9	
3/5/2004	16	23.64	2	277.26	
3/6/2004	17	23.61	3	268.39	
3/7/2004	18	23.63	5	261.67	
3/8/2004	19	23.96	1	15.45	
3/8/2004	20	25.86	2	273.81	
3/9/2004		23.73	0	55.46	
3/9/2004		25.94	0	95.63	
3/9/2004		26.99	0	4.27	
3/9/2004		32.58	0	148.87	
3/10/2004	21	33.07	0	66.88	
3/11/2004	22	32.67	0	208.81	2
3/11/2004		35.96	0	41.53	
3/11/2004		26.17	0	35.19	
3/11/2004		23.81	0	12.02	
3/12/2004	23	23.72	3	281.45	
3/13/2004		23.72	5	271.22	
3/14/2004		23.62	2	282.43	
3/15/2004	26	23.58	8	262.65	4
3/16/2004	27	23.54	4	278.84	
3/17/2004	28	23.45	9	199.55	
3/18/2004	29	23.9	0	7.43	8
3/18/2004		26.01	5	267.57	
3/19/2004					
3/19/2004					0.5
3/19/2004					

Samples from Jackson paper were filtered through with Whatman 4 and then ultrafiltered through a YM3 membrane. The TOC of both samples was measured; the results are as follows.

Day	time	Sample	Filtered			Ultra-filtered			Stickies
			TC	IC	OC	TC	IC	OC	OC-OC
3/23/2004	12:00pm	**Belt press filter**	2030	250	1780	1630	230	1400	380
3/23/2004	12:00pm	**Hydrocal In**	2450	200	2250	1690	180	1510	740
3/23/2004	12:00pm	**Hydrocal out**	2430	210	2220	1680	170	1510	710
3/23/2004	12:00pm	**Sludge Feed**	2720	200	2520	2280	170	2110	410

Day	time	Sample	Filtered			Ultra-filtered			Stickies
			TC	IC	OC	TC	IC	OC	OC-OC
3/26/2004	7:30am	**Belt press filter**	2140	260	1880	1635	230	1405	475
3/26/2004	7:30am	**Hydrocal In**	2590	190	2400	1725	170	1555	845
3/26/2004	7:30am	**Hydrocal out**	2610	190	2420	1680	170	1510	910
3/26/2004	7:30am	**Sludge Feed**	2840	200	2640	2280	180	2100	540

Day	time	Sample	Filtered			Ultra-filtered			Stickies
			TC	IC	OC	TC	IC	OC	OC-OC
4/26/2004	12:00	**Belt press filter**	1750	310	1440	1200	280	920	520
4/26/2004	12:00	**Hydrocal In**	1980	280	1700	1255	250	1005	695
4/26/2004	12:00	**Hydrocal out**	1950	280	1670	1260	260	1000	670
4/26/2004	12:00	**Sludge Feed**	2330	380	1950	1665	310	1355	595

Day	time	Sample	Filtered			Ultra-filtered			Stickies
			TC	IC	OC	TC	IC	OC	OC-OC
4/27/2004	9:00	**Belt press filter**	1750	400	1350	1240	320	920	430
4/27/2004	9:00	**Hydrocal In**	1900	270	1630	1240	240	1000	630
4/27/2004	9:00	**Hydrocal out**	1870	280	1590	1225	250	975	615
4/27/2004	9:00	**Sludge Feed**	1910	440	1470	1460	350	1110	360

Day	time	Sample	Filtered			Ultra-filtered			Stickies
			TC	IC	OC	TC	IC	OC	OC-OC
4/28/2004	3:30am	**Belt press filter**	1580	400	1180	1120	350	770	410
4/28/2004	3:30am	**Hydrocal In**	1810	270	1540	1270	250	1020	520
4/28/2004	3:30am	**Hydrocal out**	1880	280	1600	1195	260	935	665
4/28/2004	3:30am	**Sludge Feed**	2300	340	1960	1770	320	1450	510

Plans for the Next Quarter:

- Complete trials at Stora Enso, Duluth.

Budget Data (as of 3.31.04)

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			**DOE Amount**	Cost Share	Total	**DOE Amount**	Cost Share	Total
	From	To						
Year 1	1.01.02	12.31.02	132,000	60,000	192,000	68,567		
Year 2	1.01.03	12.31.03	143,000	60,000	203,000	132,746		
Year 3	1.01.04	12.31.04	166,000	100,000	266,000	58,303		
		Totals	441,000	220,000	661,000	259,616	284,222	

ID Number	Task/Milestone Description	Planned Completion	Percent Completion	Actual Completion	Comments
1.1	Laboratory studies on the effect of sparking on stickies, filler, and fiber separately and in combination	3.03	100	3.03	
1.2	Laboratory work on spark-induced de-gassing.	9.02	100	9.02	
1.3	Development of a relationship relating the oxidative potential of the acoustic wave to the properties of the particle surface.	12.03	15		
2.1	Mill trials and lab support dealing with stickies removal.	6.03	60		
2.2	Mill trials and lab support dealing with particle agglomeration.	6.04	60		
2.3	Mill trials and lab support dealing with water clarification.	10.04	70	3.03	new sub-objective
2.4	Lab work on spark-induced emulsification	12.03	15		new sub-objective
2.5	Effect of sparking on foam removal	6.03	100	6.03	new sub-objective
2.6	Flotation: lab work	4.04	100		new sub-objective
2.7	Flotation: mill trials.	10.04			
3.1	Long term trials at two mills to demonstrate feasibility with regard to stickies control & debris removal.	10.04	50		
3.2	Final report.	12.04			

High-Speed Microwave Treatment for Rapid Wood Drying

Compere: Oak Ridge National Laboratory

CPS#00786

QUARTERLY PROGRESS REPORT

Project Title: Microwave Pretreatment: In-Mill Evaluation, Kiln Schedule, and Process Model

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: August 6, 2004

Recipient: Oak Ridge National Laboratory (ORNL), operated by UT-Battelle
P. O. Box 2008
Oak Ridge TN 3783106150

Award Number: DE-AC05-00OR22725

Subcontractors: W. W. Moschler, Jr., Tennessee Forest Products Center, University of Tennessee

P. N. Peralta, Wood and Paper Sciences Department, North Carolina State University (NCSU)

Other Partners: W. L. Gardner, W. L. Griffith, and T. L. White ORNL

R. D. Little, Manager, Wood Technology, Armstrong Floor Products

D. Straka, Averitt Hardwoods International

D. Parent, Communications and Power Industries

P. G. Altham, Huntersville Hardwoods

A. Bangi and B. Kasal, NCSU

B. G. Williams, Rhyne Lumber Company

D. Mathews, SII Dry Kilns, Inc.

Contact(s): A. L. Compere (865-574-4970) compereal@ornl.gov

Project Team: Dickson Ozokwelu, DOE program manager; Buddy Showalter, AF&PA program manager; Wood and Wood Composites Task Group (mentors).

Project Objective: This project will demonstrate, at mill scale, the utility of rapid microwave pretreatment in decreasing time, energy, and cost of drying hardwoods for later use in lumber, furniture, flooring, and composite or laminate boards and panels. It will also develop the information which will permit project partners to develop designs for near-commercial units and the forest products community to assess the viability of the technology. The project goal will also develop a predictive understanding of the relationship between rapid microwave/RF - wood pretreatment of hardwoods and increases in permeability which enhance both drying rate and value in lumber, fine hardwood, and specialty hardwood products.

Background: Drying is the most energy intensive and, therefore most costly, step in lumber processing. Particularly for refractory or impermeable species, such as white oak, the development of pretreatments which increase the rate at which water vapor can be removed from wood, has the potential to dramatically cut kiln drying time and energy. Moisture content is decreased by removal of liquid water and steam from wood during processing. High-speed microwave pretreatment also increases wood permeability by opening the internal microstructure of wood, including pit membranes and the ends of vessel cells. Early studies by Paul Winistorfer and Bill Moschler of UT on microwave pretreated fungally-blocked white oak showed that it would be possible to significantly increase the drying rate of white oak with minimal changes in strength and stiffness. In FY 1998, a large factorial experiment, using a 915 MHz, 60 kW microwave applicator was initiated. Paired strips of red and white oak, maple, beech, yellow poplar, and other hardwoods were pretreated and kiln dried at UT. Effects of power levels and application were evaluated, and methods for scoring wood quality were developed. The factorial experiment was completed in FY 1999, and mechanical and machining properties of treated wood were assessed. In all of the species tested, there was a significant increase in drying rate, and the mechanical properties of pretreated and control samples were comparable.

Use of large-scale generators was obtained from earlier Fusion projects. Simulations to support design of these larger applicators for processing dimensional lumber, cants, and logs were performed and work on electric power and cooling water systems, power supplies, and controllers was started. These applicators are expected to be operational shortly. In all of these experiments, industrial partners worked closely with ORNL and UT to identify and resolve process-related issues. In addition to electronic exchanges, there have been and continue to be a number of visits.

Status: In the last quarter, evaluations to determine how far down the moisture content of yellow poplar and pine dimensional lumber can be pushed using the prototype applicator were performed. Because the prototype applicator provides very even application of 915 MHz microwaves, it appears to be possible to remove moisture down to the fiber saturation using two or three rapid cycles through the applicator. Industrially, this is tractable and would be accomplished using a series of applicators spaced along a process line.

The effect on the drying rate of the pretreated 4/4 and 5/4 lumber and paired controls was determined and, as might be expected, the pretreated boards dried in 35-45% of the time

required for untreated controls even though the mixed-load kiln was controlled based on the controls. The quality of dried pretreated and untreated lumber was similar.

These results indicate that microwave pretreatment could improve the energy efficiency of the hardwood industry both by decreasing kiln drying time and by minimizing losses, such as fungal degradation, surface checking, or cracking, due to holding lumber outdoors prior to processing.

Drying fundamentals studies which provide a basis for determination of three dimensional diffusion coefficients for water in wood continued. The North Carolina State University staff has been evaluating moisture content loss of paired untreated and microwave pretreated maple and white oak samples.

Kiln drying. Because yellow poplar and pine are relatively fast-drying woods, studies in this quarter concentrated on slow drying dimensional red oak lumber. Approximately 300 board feet of 5/4 red oak lumber was obtained from Mountain City Lumber Inc., one of the original industrial partners for this project. The lumber was random width, 8' length, one face FAS.

The lumber was ripped to nominal 6" widths. Paired samples 47" long were cut from each 8' board. One half of each board was pretreated and the other half was used as a paired untreated control. All samples were wrapped in plastic sleeves in bunches of 2 samples per sleeve to prevent surface checking during transportation to ORNL.

After weighing, the samples were placed in small fiberglass trays for pretreatment. The samples were stacked on edge with spacers between each board and the bottom of the tray to allow water to drain. Two trays of 4 sample each (total 8 samples) were treated side by side in the 915 MHz prototype applicator supplied by industrial partner Communications and Power Industries, Inc. The generator seems to couple with a load in this applicator better at certain settings.

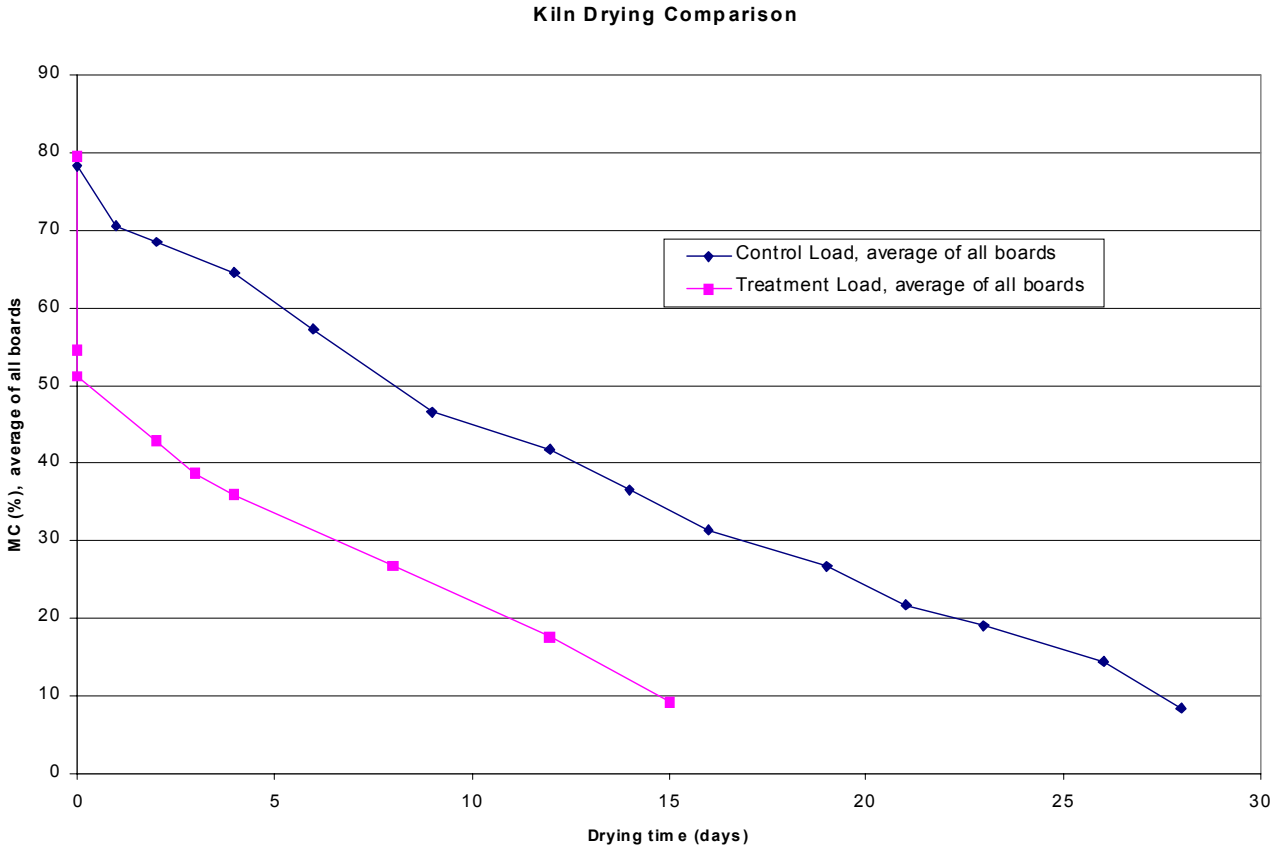
After the initial power determinations, most of the samples were treated at 0.5 inch/second feed rate, and 2 passes through the system. This provided an initial removal of approximately 25% moisture content. To permit control of the kiln schedule with pretreated wood, all pretreated samples were dried together in a separate first kiln run. The samples were then dried in the same kiln following the a standard Forest Products Society kiln schedule, Schedule 29 (T-4, D-2, Modified), which is based on the moisture content of samples selected from the wood being dried. As the kiln samples reach specified levels of moisture content, the temperature is increased and the relative humidity decreased.

During the 15 days required for the pretreated boards to reach 10% moisture content, the untreated control samples were wrapped in plastic sleeves and stored in an air-conditioned laboratory. To reach 10% moisture content, the untreated samples required 27 days using the same kiln schedule.

The results for these drying runs have not been fully analyzed. The graph below shows the average of all the boards in each of the 2 drying runs. The pre-treated samples started at a

lower moisture content both because of the initial removal of about 25% moisture content by the microwave and moisture loss from the lumber surface during kiln loading. The pretreated samples also dried at a slightly faster rate throughout the drying run.

The wood quality was similar: 1 each of the untreated and pretreated samples showed honeycomb checking, probably related to bacterial infection of the wood which blocks the transfer of moisture. Three pretreated samples showed light internal checking.



Drying fundamentals. The NCSU staff is continuing their evaluation of radial, tangential, and longitudinal moisture content loss in paired pretreated and untreated maple and white oak samples. For both woods, evaluation of several paired samples in the high moisture region and the mid-moisture content region has been completed. Studies in the low moisture region are in progress. When all of the samples have been evaluated, the normalized data will be used to calculate diffusion coefficients for water in the radial, tangential, and longitudinal directions. Kiln schedules can be calculated for most common lumber dimensions using diffusion data.

Plans for Next Quarter: Work on larger sections of wood and on wood which is showing moisture variation in wood exiting the kiln will continue. Kiln drying evaluated against the

process model. The NCSU group will complete their final statistical evaluations and create the drying models for wood species as diffusion tests are completed. These will be verified against kiln drying data for each wood species. Some Southern lumber manufacturers have requested pretreatment evaluations to determine whether hard-to-dry lumber which has unacceptably high moisture contents after completion of a kiln cycle can be improved. Evaluation of drying larger lumber moves the microwave pretreatment process closer to commercial utilization because it meets technology verification and demonstration needs expressed by microwave development partners and Agenda 2020 advisors.

Patents: None

Publications/Presentations: Presented paper, *"Microwave Pretreatment to Decrease Drying Time and Energy*" as a part of DOE projects session at the TAPPI Spring 2004 Technical Conference and Environmental Conference, 2-5 May, and participated in annual review.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1.1	Evaluation of "aggressive" kiln schedules for pretreated wood	9/2001	9/2001	
2.1	Initiate studies on softwood lumber	6/2002	6/2002	
2.2	Development of a process model applicable to kiln drying of dimensional pretreated lumber	9/2002	7/2002	
3.1	Initiate studies of uptake of environmentally-friendly preservatives / fire retardant	1/2003	1/2003	
3.2	Complete evaluations of pretreatment process + kiln drying.	9/2004		Moved as funding received a year late.

Budget Data (as of June 27, 2004):

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	10/00	9/01	250000	189800	439800	199588	142350	341938
Year 2[a]	10/01	9/02	200000	189800	389800	218287	189800	408087
Year 3[a]	10/02	9/03	200000	189800	389800	212528	189800	402238
Year 4	10/03	9/04	200000	189800	389800	110258	142350	252608
		Totals	850000	569400	1419400	740661	664300	1404961

[a]Only $200,000 in DOE funding was received during FY.

Rapid, Low Temperature Electron, X-Ray, and Gamma Beam Curable Resins

Griffith: Oak Ridge National Laboratory

CPS#01698

QUARTERLY PROGRESS REPORT

Project Title: Rapid, Low-Temperature Electron, X-ray, and Gamma Beam-Curable Resins

Covering Period: April 1, 2004 through June 30, 2004.

Date of Report: July 28, 2004

Recipient: Oak Ridge National Laboratory
Managed by UT Battelle, L.L.C for the Department of Energy
Post Office Box 2008
Oak Ridge TN 37831-6150

Award Number: DE-AC05-00OR22725

Subcontractors: P. M. Winistorfer, Department of Wood Science and Forest Products, Virginia Tech

G. F. Dorsey, W. W. Moschler, Jr., T. G. Rials and Ting Song, Tennessee Forest Products Center, University of Tennessee

Other Partners:: J. B. Eppner, Dow Chemical Company, 2301 N. Brazosport Blvd., Freeport, TX 77451.

L. A. Parks and Chang Song, IBA SteriGenics International, Inc., 7695 Formula Place, San Diego CA 92121-2418.

A. G. Landers, J. M. Huber Corporation, Engineered Woods, P. O. Box 670, Commerce GA 30529.

A. W. Boehner, TrusJoist, a Weyerhaeuser Business, P. O. Box 8449, Boise ID 83707-2449.

Contact(s): William L. Griffith, (865) 574-4970, griffithwl@ornl.gov

Project Team: Project Team: Dickson Ozokwelu, DOE program manager; Buddy Showalter, AF&PA program manager; Wood and Wood Composites Task Group (mentors).

Background: Approximately 50% of all wood used today is some type of glued-wood assembly. The manufacture of most glued-wood assemblies requires process heat. Process heat is required to dry the parent wood material, is used to assist in consolidation of the product (flat-pressed panel products) and is used to polymerize and cure the resin system. Glued-wood products range from structural laminated beams and flat-pressed panels to furniture assemblies and non-structural wooden assemblies. Many of these products are referred to as wood composites. Because process heat is required to polymerize and cure the resin system, the moisture content of the wood materials must be reduced to low levels and then be carefully controlled during manufacture. Moisture must be closely controlled to ensure efficient resin polymerization

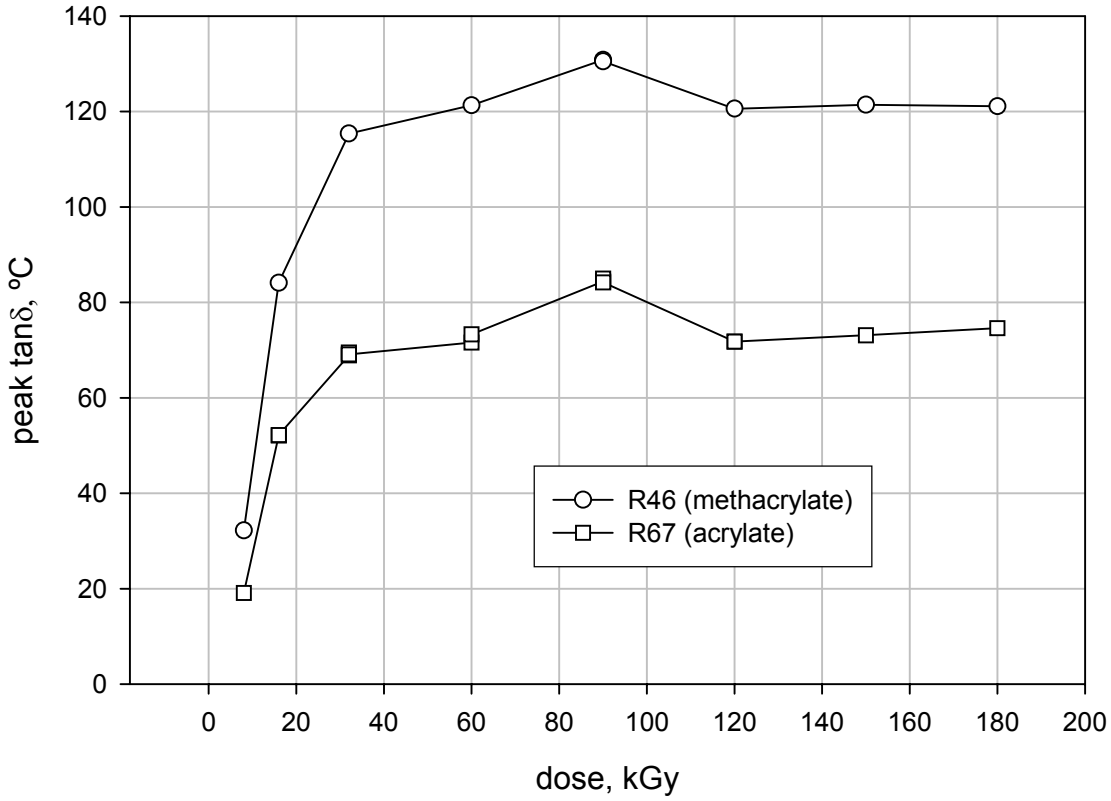
and eventual resin curing and to avoid generation of excessive steam vapor pressure internal to the product. Drying the wood furnish materials and controlling the substrate moisture content is a major consumer of energy in the manufacturing plant. "Hot-pressed" wood panels such as oriented strand board, medium density fiberboard (mdf) and particleboard can be mismanufactured by lack of moisture control. High moisture levels can result in excess steam vapor pressure leading to a condition known as internal blows. Low moisture can result in poor resin bond development. Both conditions can be fatally defective to product performance and quality and ultimately waste wood and energy resources. Development of rapid, low-temperature electron, x-ray, and gamma beam-curable resin systems offers tremendous energy savings potential to the wood composites industry, as well as unique opportunities to develop novel products and processes.

Status: The adhesive properties of three of the more promising resins in previous tests, R08, R14 and R49, epoxy acrylate, aliphatic urethane acrylate, and an aromatic methacrylate half ester, respectively, were evaluated as a function of applied dose in cure Set I. The samples were cured at 4, 8, 16 and 32 kGy to help evaluate the optimum dose required. The maple block specimens were selected and tested to ASTM D905 as in Set G using one bonded assembly per resin/test dosage. The average breaking stresses in Set I and the data from Set G (at 80 kGy) were plotted against dose for each resin and the plots were compared. Due to problems in testing or with sample preparation some of the data were missing or incomplete. Still, the plots indicate an overall increase in strength with dose. The data indicate also that 32 kGy will be required to give maximum strengths for the resins in this test.

Evaluations of these candidate resins for wood composites were continued. Activities for this reporting period included cure evaluations of Set I using dynamic mechanical analysis (DMA), and curing and testing of the corresponding bonded maple-block assemblies. In addition, evaluations were begun on curing Set H, a set of samples prepared from two materials differing only in functional group (acrylate vs. methacrylate) cured at a very wide range of doses. Analyses were carried-out with DMA, pyrolysis-molecular beam mass spectrometry (py-MBMS), Differential Scanning Calorimetry (DSC)and near infrared spectroscopy. Electron-beam exposures were as before at the IBA Sterigenics facility in San Diego.

Samples for cure Set H were prepared using R46 (Sartomer SR540, ethoxylated(4)bisphenol-A dimethacrylate) and R67 (Sartomer SR601, ethoxylated(4)bisphenol-A diacrylate) to give six samples each at 14 cures ranging from 0.1 to 180 kGy. Doses to 4 kGy could cure the materials no further than a weak gel; at 8 kGy and above the samples cured to hard solids.

DMA data were obtained as in previous reports and the data evaluated. The glass transition temperature, T_g, measured as the peak in the tan□ vs. temperature curve, was plotted against dose for each set of resins. Disregarding the data at 90 kGy, which at first glance appears to be an outlier for each resin, the curves smoothly increase to plateau maxima in T_g at 40 to 60 kGy–R_{46} at ~121ºC and R67 near 72ºC with some indication of further increase from 150 to 180 kGy. However, when the data at 90 kGy are included, the interpretation is not as clear. Each resin showed a maximum T_g at 90 kGy of ~131 and ~85ºC for R46 and R67, respectively. Tests of additional 90 kGy samples confirmed the DMA results. Other than some peculiarity in the e-beam exposure, the results seem to be a real physical phenomenon. A possible



explanation of the curves is a steady increase in T_g with increasing curing dose to near 90 kGy, then some degradation at greater dose (120 kGy and above). In fact, early evaluation of the infrared data does indicate degradation with higher doses. The py-MBMS, DSC and near infrared spectroscopy data will be covered fully in the next progress report.

Plans for Next Quarter: An updated energy balance will be completed. Additional resins and assemblies for shear-block and bond fracture tests will be prepared and evaluated. Evaluation of the detailed dore-cure relationships will be continued. Larger wood composite samples will be prepared for evaluation.

Patents: None

Publications/Presentations: A program review paper was presented at the TAPPI Spring Technical Conference May 2-5, 2004. The full paper was published in the proceedings.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1.1	Survey existing wood adhesive systems and industrial practice	09/30/02	09/30/02	
1.2	Evaluation of initial resin systems	12/31/02	12/31/02	
1.3	Develop test protocol for block-tests	12/31/02	11/05/02	
1.4	Initiate adhesion studies	03/31/03	03/01/03	
1.5	Ethylenic and acetylinic bond systems	09/30/03	09/30/03	
1.6	Downselect promising resin systems	05/01/04	05/01/04	
1.7	Properties of glued wood assemblies	08/30/04		
1.8	Evaluation of process energy balance	09/30/04		
1.9	Initiate testing of large sections	01/01/05		
1.10	Evaluate alternative beam application methods including X-rays	09/30/05		
1.11	Select large-scale systems	01/01/06		
1.12	Final Report	12/31/06		

Budget Data (as of 6/30/04):

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1[a]	10/01/01	9/30/02	200,000	71,000	271,000	116,000	65,000	181,000
Year 2	10/01/02	9/30/03	210,000	101,000	311,000	158,000	91,000	249,000
Year 3	10/01/03	9/30/04	220,000	101,000	321,000	145,000	75,000	220,000
Year 4	10/01/04	9/30/05	230,000	101,000	331,000			
Year 5	10/01/05	9/30/06	240,000	101,000	240,000			
		Totals	1,000,000	614,000	1714,000	419,000	231,000	650,000

[a]Only $150,000 in funding was received during FY 2002.

Wireless Microwave Wood Moisture Measurement System for Wood Drying Kilns

Moschler: University of Tennessee, ORNL

GO10618, CPS#01491

Quarterly Progress Report

For: Wireless Microwave Wood Moisture Measurement System for Wood Drying Kilns

Covering Period: (April 1, 2004 to June 30, 2004)
Date of Report: (July 30, 2004)

Recipient: University of Tennessee
Award Number: DE-FC36-01GO10618
Subcontractors: Oak Ridge National Laboratory

Other Partners: Kiln Drying Systems, Inc., in kind support; Averitt Hardwoods, in kind support, Communications and Power Industries, Inc., in kind support, International Paper Co., Navigations Sciences, Inc., in kind support.

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Project Team: DOE/HQ: Doug Hooker, Jim Alkire

Project Objective: The objective of this project is to develop a prototype of a microwave based moisture sensor to be used in lumber drying kilns. The sensor should be accurate from about 50% mc down to 7% mc. The moisture sensor will be combined with spread spectrum wireless telemetry to provide continuous readings during the entire drying cycle.

Background: Existing moisture sensors for a dry kiln are accurate only over the range of 25% to 6% MC. Weight based moisture content sensors that work over a larger MC range are large and currently may only be mounted in the kiln plenum. Weight based sensors are expensive and consequently an inadequate number of measurements is used. The sensors we are developing in this project will be sized so that they may be inserted into the lumber pack in various locations in the kiln. These new sensors will provide better information about the average and the distribution of moisture within the kiln. This increased knowledge of moisture content, particularly at the critical region of 35% to 25% MC will allow kiln operators greatly increase the drying rate without risk of excessive lumber degrade. These sensors will interface with existing PLC based control systems used in the hardwood and softwood drying industry. The current phase of the project is to identify and test suitable microwave moisture measurement techniques to identify suitable sensor technology.

Status:

During this quarter (4/04–6/04) the second design of the electronics to generate the microwave signal and read the response were tested. The results of these tests were presented at the TAPPI Spring Meeting and project review. This miniature custom electronics provided moisture measurement results with essentially the same accuracy and precision as obtained using the standard laboratory Network Analyzer. With the new electronics and improved analysis algorithms, MC measurements with standard deviations of less than 1% MC over a MC range of 5% to 100% was achieved. Since the review meeting, we have worked on making the analysis

software more user friendly to allow further testing at UT without more funding, developing a conceptual design for a newer, very low cost version of the microwave electronics, and on finding commercial partners to pursue follow-on pre-commercial development of this technology.

During this past quarter, ORNL tested wireless (RF) communications in the UT kiln utilizing the ORNL developed Hybrid Spread-Spectrum. These tests showed very successful communications. The units tested were built by ORNL as part of CRADA with Tarallax Wireless, Inc. and Navigational Sciences, Inc. These first prototypes represented an initial $1M investment by the CRADA partners and were made available to this project as in-kind support by Navigational Sciences, Inc. An ORNL Invention Disclosure has been filed during this quarter.

Plans for Next Quarter:

We have a conceptual design for a new sensor electronics circuit that will further reduce the cost and complexity of the RF electronics. We will perform bench top testing of this new design to aid in showing a path to a cheaper system implementation. This new electronics design should bring the component cost of the moisture sensor system (without the wireless telemetry system) down to less than $400. The present system design has a component cost of about $1000. We believe this will greatly improve our ability to market this technology for commercialization. We have communicated with two commercial companies with interest in our technology. We will pursue technology transfer or pre-commercial development projects with these companies.

Note: We have changed Milestone #5 to testing the wireless telemetry system in a UT kiln without connection to the microwave moisture sensor. This change is necessary because the telemetry system built for Navigations Sciences, Inc. is not presently designed to handle the amount of data that must be sent for the moisture sensor. Modifying the present telemetry system to handle this much data would use the remainder of our funds. Navigations Sciences will be funding a new project starting in summer of 2004 to improve and miniaturize the telemetry system for a different application. If project funding is available, Navigational Sciences will provide for testing in a kiln the new version of the telemetry system. This system will better able to be deployed with the moisture sensor system without incurring significant costs.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
	First quarter, 1st year (project started Jan., 2001)			
Task	Develop guidelines and begin sensor testing	March, 01	March, 01	
Task	Develop sensor testing technique	Mach, 01	March, 01	
	Second quarter, 1st year			
Task	Detailed testing of sensor design	June, 01	July, 01	
	Third quarter, 1st year			
Milestone #1	Demonstration of capability to determine average moisture content of the lumber at various stages of the drying process using microwaves.	September 31, 2001	September 31, 2001	We have successfully demonstrated the measurement of MC over a range of 6% mc to 80% mc on lumber samples.
	Fourth quarter, 1st year			

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
Task	Develop lower-frequency sensor prototypes, which will have a lower cost and will measure the average MC over a larger volume.	December, 01	December, 01	We have successfully tested 2 different launcher designs both working at a lower frequency band than that of the first measurements.
	First quarter, 2nd year (Jan.-Mar., 2002)			
Milestone #2	Test the lower-frequency sensor designs for sensitivity to temperature, species (density), and MC distribution.	March 31, 2002	March 29, 2002	
Task	Design and build prototype microwave electronics system for MC measurement.	March, 02		microwave electronics system designed and parts ordered.
	Second quarter, 2nd year			
Task	Select best sensor design from the two candidate designs tested in previous quarter.	May, 02	May, 02	
Task	Integrate microwave electronics with sensor. Test assembly in the laboratory.	June, 02	September, 02	
Task	Begin evaluation of kiln environment for wireless telemetry system.	June, 02	June, 02	The UT kilns were examined to determine the basic path lengths for the multipath signals.
Task	Develop and evaluate a surface MC sensor which can be integrated with the microwave MC sensor (volume averaged measurement) to allow determination of the MC profile. Determine whether to incorporate surface MC sensor into the sensor system.	June, 02	June, 02	Surface moisture evaluated and promising results obtained. Sensor development suspended due to insufficient funds
	Third quarter, 2nd year			
Milestone #3	Demonstrate operation of the prototype microwave MC sensor in a Kiln during a drying charge.	September 30, 2002	October 14, 2002	Short delay in meeting milestone due to problems with the microwave electronics.
Task	Perform design study for the spread-spectrum wireless telemetry system.	September, 02	September, 02	
	Fourth quarter, 2nd year			
Task	Order hardware for wireless telemetry system and start fabrication of telemetry system.	December, 02	December, 02	
	First quarter, 3rd year (Jan.-Mar., 2003)			
Milestone #4	Perform laboratory testing of wireless telemetry system.	June 30, 2003	June 15, 2003	Delay Milestone date by 1 quarter due to delay in funding.
Task	Complete evaluation of first generation microwave electronics circuit and design of second generation microwave electronics circuit	June, 03	June, 03	
	Second quarter, 3rd year			
Task	Perform testing of prototype wireless telemetry system in the UT kiln.	September, 03	postponed	This test planned on using commercially available prototyping modules for the telemetry system. These modules have proven unreliable and so kiln test postponed until new telemetry system available in June, 2004.
Task	Fabricate and test the second generation microwave electronics circuit.	September, 03	September, 03	
Task	Identify industry requirements for a commercial MC sensor and investigate methods to integrate MC sensor into existing kiln control systems.	September, 03	Initiated	Industry requirements defined. Integration methods explored. Will need to do further programming when actual output of sensors is available.
	Second quarter, 4th year (Ari.-Jun., 2004)			
Milestone #5	Field test wireless telemetry system in UT Kiln at room temperature.	June 30, 2004	April, 04	Custom telemetry system, provided by ORNL CRADA partner, successfully demonstrated in kiln.
Task	Test custom moisture sensor electronics in UT kiln at kiln high temperature.	June 30, 2004	cancelled	Custom electronics perform well on bench top, but will not last long in kiln. Need to improve design and packaging for kiln test.
	Third quarter, 4th year (Sep.-Dec., 2003)			
Milestone #6	Prepare report detailing future work required to commercialize prototype MC sensor.	September 30, 2004		

Budget Data This data represents the University of Tennessee portion of the budget. ORNL is budgeted separately for this project:

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	1/01	9/01	28,000	48,000	76,000	28,000	48,000	76,000
Year 2	10/01	9/02	40,000	70,000	110,000	40,000	70,000	110,000
Year 3	10/02	9/03	55,000	75,000	130,000	40,000	75,000	115,000
Year 4	10/1	12/31	7,000	12,000	19,000	4,000	112,000	116,000

Oak Ridge National Laboratory budget (all cost share shown in the UT budget).

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	1/01	9/01	130,000		130,000	130,000		130,000
Year 2	10/01	9/02	235,000		235,000	235,000		235,000
Year 3	10/02	9/03	235,000		235,000	235,000		235,000
Year 4	10/03	9/04	60,000		60,000	35,000		35,000

Improving Dryer and Press Efficiencies Through Combustion of Hydrocarbon Emissions

Banerjee: Institute of Paper Science and Technology

GO10620, CPS#01482

QUARTERLY PROGRESS REPORT

Project Title: Improving Dryer and Press Efficiencies Through Combustion of Hydrocarbon Emissions

Authors: Jennifer Cowan, Sujit Banerjee

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 16, 2004

Recipient: Institute of Paper Science and Technology

Award Number: DE-FC36-01GO10620

Other Partners: Lawrence Otwell, Georgia-Pacific; Ernie Hsu, Louisiana-Pacific; Ed Fouche, EPRI.

Contact: Sujit Banerjee (404) 894-9709; s.banerjee@ipst.edu

Project Objective: The objective of this project is to determine the feasibility of isolating dryer and press emissions in high-concentration low-volume streams, and to develop process changes to minimize the air volume that would need to be treated.

Background: Emission control devices on dryers and presses have been legislated into the industry, and are now an integral part of the drying system. The recommended device is the RTO (Regenerative Thermal Oxidation) unit, which is energy-intensive (natural gas) and has high operational and maintenance costs. Rather than focus on control devices, we plan to develop process changes that should minimize the need for controls. Where control devices will still be required, they will be smaller and will run more efficiently. The end result is expected to be a substantial decrease in natural gas use coupled with a reduction in capital cost.

Status:

- OSB panels with aspen flakes on the faces and pine in the core emit 90% less pinene in the press than all-pine panels.
- The concentrations of formaldehyde and methanol are reduced by 95 and 75%, respectively, when contacted with bask boiler ash in a fluidized bed. Best results are obtained with small ash particles and when the ash is slightly wet at about 3% MC.

Emissions from pine and aspen/pine OSB panels at different press times

OSB panels made of pine flakes or a mixture of aspen and pine flakes (aspen on faces, pine in core) were prepared and emissions were collected. Table 1 gives the panel preparation conditions. The panels were pressed in a closed caul through which compressed air was passed (5 psi). The emissions-laden air was directed through a reflux condenser and emissions were trapped in water or acetone. When water was used, two 500-mL Erlenmeyer flasks in series (each filled to about 200 mL) were connected to the outlet of the condenser to trap the emissions. The amount of emissions trapped in the second flask was less than 15% of the amount trapped in the first. The water-soluble emissions were analyzed for formaldehyde and methanol, by the acetylacetone method and by GC, respectively. With acetone, only one 500-mL flask with about 250 mL of acetone was used. The acetone-soluble emissions were analyzed by GC for α- and β-pinene. Two replicates of each panel were prepared.

Table 2 and Figures 1-3 show the average amounts of emissions that were collected. All emissions decrease significantly when the press time is reduced from 6 minutes to 3 minutes. The differences in emissions between panels pressed for 3 minutes and those pressed for 2.5 minutes are more subtle, but in some cases also significant.

Comparison of pine panels pressed at 2.5 and 3 minutes

For pine panels, about one-third less methanol is emitted from panels pressed for 2.5 minutes as compared to those pressed for 3 minutes (Figure 1). Average α-pinene emissions for all-pine panels are 36% less at the 2.5 minute press time versus the 3 minute press time, while the difference for β-pinene emissions is 30% (resulting in an overall reduction of total pinenes by 34%) (Figure 1). There is probably no difference between the formaldehyde emissions of pine panels pressed for 2.5 and 3 minutes.

Comparison of aspen/pine panels pressed at 2.5 and 3 minutes

Aspen/pine panels pressed for 2.5 minutes emit about half the methanol of those pressed for 3 minutes (Figure 2). Aspen/pine panels pressed for 3 and 2.5 minutes emit about the same amount of pinenes (Figure 2). The average formaldehyde emitted from aspen/pine panels pressed for 2.5 minutes appears to be greater than those for 3 minutes, but this surprising result may be due to the small sample size.

Table 1: Panel preparation conditions.	
Resin	GP120C92 (powder), 2% throughout
Wax	1% slack wax
Moisture content	6.5%
Panel size	16” x 16” x 3/4"
Press time	6, 3, or 2.5 min
Press temperature	400 °F
Ram pressure	115 tons

Table 2: Average emissions from pine and aspen/pine panels.						
		mg/kg panel (std. dev.)				
	press time (min)	**formal-dehyde**	**methanol**	**α-pinene**	**β-pinene**	**total pinenes**
pine panels (average values)	6	56 (2)	34.3 (3)	470 (9)	161 (7)	630 (16)
	3	11 (2)	16.8 (1)	270 (20)	117 (9)	380 (30)
	2.5	7 (2)	11 (4)	171 (6)	82 (10)	253 (16)
aspen/pine panels (average values)	6	60 (1)	35 (2)	168 (1)	57 (4)	225 (5)
	3	12 (1)	17 (2)	26.3[1]	10.5[1]	36.8[1]
	2.5	16.0 (0.4)	8.3 (0.1)	22.5 (7)	8 (4)	31(11)
[1]only one panel was analyzed.						

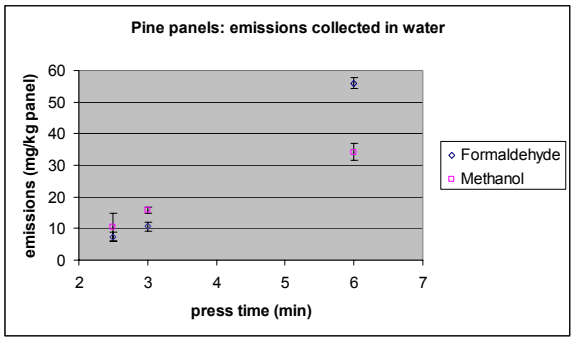
Comparisons between aspen/pine and all-pine panels

Comparing all-pine panels to aspen/pine panels, there is a large difference in the amount of pinenes emitted (Figure 3). Aspen/pine panels contain 50% by weight of each wood species, so if the temperature were uniform throughout the panel during pressing, one would expect pinene emissions of aspen/pine panels to be half that of all-pine panels. However, at both 2.5 and 3 minute press times, aspen/pine panels emit only about 10% of the pinenes emitted by all-pine panels at the same press times. This strongly indicates that the layer of aspen on the faces thermally shields the pine flakes from the press platens, leading to lower pinene emissions. At the 6 minute press time, aspen/pine panels emit 40% of the pinenes emitted by all-pine panels; however, this is a long press time which is not representative of typical mill conditions. Formaldehyde and methanol emissions at the same press times are similar, regardless of the panel construction.

Formaldehyde and methanol adsorption by ash in a fluidized bed

We have previously shown that ash containing a significant amount of carbon can adsorb formaldehyde from a low-flow (0.3 L/min) air stream. In those experiments, the ash was contained in a heated stainless steel column. In this project period we have measured the sorptive capacity of bark boiler ash using (a) a fluidized bed reactor that can accommodate higher flow rates, and (b) a bottle with a gas-permeable glass frit for lower-flow air streams.

Ash was obtained from a pulp mill (Bowater, Catawba, SC, bark burner) and several plywood mills (Georgia-Pacific Whiteville, NC, Skippers, VA, and Ahoskie, NC bark and sander dust burner). The ashes were analyzed for metals, silicon, and carbon as shown in Table 3. All but the Skippers sample contained a substantial fraction of organic carbon. The Skippers ash will be studied next to determine whether the presence of carbon is critical as indicated in our previous experiments.



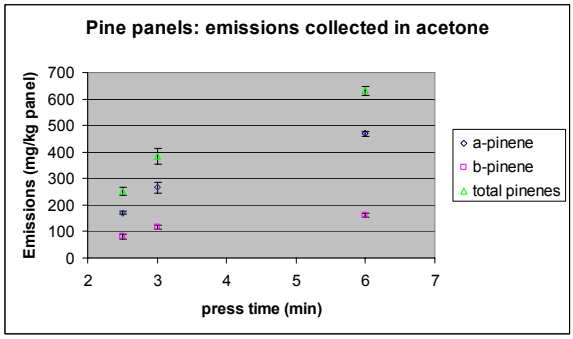
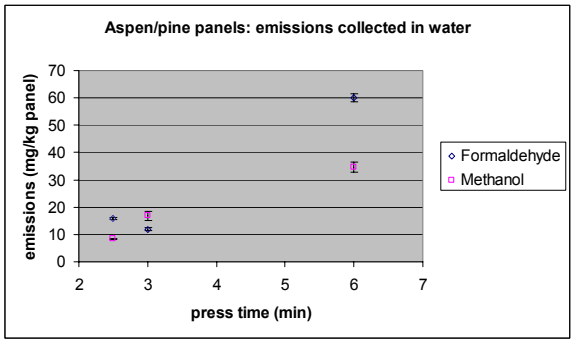


Figure 1: Water-soluble (left) and acetone-soluble emissions (right) from pine panels. Error bars represent one standard deviation.



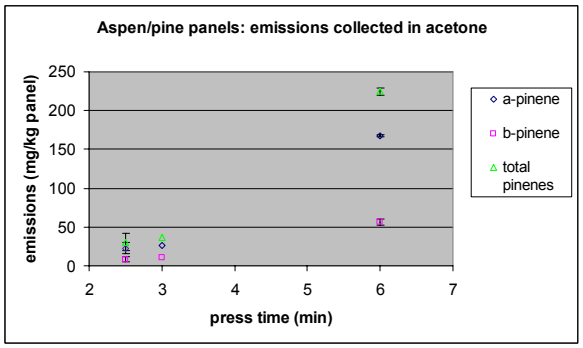


Figure 2: Water-soluble (left) and acetone-soluble emissions from aspen/pine (face/core) panels. Error bars represent one standard deviation (except for 3-minute figures, which are based on one panel).

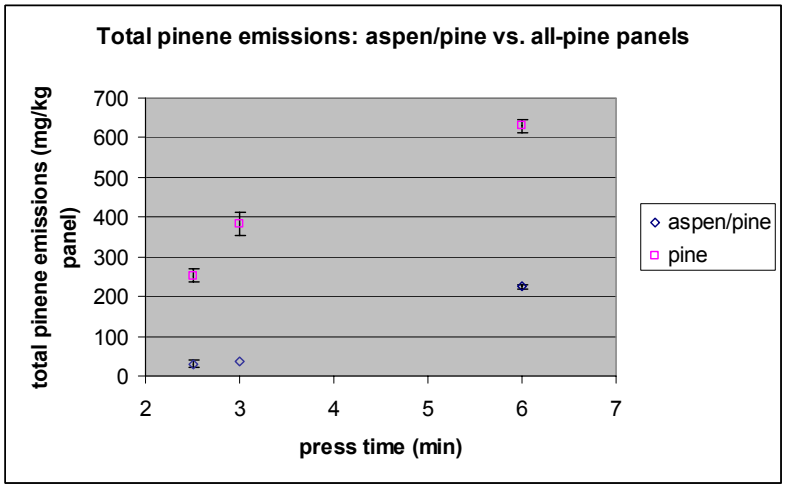


Figure 3: Comparison of total pinene emissions from aspen/pine and all-pine panels.

Table 3: Chemical analysis of ash.				
	Bowater	**Whiteville**	**Skippers**	**Ahoskie**
C (inorg., %)	0.42	3.38	0.55	0.54
C (org., %)	21.40	19.49	5.95	44.3
SiO2 (%)	53.6	16.8	51.0	21.1
Cr (mg/kg)	29.7	15.3	20.6	11.1
Mn (mg/kg)	687	1,840	4,240	1,430
Fe (mg/kg)	25,800	8,160	8,780	4,270
Co (mg/kg)	12.7	4.31	4.32	3.89
Ni (mg/kg)	26.9	10.7	14.9	7.30
Cu (mg/kg)	64.1	95.0	60.0	35.4
Zn (mg/kg)	1680	654	165	152
Al (mg/kg)	20000	18,400	14,500	8,580
B (mg/kg)	13.9	302	147	85.6
Si (mg/kg)	386	5,090	1720	1,650
P (mg/kg)	3,020	9,440	8,430	4,260
S (mg/kg)	1,590	2,340	2,180	653
Se (mg/kg)	74.4	73.3	73.5	66.2
As (mg/kg)	56.5	55.7	55.9	50.3
Mo (mg/kg)	10.5	10.4	10.4	9.36
Cd (mg/kg)	3.00	9.39	5.84	3.06
Sn (mg/kg)	28.7	28.3	28.4	25.6
Sb (mg/kg)	33.5	33.1	33.1	29.8
Pb (mg/kg)	75.4	35.2	35.3	31.8
Tl (mg/kg)	75.3	74.3	74.4	67.0
Sr(mg/kg)	232	236	514	113
Ba (mg/kg)	440	338	1200	276
Be (mg/kg)	2.73	0.134	0.135	0.121
Na (mg/kg)	757	26,700	13,200	964
Mg (mg/kg)	4,350	14,700	13,800	6,080
K (mg/kg)	4,060	12,200	25,400	10,600
Ca (mg/kg)	20,400	109,000	118,000	27,600
Ti (mg/kg)	712	806	1213	546
V (mg/kg)	64.5	11.5	14.0	7.51

Large-scale experiments

Ash was injected into a 1.5 liter fluidized sand bath and the exiting air was sampled and analyzed for formaldehyde and methanol by IR spectroscopy. The bath contains a porous ceramic plate that supports the ash, which is heated by a heating element inside the bath. Air fed through the plate fluidizes the ash. In order to prevent the very fine ash particles from escaping from the bath, a vacuum cleaner bag (Hoover type Z) was cut open and stretched over the top of the bath like the head of a drum as shown in Figure 4. The bag was secured to the fluidized bed with a large hose clamp. Formaldehyde and methanol were added to the airstream by passing air

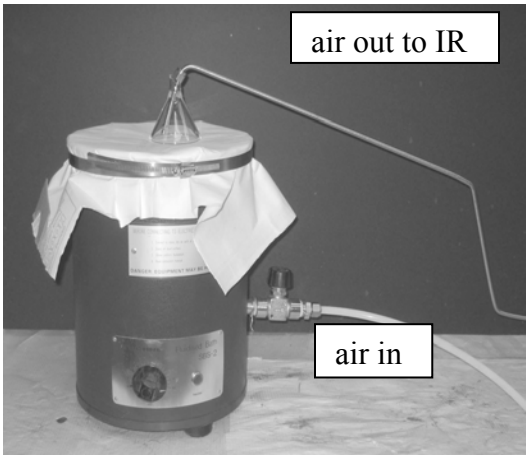


Figure 4: Photograph of the fluidized bed assembly.

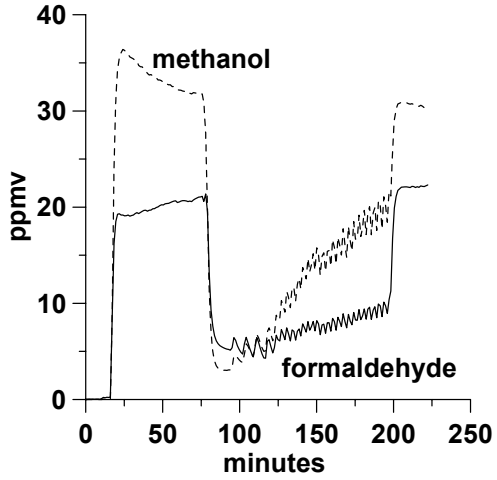


Figure 5: Concentrations of formaldehyde and methanol in an airstream passing through a fluidized bed of Bowater ash. The central dip reflects the contact period.

at 1 L/min through a gas washing bottle filled with a diluted solution of formalin. The dosed airstream was mixed with ambient air (35 L/min) in a mixing tee as it entered the fluidized bed. The flow rates of both air streams were monitored throughout,

In order to sample the air exiting the fluidized bed, a glass funnel was inverted atop the vacuum cleaner filter on the bed as shown in Figure 4. One end of a ¼" stainless steel pipe was inserted into the narrow end of the funnel, and the other end was connected to the IR cell using a pressure fitting. A vacuum was pulled on the IR cell to draw air through the pipe. The flow rate was about 2 L/min. This was initially performed without ash in the bed to determine the concentration of formaldehyde and methanol in the feed stream. The concentrations of formaldehyde and methanol in the feed were also determined by placing the end of the inlet tube inside a glass bottle and drawing the IR sample from inside the bottle. The two methods gave the same results, proving that the filter does not adsorb formaldehyde or methanol or otherwise impede airflow.

Figure 5 shows the IR data from a typical adsorption experiment. The flow rate through the bed was 35 L/min, and the amount of ash in the bed was 550 g. The temperature in the ash bed was ca. 110 °C. The central trace reflects the concentrations of formaldehyde and methanol in the air after contact with the ash. Passage through the ash bed reduced the concentrations of formaldehyde and methanol to 5-7 ppm for about 40 minutes, after which the concentration began to increase gradually. The sinusoidal shape of the curve is caused by the cycling on and off of the heating element. A similar trend is observed for methanol, except the initial concentration drop is greater and the rate of increase is faster.

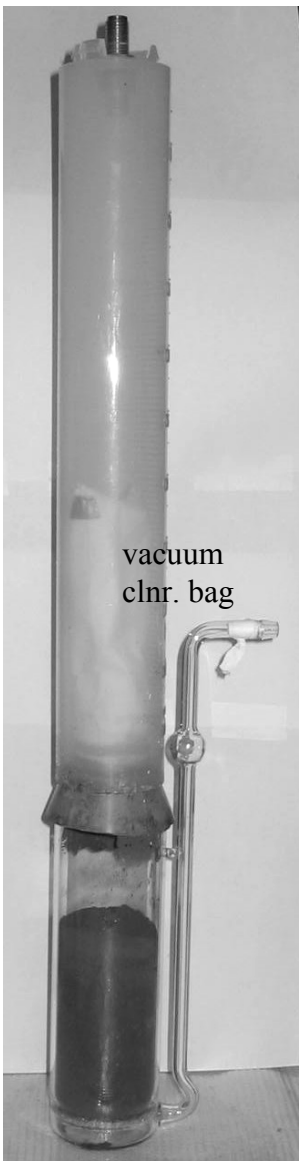


Figure 6: Gas washing bottle with ash.

Small-scale experiments

Owing to the large amount of ash necessary for the fluidized bath work, a gas washing bottle was also used for exploratory purposes. The ash was place on the fritted disk and air was passed through the disk. To prevent the ash escaping from the vessel, a vacuum cleaner bag was cut into a cylinder and placed over the neck of the vessel as shown in Figure 6. Stretching the vacuum bag paper over the top of the vessel as in the larger fluid bed setup did not provide enough surface area for filtration and led to pressure buildup. The air exiting the ash bed was trapped by placing a plastic cylinder over the filter and onto the shoulders of the vessel. A bulkhead fitting was installed in the top of the plastic cylinder, and a 1/4"' stainless steel pipe with pressure fittings was used to connect the cylinder to the IR cell.

Experiments at 1 L/min flow rate

At this flow rate, it was necessary to agitate the ash bed to prevent channeling. Agitation was provided by placing a vortex mixer beneath the ash bed, which was clamped to a ring stand and positioned in slight contact with the mixer. The ash was screened and placed in the glass cylinder atop the fritted disc. The bed was wrapped with heating tape and heated to 105 °C. Air was passed through a formalin solution in a gas washing bottle at 1 L/min, and the outlet was fed either to the IR cell directly (to obtain blank values before and after the adsorption experiment) or to the ash bed and then to the IR cell. The results of these experiments are summarized in Table 4. The best performance was obtained by ash with a moisture content of 3.2% that had been screened through a 60 mesh sieve (0.25 mm opening size). The results of this experiment are shown in Figure 7.

The concentration of formaldehyde decreased from 20 to 0.4 ppm, and methanol was reduced from 54 to 12 ppm. In addition, the formaldehyde level was maintained below 1 ppm for at least 4 hours. Methanol gradually increased during this time to 29 ppm. The best results with Bowater ash screened through an 18 mesh sieve (1.0 mm opening size) were obtained with 85 g of ash at 3.2% moisture. The formaldehyde concentration was lowered from 20 ppm to less than 2 ppm for 110 minutes, while the methanol concentration decreased from 52 ppm to 13 ppm at the beginning of the experiment, and gradually increased to 35 ppm over the same period. Dry ash (experiments 83 and 84), whether screened through 18 or 60 mesh sieves, is not able to decrease the concentration of formaldehyde to less than 3 ppm, although the adsorption of methanol may be initially a little better. A critical mass of ash may be also required for effective adsorption, as 50 g of ash (experiment 80) did not decrease the concentration of formaldehyde or methanol to the low levels observed in the other experiments where at least 75 g of ash were used. Ash from a different source, Georgia-Pacific's Whiteville, NC plywood mill, was also used in one of the experiments in this series. While the initial drop

Table 4: Experiments with Bowater ash at 1.0 L/min air flow and 105 °C ash bed.							
Expt. No.	Ash (g)	Airstream [HCHO] (ppm)	Airstream [MeOH] (ppm)	Minimum [HCHO] (ppm)	Minimum [MeOH] (ppm)	Ash moisture content (%)	Screen no.
80	50	40	100	6	50	3.2	18
82	85	20	52	0.9	13.3	3.2	18
83	75	22	48	3	10	Dry	18
84	85	20	54	3	8	Dry	60
85	85	21	54	0.4	12	3.2	60
86[1]	85	25	56	2	42	1.8	60

[1]ash for this experiment was from G-P Whiteville, NC

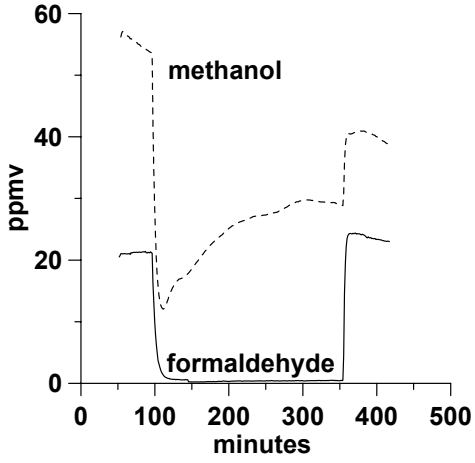


Figure 7. Adsorption of formaldehyde and methanol by Bowater ash. The central dip reflects the period when the air contacted the ash.

in formaldehyde concentration of the airstream upon contact with the ash bed was from 25 to 2 ppm, the concentration gradually increased to 7.3 ppm over 85 minutes. Performance may improve with a higher moisture content than the 1.8% used here.

We tentatively conclude that adsorption is inversely related to particle size, and that particles with moisture are better at adsorbing formaldehyde. Moisture could promote sorption of formaldehyde by dissolving the gas.

Experiments at 2 L/min flow rate

Several experiments have been performed at the 2 L/min flow rate. The higher flow rate causes the ash bed to remain fluidized without the need for external agitation. The data are summarized in Table 5. At 2 L/min, the ash is able to reduce the concentration of formaldehyde in the airstream to levels similar to those obtained at 1 L/min. However, thus far, none of the 2

Table 5: Adsorption experiments with Bowater ash at 2.0 L/min air flow and 105 ºC ash bed.						
Expt. No.	Ash (g)[1]	Feed [HCHO] (ppm)	Feed [MeOH] (ppm)	Minimum [HCHO] (ppm)	Minimum [MeOH] (ppm)	Ash moisture content (%)
95	80	19	25	4	8	3.2
97	100	19	42	2	No reduction	3.2
98	120	20	41	4	15	3.2
[1]screened through a 60 mesh sieve.						

L/min experiments has shown a reduction in formaldehyde to less than 1 ppm, as was demonstrated in a couple of cases at 1 L/min. In experiment 95, using 80 g of ash, the concentration of formaldehyde was maintained below 4 ppm for 110 minutes. In experiment 97, using 100 g of ash, the concentration of formaldehyde penetrating the ash bed was initially about 2 ppm, but gradually increased to 3 ppm over the first 20 minutes. This concentration was maintained over the next 50 minutes of the experiment. In experiment 98, using 120 g of ash, the concentration of formaldehyde dropped to about 4 ppm and then gradually increased in a fairly linear fashion over the next 215 minutes to about 13 ppm. Then for about the next hour, the concentration of formaldehyde penetrating the ash bed dipped to 12 ppm and remained there. As for methanol, while there was an initial dip in airstream concentration upon contact with the ash bed, in all cases the concentration rises rapidly.

While a higher flow rate presents a greater challenge for removing formaldehyde from the air stream to the very low levels required by EPA MACT regulations, the ash is still capable of substantially reducing the concentration of formaldehyde for relatively long time periods.

Plans for the Next Quarter:

- Complete larger-scale laboratory work on the use of ash and dry fines for HAPs reduction.
- Determine whether increasing moisture content of the ash improves adsorption. Study the desorption of formaldehyde and methanol to determine whether the ash is adsorbing or reacting with the substrates. Study the performance of the other ash samples.
- Complete pilot work on reducing press VOCs through sandwiching a softwood mat with hardwood.

Budget Data (as of 6.30.04)

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	1/1/01	12/31/01	111,507	156,940		46,106		
Year 2	1/1/02	12/31/02	212,949	56,940		98,300		
Year 3	1/1/03	12/31/03	235,227	56,940		171,903		
Year 4	1/1/04	12/31/04				124,857		
Totals			559,684	270,820		441,166	406,137	

ID Number	Task/Milestone Description	Planned Completion	Percent Completion	Actual Completion	Comments
1	Develop relationships between VOCs and the following dryer parameters:				
1.1	furnish temperature,	3.02	100	6.02	
1.2	geometry,	3.02	100	6.02	
1.3	moisture,	3.02	100	6.02	
1.4	dryer temperature,	3.02	100	6.02	
1.5	humidity	3.02	100	6.02	
2	Construct a model incorporating item 1				
2.1	statistical	3.03			
2.2	finite element	9.03			
3	Develop relationships between VOCs and the following pressing parameters:				
3.1	furnish temperature,	6.01	100	12.02	
3.2	geometry,	12.01	100	12.02	
3.3	moisture	12.01	100	12.02	
4	Construct a model incorporating item 3	6.02	100	12.02	
5	Collect field data on drying	12.02			
6	Collect field data on pressing	6.02	100	6.02	
7	Develop a relationship between drying practice and pressing performance	12.03	100	12.01	
8	Develop dryer and press redesigns	12.03			
9	Evaluate the performance of low-temperature catalysts for HAPs removal		100	6.02	added objectives
9.1	Evaluate the performance of ash for HAPs removal	12.03 3.05	100 40	3.03	
9.2	Evaluate the performance of wood dust for HAPs removal	6.04	100	12.03	
10	Develop & validate a model for veneer dryers	3.04	20		
11	VOCs from steam-injected pressing	6.04	60		added objective
12	Reduce press VOCs through sandwiching a SWD mat with HWD				added objective
12.1	lab work	6.04	100		
12.2	pilots	3.05	10		
13	Economic analysis	3.04			
14	Final report.	3.04			

Fast Curing of Composite Wood Products

Ragauskas: Institute of Paper Science and Technology

GO10625, CPS#01487

QUARTERLY PROGRESS REPORT

Project Title: Fast Curing of Composite Wood Products

Covering Period: April 1 – June 30, 2004

Date of Report: July 30, 2004

Recipient: Institute of Paper Science and Technology
500 10th St., NW, Atlanta, GA 30318

Award Number: DE-FC36-01G010625

Subcontractors: T.J. Elder, Auburn University, Auburn, AL
Recently re-located to USDA Laboratory
Southern Research Station, 2500 Shreveport Highway
Pineville, LA 71360

Other Partners: Georgia-Pacific Resins, Inc.
. Louisiana-Pacific Corporation
Weyerhaeuser OSB Business

Contact(s): Arthur J. Ragauskas, 404-894-9701, arthur.ragauskas@ipst.edu

Project Team: AF&PA Agenda 2020 Capital Effectiveness - Task Group, United States Department of Energy, Elmer H. Fleischman//INEEL/US

Project Objective:

The overall objective of this program is to develop low temperature curing technologies for UF and PF resins. This will be accomplished by:

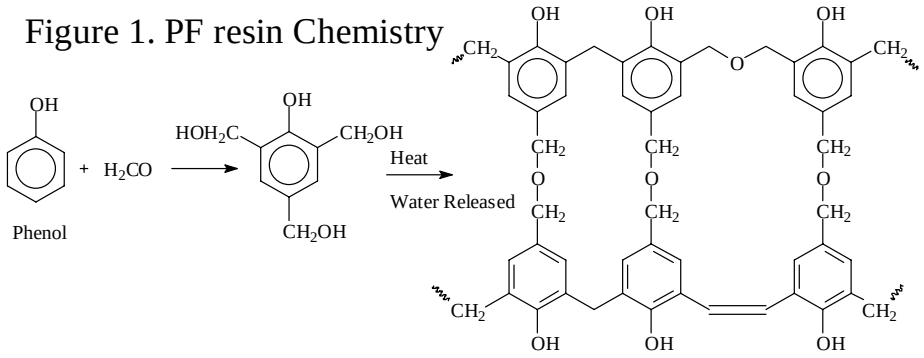
- Identifying the rate limiting UF and PF curing reactions for current market resins;
- Developing new catalysts to accelerate curing reactions at reduced press temperatures and times.

In summary, these new curing technologies will improve the strength properties of the composite wood products and minimize the detrimental effects of wood extractives on the final product while significantly reducing energy costs for wood composites. In turn, these results will provide US manufacturers a new competitive advantage in the production of composite wood products for the market.

Background:

The low cost and proven performance of urea-formaldehyde (UF) and phenol-formaldehyde (PF) resins have made them the most important adhesive systems for composite wood products such as, oriented strandboard (OSB), medium-density fiberboard (MDF), and particleboard (PB). Both UF and PF are most commonly applied to wood fibers, particles, and veneer as aqueous solutions. PF resins are manufactured from phenol and formaldehyde and have an affinity for wood surfaces. In the presence of sodium hydroxide and heat (215-235^{o}C), the PF resin polymerizes into a three-dimensionally crosslinked network thereby providing bonding. The overall chemistry of PF polymerization is summarized in Figure 1.

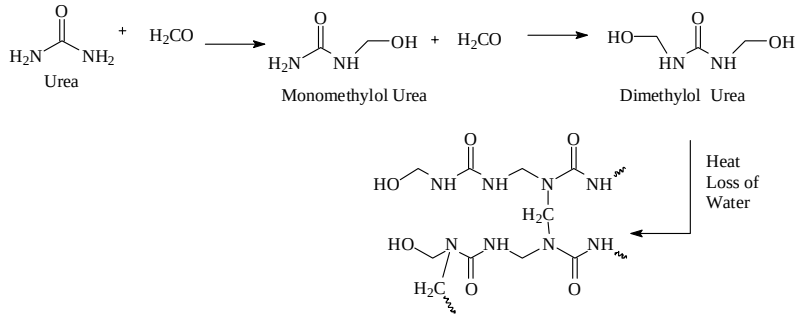
Figure 1. PF resin Chemistry



The curing chemistry can be accelerated using organic esters such as, proplyene carbonate, methyl formate or triacetin (i.e., α- and β-sets acceleration). These catalysts decrease press-time by a factor of 2 – 7. The inclusion of the ester accelerator also improves the I.B. strength for dry and boiling tests.

UF resins are prepared from urea and formaldehyde and are applied to wood fibers, particles, and flakes as an aqueous solution. These resins are the dominant adhesives for MDF and PB products. This resin has a natural affinity towards wood surfaces and in the presence of heat (190-225^{o}C) and an acidic catalyst (or hardener), UF condenses into a 3-dimensionally crosslinked network thereby providing bonding. The overall chemistry of UF polymerization for board production is summarized in Figure 2.

Figure 2. UF Curing Chemistry



The formulation of UF resins was initially accomplished using a two-stage alkaline/acid set of reactions. The use of acid catalysts has significantly improved the curing process providing improved curing rates and products. Neither UF nor PF resins are chemically attached to the wood fibers; instead, the adhesion is attributed to secondary bonding and/or physical bonding. The lack of chemical bonding to wood makes the physical performance of the cured

resins susceptible to the presence of extractives in wood. One of the main differences between PF and UF products lies in the water resistance of PF as opposed to UF.

In summary, UF and PF resins provide excellent bonding for the preparation of composite wood products. These products typically require curing temperatures of 215 -240^{o}C for 2 – 4 minutes of press time. The industry as a whole consumes approximately 40 trillion BTU/year in curing. It is known that the chemistry involved in the formation of OSB, MDF, or PB can be accelerated using catalysts. The goal of this project is the development of new curing catalysts designed to lower curing temperatures to 125 – 140^{o}C, with times of 0.5 – 1 minute that will reduce curing energy requirements by 40%. The chemistry of curing UF and PF resins can be uniquely determined using liquid and solid-state NMR. ^{13}C NMR techniques can define the exact structure of the cured resins and establish how catalysts can alter the chemical mechanisms involved in curing. For UF resins, ^{15}N NMR can be used in addition to ^{13}C NMR to define the polymerization chemistry occurring during curing. This project will employ these advanced analytical chemistry tools to develop and optimize the next generation of catalytic treatments that will accelerate UF and PF curing at lower temperatures, thereby providing US manufacturers a competitive advantage in the market place.

Status: Research Accomplishments over Past Quarter

Research Highlights

Research studies over the past quarter were directed at evaluating the overall benefits of the cure catalysts we have identified in this program. Laboratory studies were focused on a preparing UF PB boards at several lower temperatures and testing their physical properties.

Research Details:

Research efforts in this quarter have been directed at determining if the curing catalysts identified in this program could be successfully employed to reduce the energy requirements needed for formation of composite board formation. To accomplish this goal, the three most promising cure additives and control experiments (i.e., no-cure additives) were used to manufacture UF-particleboards at varying press temperatures of 200^{o}, 250^{o}, and 300^{o} F.

Our experimental procedure consisted of blending five kg of pine particles with 8% UF resin and 1% of paraffin wax (based on particle weight). This mixture was hand felted into a form box with aluminum cauls. Mat consolidation and curing were accomplished using a laboratory Carver hydraulic press. Two boards were prepared at each cure temperature and these were then conditioned and cut into test-boards for dimensional stability tests. The thickness swelling and water adsorption have been initiated and will be completed shortly. The results of these studies will determine the impact of cure additives at lowering cure temperatures will maintain physical properties.

The parameters for Particle boards manufacture were as follows;
1) Particles: Pine
2) Resin: UF
3) Moisture content: 9.7%
4) Mat dimension: 150 X 150 X 10(mm)
5) Mat formation: One layer
6) Target density: 700 cm/g3
7) Press temp: 200, 250, 300oF
8) Press pressure: 7,000 pounds
9) Hot press curing time: 5min
10) Resin content: PB-8% (based on oven dry wood particles)
11) Paraffin wax: 1%(based on oven dry wood particles)
12) Cure Additive Charge: 5% (based on resin solid content)
13) Replication: 2 boards

We have also continued to examine the curing chemistry of PF and UF resins in the presence of cure additives. This past quarter we examined the curing of PF and UF resins in the presence and absence of curing additives. Figure 3 provides an illustrative example of the data acquired to-date. This spectral date suggests that the cured UF and PF resins do not undergo any substantial change in the chemical structure in the presence of the cure additives studies to date. This further supports our hypothesis that these cure additives could be employed without significant process changes.

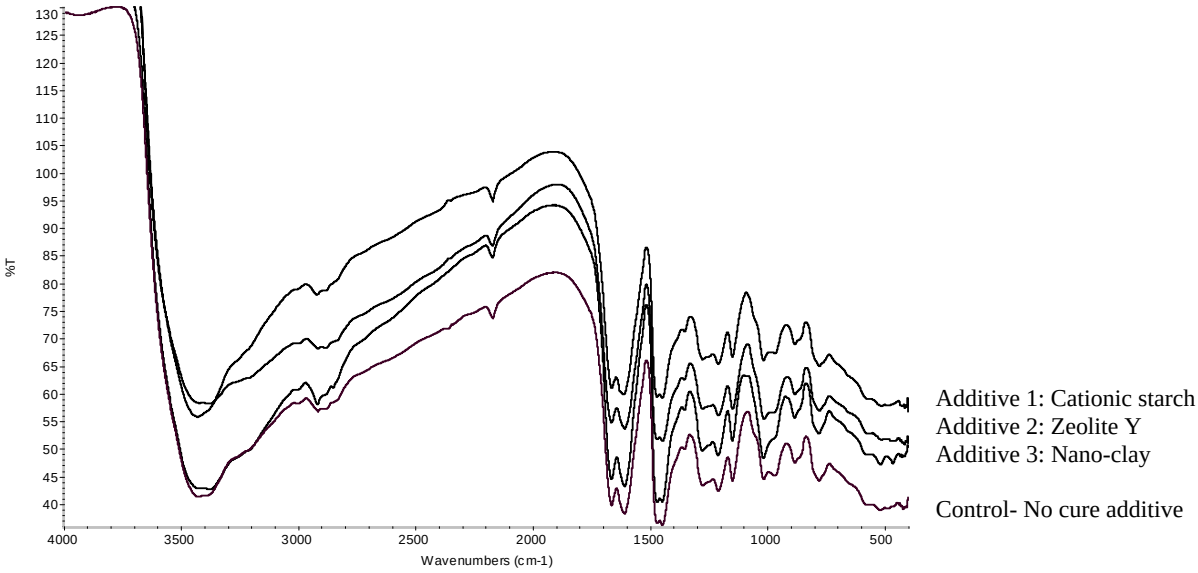


Figure 3. FT-IR stack plot of PF resin cured in the presence and absence of cure additives.

Plans for Next Quarter:

Research efforts this next quarter will be directed at Tasks 2.2.1 and 2.2.2. These two tasks and a final energy evaluation of the new curing catalyst will be the focus of the remaining research activities.

Industrial Reviews

A program review of research deliverables accomplished under this program is scheduled on August 3rd at Georgia-Pacific Resins, Inc., Decatur, GA 30035

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion**	Comments*
10625	Fast Curing of Composite Wood Products Recipient, PI	Fr 10/1/00 To 10/1/03		As of 9/30/00
1	Year 1			
1.1	Characterize SW and HW woodchips and prepare OSB, MDF, and PB board.	6/1/01	3/2002	Completed
1.1.1	Physical properties.	6/1/01	3/2002	Completed
1.1.2	NMR/DSC analyses.	8/1/01	3/2002	Completed
1.2	Evaluate impact of extractives on OSB, MDF, and PB board on physical properties.	10/1/01	3/2002	Completed
1.3	Determine curing chemistry of PF/MDI and UF for production of OSB, MDF, and PB, respectively.	10/1/02	12/2003	Completed
1.3.1	Examine impact on plate pressure and curing temperature.	10/1/01	3/2002	Completed
1.3.2	Establish effect of catalyst for UF and PF curing chemistry via NMR.	12/1/02	1/2004	Completed
	Year 1 report.	9/3/02	10/2002	Completed
2	Year 2			
2.1	Evaluate pretreatments to minimize detrimental impact of wood extractives on OSB, MDF, and PB.	8/1/02	11/2003	Completed
2.2	Test new catalyst technology for OSB, MDF, and PB production.	12/30/03	1/2004	Completed
2.2.1	Evaluate optimal curing chemistry at low temperature profiles.	6/1/03		Ongoing
2.2.2	Characterize physical properties of new, fast cured composite wood board.	8/1/03		Ongoing
2.3	Perform energy audit of new catalyzed OSB, MDF, and PB production techniques.	9/1/03		
	Final report.	10/1/03		

*initiation of the project was delayed due hiring issues** one year no-cost extension granted

Low VOC Drying of Lumber and Wood Panel Products

Banerjee: Institute of Paper Science and Technology

ID13439, CPS#00687

QUARTERLY PROGRESS REPORT

Project Title: Implementing Strategies for Drying and Pressing Wood Without Emissions Controls

Authors: Sujit Banerjee, Jennifer Cowan, Rallming Yang, Institute of Paper Science and Technology at Georgia Tech;
Paul Stiglbauer, Terry Conners, University of Kentucky

Covering Period: April 1, 2004 to June 30, 2004

Date of Report: July 16, 2004

Recipient: Institute of Paper Science and Technology

Award Number: DE-FCO7-96IDI3439

Other Partners: Lawrence Otwell (Georgia-Pacific), Ernie Hsu (Louisiana Pacific)

Contact: Sujit Banerjee (404) 894-9709; s.banerjee@ipst.edu

Project Objective: The objective of this project is to devise strategies for sizing down control devices needed for treating VOC emissions from dryers and presses for wood products such as OSB and veneer.

Background: Our previous work has brought us to the point where we can dry wood full-scale for brief periods without emissions controls. We now need to do this consistently and without adversely affecting throughput and production economics. Our first objective is to identify the mechanisms of release of some of these HAPs, to identify second-order variables that affect HAPs generation, and to develop and field-demonstrate a comprehensive strategy. Our second goal is to reduce resin use during pressing through droplet control. An ancillary goal is to determine the feasibility of applying urea as a fine mist to the mat in order to quench formaldehyde emissions.

Status:

- A trial at the Norbord, Guntown mill showed that a 26^{o} knife angle produces less variation than either 29 or 32^{o} knife angles. Fewer fines were generated from the 26^{o} knives and they did not appear to increase with the number of flaker strokes.
- Treating green flakes with a urea solution and then drying and pressing reduces press formaldehyde emissions by 45%.

Trials at Norbord, Guntown

An initial trial was conducted between April 23-25, 2004 at the Norbord OSB mill in Guntown, MS. The following conclusions were drawn:

- At a 32^o knife angle, the percentage of fines generated for small (< 5 inches diameter) and large logs is not significantly different.
- At a 29^o knife angle, the percentage of fines generated is significantly lower for large logs (4.8 percent versus 7.4 percent for small logs).
- Overall, logs processed utilizing a 29^o cutting angle display a lower fines generation (6.2 percent versus 8.7 percent for 32^o)
- Overall, large logs processed yielded a lower fines generation (6.9 versus 7.9 for small logs)

Flakes are transported from the flaker on a conveyor belt to another conveyor, which transports the flakes to collection bins. Samples were collected as the flakes dropped from the flaker outfeed conveyors. This location provided the most representative flake samples. This first trial demonstrated an increase in mean fines generation as flaker stroke increased. A stroke is defined as the cycle of a flaker progressing through a stack of logs and back to its starting point. However, the trial only ran for 600 flaker strokes. The mill changes flaker knives after 1,000 strokes. A follow-up trial was conducted during June 7-9, 2004 to determine the effects of knife angle on fines generated from a CAE disk flaker. Samples were collected every 50 flaker strokes from 50 to 1,000 strokes for each knife angle. Fines were defined as particles that passed through a 1/8-inch mesh screen. Three knife angles, 26, 29, and 32^o, were employed; the mill currently utilizes knives ground to 29^o. According to International Knife and Saw, flaker knife angles are normally honed between 29-32^o.

Knife angles

The first step of the analysis was to examine the effects of knife angles on mean fines generation. The 32^o study was limited to 600 strokes because the disk hit a hard object at that point causing the knives to be pushed back into the disk. The results, presented in the Appendix (Table A1) are summarized in Table 1. They are also illustrated in Figure 1, which shows that fines increase with increasing flake angle.

The following conclusions were drawn:

- the 26^o knife angle produces less variation than either the 29 or 32^o knife angles;
- fewer fines are generated from the 26^o knives and they do not appear to increase with the number of flaker strokes.

Table 1: Dependence of fines generation on knife angle.

knife angle	flaker strokes	percent fines (sd)
26	1,000	5.9 (1.6)
29	1,000	7.4 (2.6)
32	600	8.0 (3.2)

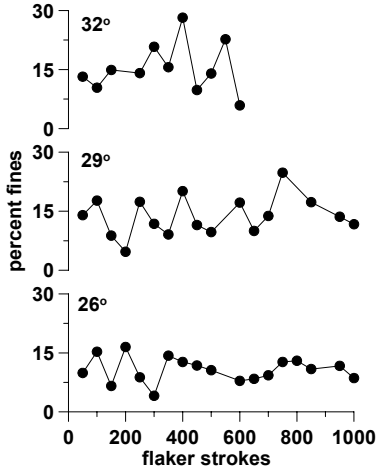


Figure 1: Fines generation at various knife angles.

Carmanah Design and Manufacturing Co.

Carmanah Design and Manufacturing Co. provided unpublished information regarding several factors that accelerate tool wear and increase fines production. One factor is the diameter of the log being chipped. Carmanah concluded that smaller diameter logs lead to an increase in fines generation. They also observed an increase in fines generation with an increase in flaker knife angle. Finally, they indicated that problems associated with feed systems may result in fines generation. This increase may result from feed systems not holding logs parallel as they are chipped.

International Knife and Saw

International Knife and Saw (IKS) supplies flaker knives to the Louisiana-Pacific (LP) in Athens, Georgia. IKS indicated that the LP knives were uncoated and had the following composition: 0.55 C, 1.20 W, 8.0 Cr, 1.25 Mo, 0.90 Si, and 0.30 percent Mn. Our analysis (XRF) gave: 0.5 C, 0.06 W, 7.87 Cr, 1.33 Mo, 0.93 Si and 0.40 Mn, V 0.4 and Ni 0.4%). IKS indicated that this composition was an industry standard.

Treating OSB flakes with urea for reducing formaldehyde emissions

We previously showed that treating dry flakes with a urea solution prior to pressing greatly reduced press formaldehyde emissions. However, as this adds water to the flakes it will probably not be feasible. We reasoned that treating green flakes with urea might be a better strategy, since these flakes would need to be dried anyway. Accordingly, measurements were made to determine whether formaldehyde released in the press would be reduced through such a approach.

Green flakes (ca. 50% MC) from G-P Dudley, NC, were soaked in either a 1.0 or 0.1 % urea solution for 1 minute. They were then dried in a 105 °C oven to 7% MC. Control flakes were dried similarly but were not urea-treated. Flake mats were prepared using 15 g of flakes and 2.5% GP 145C48 OSB core resin. The mat was carefully placed in an aluminum bag (6x12", McMaster) that had been modified to have an outlet tube and an inlet tube. After placing a strip of Teflon tape in the edge of the bag opening, the edge was folded twice and hammered flat. The bag was finally sealed by applying a strip of glass tape on the folded edge, as indicated in Figure 1. The outlet of the bag was connected to a fritted glass impinger, which was connected to a water aspirator. Before pressing, the water was turned on so that negative pressure was generated in the sealed aluminum bag. During hot pressing in our MTS press, the emissions were withdrawn from the bag and trapped in the impinger tube, which contained about 15 mL of chilled water. The flow rate of air withdrawn from the bag was 0.5 L per minute.

The mats were pressed at 156 psi for three minutes. The upper platen temperature was 210°C, while the bottom platen temperature was 110°C. After the press was opened, the water

aspirator was kept running for another three minutes. The formaldehyde trapped in the impinger was quantified by the chromotropic acid method (NIOSH Method 3500). The results are summarized in Table 2 and show that treatment with the 0.1 and 1% urea solutions decrease formaldehyde emissions by 20 and 46%, respectively.

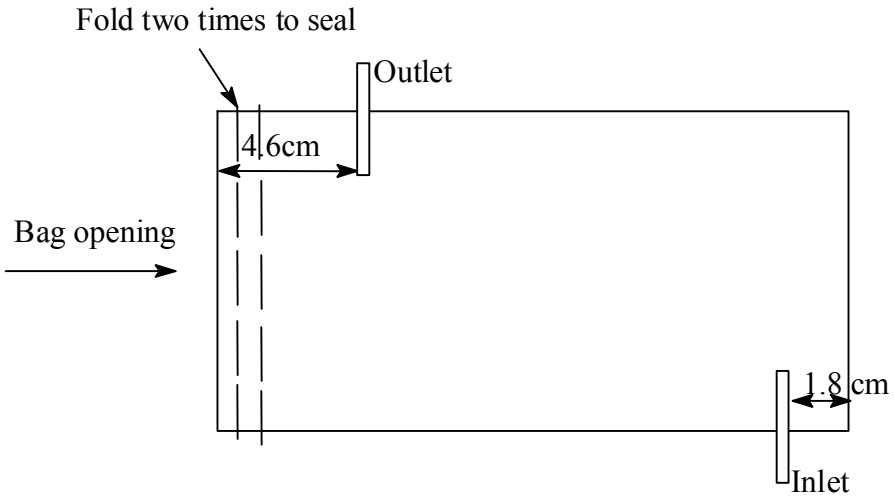


Figure1: Aluminum bag used for the press.

Table 2. Formaldehyde released from pressing urea-treated flakes.		
flake weight (g)	**urea (%)**	**formaldehyde (μg/g flake)**
15.23	0	43.2
15.20	0	45.3
15.17	0	46.3
	average	**44.9**
15.14	0.1	32.0
15.31	0.1	34.6
15.24	0.1	40.7
	average	**35.8**
15.24	1.0	18.6
15.20	1.0	24.8
15.31	1.0	29.9
	average	**24.4**

APPENDIX

Table A1: Fines generation at various flake angles.

ID	Angle	Stroke	Screen weight (g)							Percent	
			Total	7/8	5/8	3/8	1/4	1/8	Pan	Pan	Pan+1/8
29-1	29	50	771	590	11	33	29	50	58	7.5	14.0
29-2	29	100	1619	1099	33	96	104	158	130	8.0	17.7
29-3	29	150	1346	1171	14	20	24	41	77	5.8	8.8
29-4	29	200	1078	964	16	27	20	23	28	2.6	4.7
29-5	29	250	1055	761	17	48	46	87	97	9.2	17.4
29-6	29	300	1016	772	26	48	50	61	59	5.8	11.8
29-7	29	350	999	833	17	35	23	44	46	4.6	9.1
29-8	29	400	1230	796	34	84	69	101	146	11.9	20.1
29-9	29	450	1361	1144	12	23	26	51	106	7.8	11.5
29-10	29	500	1151	946	18	36	39	48	64	5.6	9.7
29-11	**29**	**550**	**998**	**949**	**7**	**9**	**9**	**8**	**18**		
29-12	29	600	1346	1001	13	42	59	106	125	9.3	17.2
29-13	29	650	1028	840	18	37	31	47	55	5.4	10.0
29-14	29	700	1079	813	30	47	41	71	78	7.2	13.8
29-15	29	750	1112	683	22	61	71	127	149	13.4	24.8
29-16	**29**	**800**	**867**	**727**	**10**	**29**	**24**	**31**	**47**		
29-17	29	850	1104	820	7	33	53	103	88	8.0	17.3
29-18	**29**	**900**	**1099**	**870**	**21**	**44**	**38**	**57**	**70**		
29-19	29	950	1356	1055	20	48	48	79	105	7.8	13.6
29-20	29	1000	1398	1141	14	34	45	79	85	6.1	11.7
32-1	32	50	928	720	8	41	36	61	62	6.7	13.2
32-2	32	100	1313	1070	20	44	43	69	67	5.1	10.4
32-3	32	150	851	516	19	34	41	63	63	7.4	14.9
32-4	**32**	**200**	**1075**	**812**	**8**	**28**	**25**	**45**	**54**		
32-5	32	250	1545	1091	23	50	55	106	112	7.3	14.1
32-6	32	300	1337	824	15	44	66	131	146	10.9	20.8
32-7	32	350	1302	908	14	37	38	91	112	8.6	15.6
32-8	32	400	1317	583	32	99	127	174	198	15.0	28.2
32-9	32	450	1461	1127	11	31	29	55	89	6.1	9.8
32-10	32	500	946	584	21	40	49	66	66	7.0	14.0
32-11	32	550	1181	620	22	76	95	147	122	10.3	22.7
32-12	32	600	1249	1003	11	24	27	31	42	3.4	5.9
26-1	26	50	1334	1025	13	29	34	61	71	5.3	9.9
26-2	26	100	1536	1040	19	51	80	111	124	8.1	15.3
26-3	26	150	995	764	6	17	17	34	32	3.3	6.6
26-4	26	200	1255	813	14	52	63	98	108	8.6	16.5
26-5	26	250	1080	824	13	21	21	40	55	5.1	8.8
26-6	26	300	977	805	4	9	6	16	25	2.5	4.1
26-7	26	350	1296	871	9	51	64	90	95	7.3	14.3
26-8	26	400	944	637	14	35	35	55	64	6.8	12.7
26-9	26	450	1069	757	17	31	27	53	73	6.8	11.8
26-10	26	500	970	711	8	22	25	44	59	6.1	10.6
26-11	**26**	**550**	**732**	**443**	**8**	**25**	**29**	**47**	**71**		
26-12	26	600	1365	1072	20	25	24	43	65	4.8	7.9
26-13	26	650	1179	911	14	28	26	37	62	5.3	8.4
26-14	26	700	1231	926	14	30	31	49	66	5.3	9.3
26-15	26	750	1506	1083	19	50	49	89	103	6.8	12.7
26-16	26	800	1029	698	15	37	38	60	74	7.2	13.0
26-17	26	850	1152	830	15	27	29	50	75	6.5	10.9
26-18	**26**	**900**	**1375**	**930**	**20**	**49**	**51**	**96**	**126**		
26-19	26	950	929	609	15	35	38	58	51	5.5	11.7
26-20	26	1000	1128	842	18	30	30	40	57	5.1	8.6

Plans for the Next Quarter:

- Run a trial at Norbord, Guntown, MS, to determine flaker efficiency in terms of fine production, study the effect of the predryer in HAPs reduction, and optimize biofilter performance.
- Measure the corrosion of flaker knives and study the effects of carbon coatings on fines reduction.

ID Number	Task/Milestone Description	Planned Completion	Percent Completion	Actual Completion	Comments
1	Identify factors that lead to HAPs generation during drying				
1.1	Lab work	4.04	20		
1.2	OSB mill trials (rotary dryers)	5.05	40		
1.3	Veneer mill trials	12.04	5		
1.4	OSB mill trials (conveyor dryers)		50		new objective
2	Integrate items identified above into strategies for reducing emissions during drying				
2.1	Lab work	8.04			
2.2	OSB mill trials	3.05			
2.3	Veneer mill trials	12.05			
2.4	Effect on product properties	12.04			
3	Extend above strategies to pressing OSB and veneer	10.04			
4	Reduce press HAPs by applying urea and resin as a fine aerosol				
4.1	Lab work with urea	12.03	30		
4.2	Lab work with resin	6.04			
4.3	Effect on product properties	12.04			
4.4	Pilots				
5	Studies on knife corrosion				new objective
4.1	Rate studies and characterization	3.05	20		
4.2	Application of coatings	6.05			
4.3	Field trials	9.05			
6	Economic analysis	2.06			
7	Final report	3.06			

Budget Data (as of 6.30.04)

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
	4/1/03	3/31/06				70,183		
Totals			1,998,007	651,059	2,649,066	1,316,714	406,138	1,722,852

Experimental Assessment of Low-Temperature Plasma Technologies for Treating VOC Emissions from Pulp Mills and Wood Products Plants

Fridman: University of Illinois - Chicago, ANL, PNNL

ID13868, GO14052, CPS#01151

DOE F 4600.6
(10-94)
Replaces EIA-459F
All Other Editions Are Obsolete

U.S. Department of Energy

OMB Control No.
1910-0400

FEDERAL ASSISTANCE PROGRAM/PROJECT STATUS REPORT

OMB Burden Disclosure Statement

1. Program/Project Identification No.	2. Program/Project Title	3. Reporting Period
DE-FC36-04GO14052/A000	Plasma Pilot Test for Treating VOC Emissions from Wood Products Plants	04/01/04 to 06/30/04

4. Name and Address

Prof. Alexander A. Fridman 215-895-1542 fridman@drexel.edu

Prof. Alexander Gutsol 215-895-1485 gutsol@drexel.edu

5. Program/Project Start Date
01/01/2004

6. Completion Date
03/01/2005

7. Approach Changes

At Georgia-Pacific's direction, the Drexel project team has identified a major vendor of environmental-control technology to lead the commercialization effort. This company, Met-Pro Corporation, is proposing to build a "pre-commercial", low-temperature plasma in the beginning of 2005. This unit would be capable of processing 12,500 standard cubic feet of gaseous emissions per minute but, in order to meet this objective, the Pilot Plant demonstration needs to be conducted within nearest months. Georgia-Pacific wants to conduct the demonstration at a wood products plant on the OSB Vent Stream at Brookneal, VA.

8. Performance Variances, Accomplishments, or Problems

Some modifications were made for the pulsed-corona pilot plant for the demonstration at a wood products plant.

9. Open Items

Time of the demonstration.

10. Status Assessment and Forecast

Drexel and their industrial partners are prepared to move forward with the demonstration upon receiving permission for the demonstration at a wood products plant. Meanwhile, Georgia-Pacific is evaluating a hybrid environmental-control process for paper mills. This concept would use the low-temperature plasma technology in conjunction with another emission-control technology.

11. Description of Attachments
Quarterly Progress Report

12. Signature of Recipient and Date	13. Signature of U.S. Department of Energy (DOE) Reviewing Representative and Date

Quarterly Progress Report

For: Plasma Pilot Plant Test for Treating VOC Emissions from Wood Products Plants

Covering Period: 04/01/04 to 06/30/04
Date of Report: 07/27/04

Recipient: Drexel University
Award Number: DE-FG36-04GO14052/A000

Subcontractors: ECOS, Ltd., Kurchatov Institute, Moscow, Russia

Other Partners: Georgia Pacific, Corp. ($20,000 cash support and $150,000 in-kind support)
ECOS, Ltd. ($60,000 in-kind support)

Contact: Prof. Alexander Gutsol 215-895-1485 gutsol@drexel.edu
Prof. Alexander A. Fridman 215-895-1542 afridman@drexel.edu

Project Objective: The objective of this project is to test the Plasma Pilot Plant capabilities in wood industry. The final goal of the project is to replace the current state-of-the-art, regenerative thermal oxidation (RTO) technology by Low-Temperature Plasma Technology (LTPT) in paper and wood industry for VOC destruction in HVLC vent emissions.

Background: The forest products industry is coming under increasing pressure from the US Environmental Protection Agency as well as state and local agencies to control VOC emissions from pulp mills and wood products plants. Currently available VOC-control technologies, such as regenerative thermal oxidizers, are energy intensive, combustion-based technologies that are expensive to build and operate. Low-temperature, nonequilibrium plasmas (also called "non-thermal" plasmas) are an emerging technology for VOC-emission control. The principal advantage of these nonequilibrium plasmas is that the majority of the process energy goes into the production of highly energetic, VOC-destroying species and *not* into heating the gaseous stream, as is the case with combustion-type technologies.

In a previous study sponsored by DOE and NCASI (National Council for Air and Stream Improvements of the woods products industry), four low-temperature plasma technologies were identified — electron-beam, gliding-arc, gas-phase corona reactor (GPCR), and pulsed corona— which appear to have both lower capital costs and operating costs than the incineration-type process currently available. In discussions with the wood products industry, there were selected two process emissions for demonstration — HVLC Brownstock Washer Vent Emissions and Oriented Strandboard (OSB) Press Vent Emissions — and a third for just a laboratory evaluation — OSB Dryer Vent Emissions.

Under the DOE Office of Industrial Technologies, Forest Products program, four plasma technologies were evaluated under project DE-FC07-00ID13868 "Experimental Assessment of Low-Temperature Plasma Technologies for Treating Volatile Organic Compound Emissions from Pulp Mills and Wood Products Plants". This project was conducted by the team that included University of Illinois at Chicago (UIC); Argonne National Laboratory (ANL); Pacific Northwest National Laboratory (PNNL);

Georgia-Pacific Corporation (G-P); Ecos. Ltd., Kurchatov Institute of Atomic Energy, Moscow, Russia (KI); and Drexel University (DU). On the last stage of the project the trailored pulsed corona pilot plant was developed at Drexel University and prepared for the test at Georgia-Pacific Port Hudson mill in Zachary, Louisiana. The test supposed to be done at HVLC Brownstock Washer Vent system. As due to different reasons the pilot plant was prepared for the test with significant delay, G-P rearranged their priorities in Low-Temperature Plasma Technologies (LTPT) commercialization and put on the first place a field test and commercialization of the technology for OSB press vent emission. As this test demanded some modification of the technology and the Pilot Plant itself, this new project "Plasma Pilot Plant Test for Treating VOC Emissions from Wood Products Plants" was initiated. This project is conducted by Drexel University in cooperation with G-P and KI.

Status: G-P supposes to spend significant funs for the field test, and announced the following demands that should be satisfied before the test:

1. A commercialization team should be developed and it should have realistic commercialization plan.
2. Intellectual Property (IP) and commercialization right issues should be clarified between the team members.
3. The team should include a major vendor with well known name in the environmental control business.
4. The technology should be evaluated by the "third party" before the field test.

That is why the main efforts were spent to reach the following:

1. After couple of iterations the potential major vendor was found. This is Met-Pro Corporation, a well-known company in the environmental control business. G-P confirmed that Met-Pro can be considered as a major vendor.
2. Several tests of the Pilot Plant were run at Drexel University to demonstrate technology to Met-Pro Corporation. Met-Pro Corporation was satisfied by the results of the tests and is ready to lead the commercialization efforts.
3. As a result of the Pilot Plant tests and modifications at Drexel University two new invention disclosures were made and now two provisional patent applications are preparing by patent attorneys.
4. Mutual three-side agreement between Met-Pro Corporation, Drexel University and University of Illinois at Chicago was prepared and it is under consideration of authorities of the parties now.
5. All data about the Pilot Plant tests were made available to Concurrent Technology Corporation (CTC), the company selected by DOE as a "third party" evaluator. Now CTC is in the process of making the evaluation.
6. During the meeting with G-P representative (Mr. Lawrence Otwell), the commercialization plan was discussed. The Plan Include the following steps:

a) Field Test at G-P facility at Brookneal, VA;

b) Full-cycle one-year demonstration experiment with plasma power on the level of 100 kW. As this demonstration experiment will be relatively expansive, that the cost of the experiment will be shared by G-P, DOE, a major vendor and sub-vendors. That is why the appropriate proposal should be prepared and sent to DOE next quarter.

c) In the case of successful demonstration experiment, the prime vendor should supply about 7 full size systems in years 2006-2008.

Meanwhile some technical modifications and improvements are in the progress:

The oil-catching tanks were designed and ordered. The system of oil cooling and recirculation was installed to prevent overheating of the high voltage transformers. Matching between the power supply and pulsed corona was improved and the power of the corona system was increased. After a year of the pilot plant in use some problems appears in the control system cooling: water temperature during

summer is not low enough to run long experiments with full power. Resolution of this problem is in progress.

Plans for Next Quarter: Drexel will be finalizing intellectual property agreements between UIC, Drexel, and Met-Pro Corporation. We expect to get positive evaluation from CTC, get permission from G-P for the field test, and to start the test. As it was mentioned above the team is going to submit proposal to DOE with request to support commercialization efforts regarding the Low-Temperature Plasma Technology for HVLC gas stream cleaning in paper and wood industry.

Budget Data: The following table summarizes project spending up to June 30, 2004.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	01/04	03/05	$100,000	$271,783	$371,783	$51,263	$61,478	$112,741
Drexel			$100,000	$41,783	$141,783	$51,263	$17,907	$69,170
Ecos(KI)				$60,000	$60,000		$23,571	$23,571
G-P				$170,000	$170,000		$20,000	$20,000

VOC and HAP Recovery Using Ionic Liquids

Milota: Oregon State University

ID14432, CPS#01873

Quarterly Progress Report

Project Title: VOC and HAP Recovery Using Ionic Liquids

Covering Period: Mar. 31 - June 30, 2004

Date of Report: July 29, 2004

Recipient: Oregon State University
Award Number: DE-FC07-03ID14432

Working Partners: Weyerhaeuser, Inc., Federal Way, WA; Louisiana Pacific Corp., Portland, OR; Boise Cascade Corp., Boise ID.

Cost-Sharing Partners: Weyerhaeuser, Inc., Federal Way, WA; Louisiana Pacific Corp., Portland, OR; Boise Cascade Corp., Boise ID.

Contact: Michael R. Milota, (541) 737-4210, Mike.Milota@OregonState.edu
Kaichang Li, (541) 737-8421, Kaichang.Li@OregonState.edu
Department of Wood Science and Engineering
119 Richardson Hall
Oregon State University
Corvallis, OR 97331-5751

Project Team: Jim Alkire, IRT / DOE Golden Field Office
Elmer Fleischman, Idaho National Engineering Laboratory

Project Objective: Synthesize RTILs and optimize their chemical structures for a VOC/HAP absorption process. Evaluate of the solubility and removal of VOC compounds in the synthesized RTILs and determine other chemical and physical properties important for absorption. Construct a continuous prototype absorption system using the RTIL most suited for VOC removal. Using the prototype, determine the ability of the RTIL to clean exhaust during long-term trials on wood dryer and press exhaust.

Background: During the manufacture of wood composites, paper, and to a lesser extent, lumber, large amounts of volatile organic compounds (VOCs) such as terpenes, formaldehyde, and methanol are emitted to air. Some compounds are also hazardous air pollutants (HAPs). The air pollutants produced in the forest products industry are difficult to manage because the concentrations are very low. Presently, thermal oxidizers (TOs) are commonly used for the destruction of VOCs and HAPs. TOs consume large amounts of natural gas to heat air and moisture. The combustion of natural gas generates increased CO_2 and NO_x, which have negative implications for global warming and air quality.

Many shortcomings of TOs and other control technology are addressed by an absorption system containing a room-temperature ionic liquid (RTIL) as an absorbent. RTILs are salts, but are in the liquid state at room temperature. RTILs, an emerging technology, are receiving much attention as replacements for organic solvents in industrial processes with

significant cost and environmental benefits. Some of these processes include organic synthesis, extraction, and metal deposition. RTILs would be a excellent absorbents for exhausts from wood products facilities because of their unique properties: no measurable vapor pressure, high solubility of wide range of organic compounds, thermal stability to 200ϛC, and immiscible with water.

Preliminary results at OSU reveal that fatty acids and resins could dissolve in RTILs, although the solubility has yet to be quantified. A phase separation between a fatty acid and a RTIL was seen when a large amount of fatty acids was added to a RTIL.

Status: We have determined that methanol and alpha-pinene can be absorbed into 1-octyl-3-methyl-imidazolium hexafluorophosphate, 1-hexyl-3-methyl-imidazolium hexafluorophosphate, 1-butyl-3-methyl-imidazolium hexafluorophosphate, and 1-butyl-3-methyl-imidazolium tetrafluoroborate. More importantly, the methanol could be removed from the ionic liquids by use of vacuum. We were having a problem in the previous quarter removing alpha-pinene; however, during this quarter this was resolved with additional heat. Recylability is a key to being able to recycle the ionic liquid in industrial pollution control equipment.

To date we have been unable to replace the student that left in October. This absence has caused us to fall behind our work plan. We have hired a full-time research assistant to work half-time on this project. He will start in early July. He has good lab skills and has come up to speed over the past few weeks. We are currently advertising (interviewing on July 30) for a second full time RA to work half-time on this project to do organic synthesis. With the addition of these two employees, we will bring ourselves back on schedule over the next six months.

Plans for Next Quarter: Early in the sixth quarter, we will have two phosphomium-based ionic liquid available for testing – tetradecyl(trihexyl)phosphonium decanoate and tetradecyl(trihexyl)phosphonium bus-2,4,4-(trimethylpentyl)phosphinate.. These are reported to be more stable than the imidazolium-based structures. As the secone RA comes on board, we will synthesize and test additional ionic liquids in this class. We will also continue to design and construct a continuous device in which the ionic liquid is recycled this is 95% designed and initial orders for parts have been placed.

Patents: None
Publications / Presentations: None

Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	SPME / GC Calibration	06/30/03	10/15/03		100%	
2	Method for making standards	06/31/03	8/30/03	12/31/03	100%	
3	Method for testing equilibrium	08/30/03	10/20/03		100%	
4	Ionic liquids	12/31/03			60%	6 of 12 done
5	Equilibrium testing	12/31/03			50%	4 of 12 done
6	Test ability to clean ionic liquid	03/31/04		6/30/04	100%	

Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
7	Construct lab device for continuous testing	3/31/04	10/31/04		15%	
8	Test continuous device on lab exhaust		11/30/04		0%	
9	Test continuous device on mill exhaust		01-31-05		0%	

Current Budget Period: 04/01/03 to 03/31/04

Spending Schedule

Current Quarter: 01/01/04 to 03/31/04

Budget Category	Approved Budget	Project Expenditures This Quarter	Project Expenditures Cumulative to Date
Personnel	23,783	6511	32485
Fringe Benefits	3,256	902	15017
Travel	3,100	688	969
Equipment			
Supplies	11,700	2447	9387
Contractual			
Construction			
Other	15,358	3713	
Total Direct Charges	57,197	13261	57858
Indirect Charges	10,774	4377	19330
Total	67,971	17638	77188
DOE Share	43,291		
Cost Share	24,680		

Cost Share Contributions

Funding Source	Approved Cost Share		This Quarter		Cumulative to Date	
	Cash	In-Kind	Cash	In-Kind	Cash	In-Kind
Weyerhaeuser	10880	2300	15000	0	15000	0
Louisiana Pacific	5000	4000	5000	0	5000	0
Boise Cascade	0	2500	0	0	0	0
Total	15880	8800	0	0	20000	0
Cumulative Cost Share Contributions						

An Innovative Titania-Activated Carbon System for Removal of VOCs and HAPs ... with In-Situ Regeneration Capabilities

Mazyck: University of Florida

ID14437, CPS#01874

PROJECT INFORMATION & PLANNING REPORT

Project Title: An Innovative Titania-Activated Carbon System for Removal of VOC's & HAP's from Pulp, Paper, Paperboard Mills, and Wood Products Facilities with In-Situ Regeneration Capabilities

Covering Period May 1, 2004 through July 31, 2004

Date of Report: July 31, 2004

Recipient:
University of Florida
PO Box 116450 Gainesville, FL 32611
5th Congressional District

Award Number: DE-FC36-03ID14437

Subcontractors:
MicroEnergy Systems, Inc.
300 Industrial Drive Oakland, MD 21550
Rick Sheahan
(301) 334-3455
6th Congressional District.

National Council for Air and Stream Improvement
PO Box 141020 Gainesville, FL 32614
Ashok Jain
(352) 377-4708
5th Congressional District

Other Partners: None

Contact(s):
David W. Mazyck, (352) 846-1039, dmazyck@ufl.edu
Angela Lindner, (352) 846-3033, alind@eng.ufl.edu
CY Wu, (352) 392-0845, cywu@ufl.edu

Project Team:
Joe Springer (Project Manager), Golden Field Office
DOE/GO Project Officer
1617 Cole Boulevard, Bldg 17/2
Golden, CO 80401
Tel: 303-275-4758/1-800-644-6735, ext. 4758
Fax: 303-275-4753

Project Objective: The goal of the proposed work is to develop a cost-effective and reliable air pollution control system to remove VOCs (volatile organic compounds) and HAPs (hazardous air pollutants) in emissions from pulp, paper and paperboard mills, and solid wood products facilities. The focus of our proposed control system is a novel composite material of activated carbon coated with a photocatalyst titanium dioxide (TiO_2), herein referred to as TiO_2-coated activated carbon.

Background: Forest products provide essential resources for human civilization, including energy and materials. Compared to fossil fuels, such as coal and oil, the resources from forest products are more sustainable and diverse. In processing forest products, however, unwanted by-products, such as VOCs and HAPs, are generated. Effective control of these emissions is of seminal importance to the continuing development of the forest product industry.

Currently thermal oxidation is the most commonly applied technique for the control of VOC and HAP emissions from the forest products industry sources. While effective, these measures require a constant fuel supply to support the thermal energy requirements. Considering its operating cost involving intensive resources and the formation of NOx, thermal oxidation is not favorable in the long run. In certain facilities, the gas stream is directed to a boiler for treatment. Although the fuel cost is reduced in comparison to thermal oxidation technologies, the transport of the gas stream and the ductwork building is still costly. Hence, a cost-effective technique for in-situ treatment of these pollutants is needed.

Status: Sixth quarter activity focused on a pilot-scale trial with the TIO_2-AC at MicroEnergy Systems, Inc., bench scale evaluation of the titania-activated carbon composites, and further development and testing of the silica-titania composites. In addition, LCA data collection continued and the investigation of microbial degradation of methanol commenced.

1. Pore Volume Impregnation (TiO_2-AC)

In this reporting period, a series of experiments were conducted to measure the effect of hydrolysis conditions on TiO_2 phase transformation (i.e., anatase vs. amorphous). TiO_2-AC composites were prepared by pore volume impregnation. Approximately 3.5 g of Bionuchar 120 was filled with 5 mL of a 20% by vol. TTIP 2-propanol solution. The volume of TTIP solution was equal to the pore volume of the activated carbon. Next, the carbon saturated with the TTIP solution was placed in a hydrolysis reactor (Fig. 1). Air saturated with water from a water bubbler passed through the reactor at the rate of 0.75 L/min for 2 hours. The residence time was 0.8s. The temperature of the water bubble bottle and the temperature of the reactor were controlled by a hot plate and heating tape wrapped around the reactor, respectively. After hydrolysis, the samples were dried at 100 ^{o}C for 4 hours to evaporate the adsorbed 2-propanol followed by calcination at 300 ^{o}C for 2 hours in air.

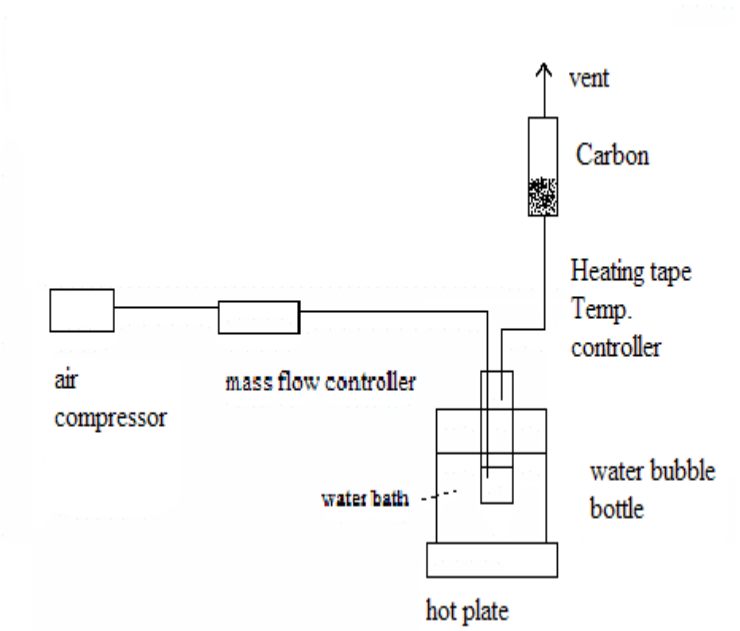


Fig. 1 Schematic of the Hydrolysis Reactor Set Up

In order to investigate the effect of hydrolysis temperature and the effect of water vapor concentration, four different hydrolysis conditions were used (Table 1). For convenience, notations in the first column are used to present different samples. The first number stands for the temperature of the water bath which is in proportion to the water concentration in the air flow; the second number represents the temperature of the reactor; the third number represents the time of hydrolysis. The specific surface areas of samples after calcination are also listed in Table 1.

Table 1 Hydrolysis Conditions and Surface Area

Sample	Water Bath Temp (^{o}C)	Hydrolysis Temp. (^{o}C)	Hydrolysis Time (hour)	Surface Area (m^2/g)
25-25-2	25	25	2	1113
25-90-2	25	90	2	1140
25-175-2	25	175	2	1018
90-90-2	90	90	2	1365

Compared with the specific surface area of the virgin Bionuchar 120, 1472 m^2/g, the specific surface area for each of the coated carbons decreased. However, the specific surface area of

90-90-2 was 1365 m^2/g, which is much higher than that of the other two samples perhaps indicating a different coating morphology.

The surface morphology of TiO_2-AC samples was characterized by SEM (JSM6330F, JEOL). The working distance was 15 mm and the voltage was 15 KV. Fig. 2 shows the SEM photo of 25-175-2. The photo reveals that TiO_2 formed a particulate film on the surface of the carbon. Fig. 3 is the SEM photo of 90-90-2. The photo shows that TiO_2 formed a solid film on the surface of the carbon. The difference between these results demonstrates that the hydrolysis condition influences the morphology of the TiO_2 on the carbon and possibly the subsequent photocatalytic performance.

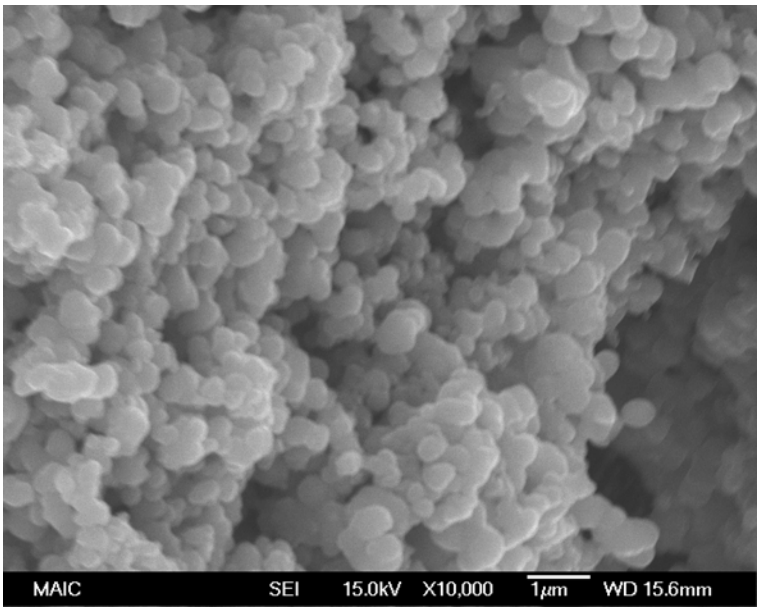


Fig. 2 SEM Photo of Sample 25-175-2

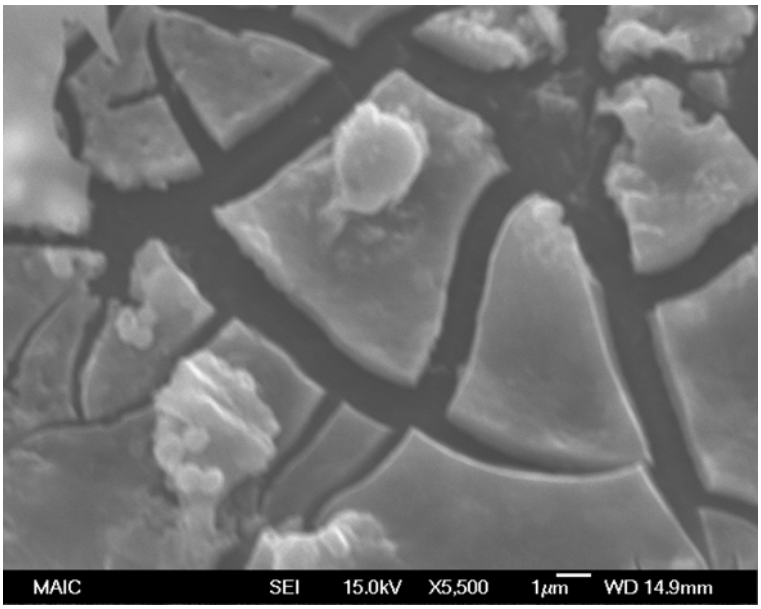


Fig. 3 SEM photo of sample 90-90-2

In addition to SEM analyses, the samples were also analyzed by X-ray diffraction (XRD 3720, Philips) for identification of crystalline species in the continuous-scan mode. The scanning speed was 0.005 ^{o}/sec and the scanning range was 20-50 ^{o}. Fig. 4 shows the XRD patterns of samples prepared under different hydrolysis conditions. Comparing the XRD patterns of 25-25-2, 25-90-2, and 25-175-2, it is clear that the anatase phase was favored at higher hydrolysis temperatures. At the higher temperatures, the diffusivity and collision rate of water vapor and TTIP is high. Therefore, the hydrolysis reaction rate is faster than that at lower temperatures. According to Kim et al. (2000), when the water concentration during hydrolysis reaction is small, large amounts of unhydrolyzed alkyls remained in the powder. These alkyls prevented crystallization to anatase; so the TiO_2 was amorphous. Therefore, when the water concentration was higher (90-90-2), the major anatase (101) peak at $2\theta = 25.4^{o}$ was higher than that of 25-90-2. Before calcination, there is no anatase peak on the XRD pattern, which illustrates that calcination is necessary for getting anatase TiO_2.

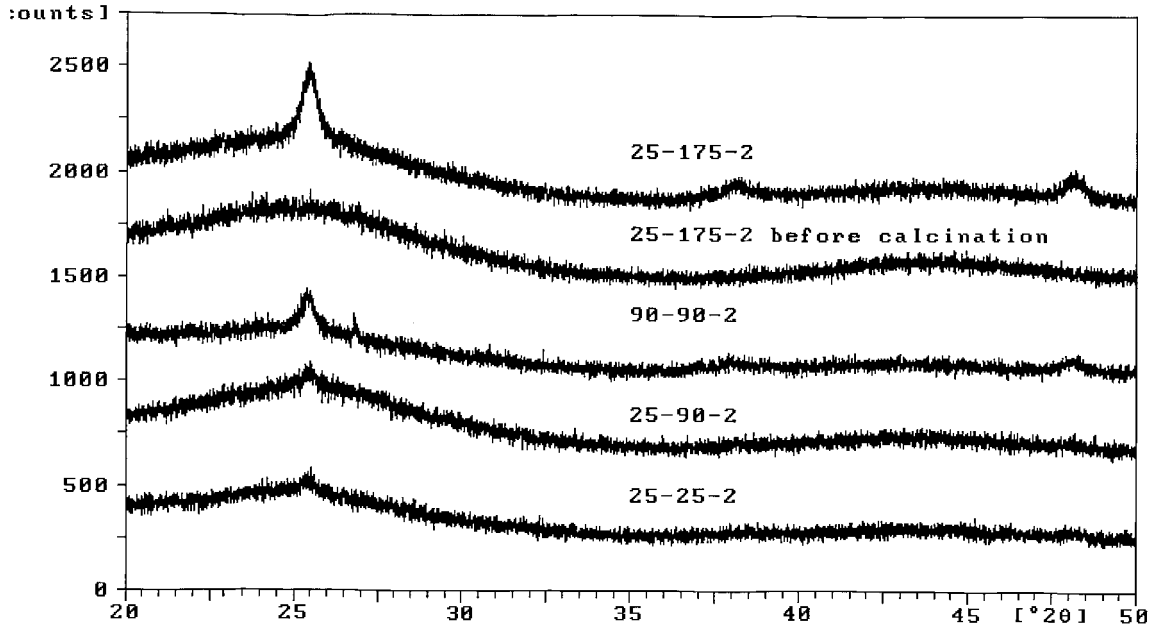


Fig. 4 XRD Patterns of Samples Prepared under Different Hydrolysis Conditions

Based on the above, high hydrolysis temperature and high water vapor concentration are the favorable hydrolysis conditions.

2. Evaluation of Methanol Removal Performance

Studies were then conducted to evaluate the methanol removal performance for the various TiO_2-AC composites. In order to simulate the true emission from the Luke, MD paper mill, low methanol concentration and high humidity was chosen. First, experiments were performed to quantify methanol adsorption only. The experimental conditions were: influent methanol concentration of 100 ppm, relative humidity at 90%, flow rate of 1.0 L/min, and a residence time of about 0.15s. Fig. 5 shows the effluent methanol concentration profiles of 90-90-2 (prepared via pore volume impregnation (PVI) method), 1.5% TiO_2-AC (prepared via boil deposition (BD) method) and the virgin Bionuchar 120. The adsorption profiles were similar for each carbon.

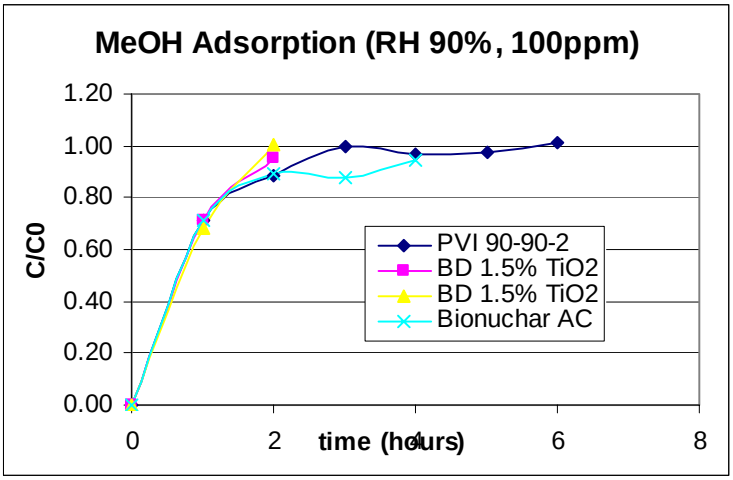


Fig. 5 Methanol Adsorption for Different TiO_2-AC Composites

Next, experiments were performed to assess the ability of TiO_2-AC to degrade methanol in the humid air via photocatalysis. Approximately 1.0 g of 9% wt TiO_2-AC (prepared by MicroEnergy using the boil deposition method) was pre-adsorbed with humidity until saturated. Methanol laden air (C_0=30 ppm; RH=96%) was then passed through the fixed bed of TiO_2-AC with and without UV light (8 W black light lamp, peak wavelength=365 nm). The residence time was about 0.35s. Fig. 6 shows the effluent methanol concentration profiles. The results showed that without UV light, methanol broke through in four hours; and with UV light the effluent methanol concentration reached steady state in two hours, which was around 20 ppm.

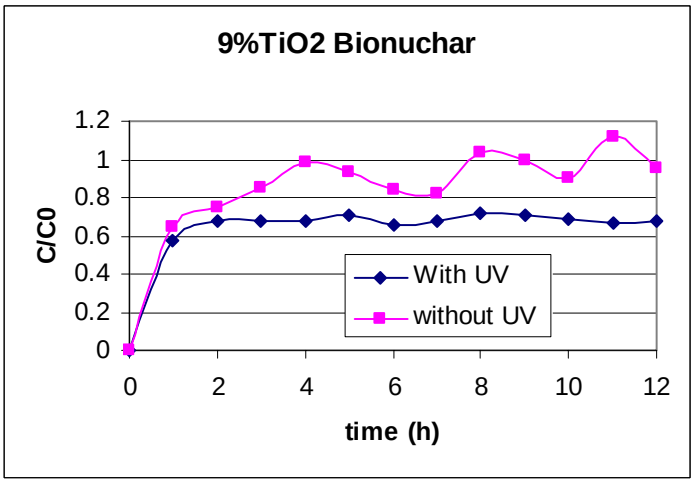


Fig. 6 Methanol Adsorption of 9% wt TiO_2-AC

3. Optimization of Titanium Dioxide Loading onto Bionuchar 120 by Boil Deposition

BET surface area, total pore volume, and destruction efficiency analyses were performed to assess the optimal titanium dioxide loading on Bionuchar 120. Titanium dioxide was added to Bionuchar 120 in varying amounts by boil deposition. Table 2 shows the results of the BET surface area and total pore volume analyses for these carbons. In general, the addition of titanium dioxide onto the surface of the carbon resulted in a decrease in specific surface area and total pore volume.

Table 2 Effect of TiO_2 Loading on Surface Area and Total Pore Volume of Bionuchar 120

GAC	% TiO2	SSA (m^2/g)	TPV (cc/g)
BioNuchar 120	0	1447	1.14
BioNuchar 120	3	1480	--
BioNuchar 120	5	1416	--
BioNuchar 120	7	1331	--
BioNuchar 120	9	1358	1.05

To assess the adsorption and destruction efficiency of the various titanium dioxide loadings, two series of batch studies were performed. In the first series of studies, 300 mg/L of GAC was added to 150mL of water, which had a methanol concentration of 10mg/L. The GAC was mixed in the solution for three hours. The amount of methanol adsorbed by the carbon was measured and the results are shown in Fig. 7.

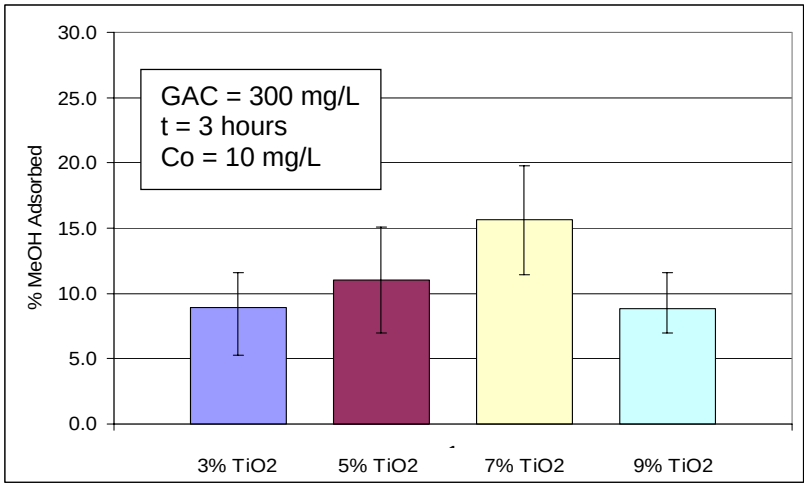


Fig. 7 Effect of TiO_2 Loading on the Methanol Adsorption Capacity of Bionuchar 120

To assess the simultaneous adsorption and destruction efficiency of the carbons loaded with various amounts of titanium dioxide, the first series of experiments (i.e., Fig. 7) were redone in the presence of UV light. The results of these experiments are shown in Fig. 8. Although the Bionuchar 120 with a 9% titanium dioxide loading had the lowest adsorption capacity for methanol, the combined adsorption/destruction ability of this carbon was greater than those with lower TiO_2 loadings.

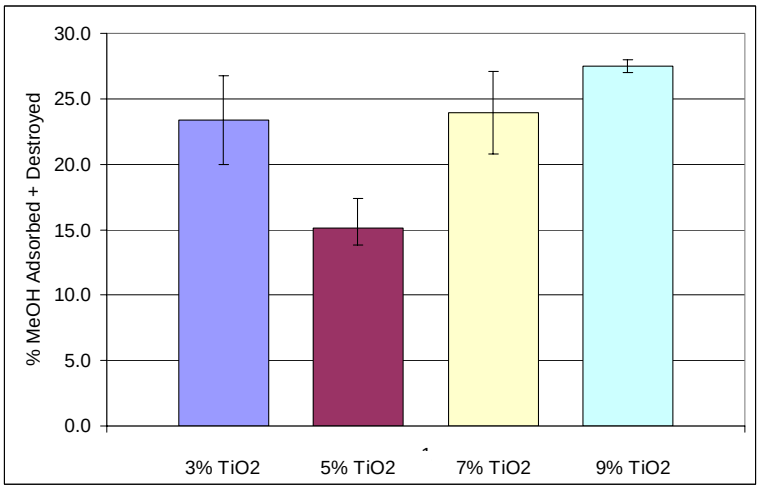


Fig. 8 Effect of TiO_2 Loading on the Simultaneous Adsorption and Destruction of Methanol

Fig. 9 shows the effect of TiO_2 loading on methanol destruction. These results were obtained by subtracting the results from the second (Fig. 8) and first set (Fig. 7) of experiments. Bionuchar 120 with a 9% TiO_2 loading showed the greatest amount of methanol destruction.

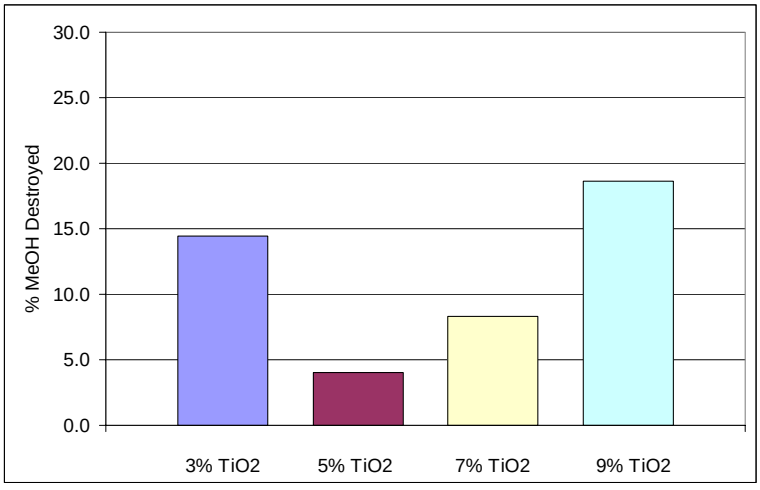


Fig. 9 Effect of TiO_2 Loading on Methanol Destruction

4. Pilot-Scale System Progress

During this quarter (May 1, 2004 –to- July 31, 2004), MicroEnergy Systems, Inc. (MSI) was involved in support activities to the work conducted by Dr. Mazyck at the University of Florida, and included:

- Development of a protocol for applying an optimum TiO2 loading to granular activated carbon (GAC).
- Methanol adsorption tests utilizing the Photocatalytic Fluidized Bed Reactor (PFBR) at the MSI Test Facility in Oakland, Maryland.
- Site visit to MeadWestvaco facility in Luke, Maryland.
- Development of a protocol, coupled with test run productions of silica gel pellets suitable for methanol adsorption and photocatalysis.

The following provides a description of each of these activities.

Protocol for Application of TiO_2 onto GAC. In the previous Quarter, a small sample of GAC was impregnated with one (1) percent of titania, by weight. This sample was then sent to Dr. Mazyck, where laboratory tests employing photocatalytic oxidation of organic dyes, showed that an increased loading of TiO_2 would be needed to achieve good contaminant destruction.

With these results in mind, the objective of this Quarter's task was to develop a methodology of producing GAC coated with an optimum dose of TiO_2 that could be replicated on a commercial scale for large quantity production.

Known quantities of Westvaco Bionuchar 120 activated carbon was dosed with slurry mixtures of distilled water and varying quantities of Degussa P-25 TiO_2 that ranged in six "steps" from one (1) percent up to nine (9) percent, by weight, based on the criteria presented in Table 3.

Table 3 Protocol for Production of GAC with Various TiO_2 Loadings

TEST NO.	**PERCENT TITANIA**	**GAC**	**WATER**		**TiO_2**
	percent	grams	Grams	oz	grams
1	1.0%	113.4	170.1	5.75	1.13
2	2.0%	113.4	170.1	5.75	2.27
3	3.0%	113.4	170.1	5.75	3.40
4	5.0%	113.4	170.1	5.75	5.67
5	7.0%	113.4	170.1	5.75	7.94
6	9.0%	113.4	170.1	5.75	10.21

Each sample was then placed in MSI's prototype external-fired test kiln to vaporize the slurry's water content; thereby, coating the GAC with TiO_2.

Samples from each of the six tests were sent to Dr. Mazyck for laboratory testing to determine the effect of percent TiO_2 loading on the adsorption/destruction of methanol in the presence of UV light. Results indicated that a nine (9) percent loading of yielded the best performance (as discussed in the previous section).

Methanol Adsorption Tests in the PFBR. With the above results and utilizing the indicated protocol, it was decided to prepare sufficient quantities of GAC with a 9% TiO_2 loading and conduct a series of methanol adsorption tests in the Photocatalytic Fluidized Bed Reactor (PFBR) at the MSI Test Facility in Oakland, Maryland.

Dr. Dave Mazyck was present during all tests and directed their performance and confirmation of protocol.

Prior to the start of testing, samples of GAC coated with 9% TiO_2 was loaded with methanol equivalent to two (2) percent, by weight. This ratio was chosen, as an initial start point, so as to: (a). "generally" learn how the PFBR performed, vis-à-vis methanol reduction, (b). determine if methanol desorbed from the carbon due to air flow through the chamber, (c). not exceed potential explosion limits of methanol, and (d). determine differences in methanol reduction with UV radiation.

During testing, a PerkinElmer Photovac MicroFID Portable Flame Ionization Detector was utilized to measure and monitor methanol levels at the inlet and outlet of the PFBR.

Although, levels of methanol did decrease during the duration of each test; unfortunately, results were less than satisfactory based on data obtained.

It was conjectured that possibly the MicroFID instrument readings were compromised due to contamination of fine carbon dust on the instrument's inlet sampling port during testing. This was an unanticipated occurrence; which apparently resulted from the fact that the Westvaco Bionuchar 120 activated carbon used during testing is relatively "soft"; thus, producing fine dust from the fluidized bed. A possible remedy for this occurrence is the selection of a "harder" activated carbon, which is being investigated by Dr. Mazyck.

Dr. Mazyck retrieved samples of the GAC before and after testing for laboratory analyses upon his return to UF. Samples were taken from the tests where GAC was loaded with (1) methanol and (2) methanol and water. In both cases, the GAC was fluidized in the FBPR for about an hour in the presence of UV light. The results showed that when the GAC was loaded with methanol only, a majority of the methanol remained in the carbon pores and, thus, was not oxidized. The GAC loaded with methanol and water desorbed about 2/3 of the methanol from its pores during fluidization. Measurements taken with the MicroFID instrument showed that only a small portion of this desorbed methanol was oxidized.

MeadWestvaco Site Visit. MeadWestvaco operates a series of brown stock washers in conjunction with its wood products processing facility in Luke, Maryland, which is located about 20 miles east of MSI's Test Facility.

The Luke facility is currently assessing options to control methanol emissions in response to new regulatory requirements. The facility's current plan entails: (a). sealing the washers to reduce tramp air ingestion; thus, reducing overall quantities of gases to treat, and (b). directing the resulting gas flow to incineration.

Luke personnel expressed interest in Dr. Mazyck's concept; and pending an acceptable arrangement and configuration, agreed to serve as host site for a prototype demonstration. Dr. Mazyck and MSI personnel visited the Luke site, and observed the washers in relation to their discharge points and potential demonstration sites. Their orientation appears conducive for a successful installation setup and demonstration.

Likewise, Luke personnel visited MSI's facility to hear a project overview and status presentation by Dr. Mazyck and inspect the PFBR in operation.

Silica Gel Pellet Production by MSI. As a result of the less than satisfactory results obtained from the methanol adsorption tests utilizing GAC + TiO_2, Dr. Mazyck decided that it would be prudent to: (1). Continue pursuing the concept of utilizing GAC + TiO_2 following further laboratory analyses and possible procurement of a "harder" activated carbon, and (2). Investigate use of silica gel as a catalyst support.

Dr. Mazyck conducted a series of laboratory tests with silica gels impregnated with TiO_2 that showed very encouraging results, which are discussed in Section 5. Based on these results, MSI proceeded to prepare samples of silica gel pellets based on the formulation developed by Dr. Mazyck. MSI's intent was to demonstrate the acceptability of replicating Dr. Mazyck's laboratory results on larger "bench-scale" quantities. This was successfully achieved as verified by MSI's samples sent to Dr. Mazyck for his laboratory analyses.

The next objective is to initially fill the PFBR with silica gel pellets to allow testing of a methanol-laden air stream through the reactor, when subject to UV radiation, to determine the efficacy of methanol adsorption and destruction by the silica gel pellets on a prototype scale.

The challenge of this task relates to the extremely large number of pellets necessary to partially or totally fill the reactor. MSI investigated various options and materials to fabricate the pellets and decided to use sheets of polyethylene with multiple holes drilled to create a mold for the pellets, followed by a scheduled heat treatment process in dual thermal chambers, per the protocol established by Dr. Mazyck.

Toward the later part of the Quarter (i.e., July 2004), MSI began preparation of equipment and facilities to prepare sufficient quantities of silica gel pellets that would allow filling a portion of the PFBR, with subsequent testing to follow.

5. Silica Gel Methanol Adsorption/Destruction Tests

During this quarter, various adsorption and destruction tests were performed in a continuous fixed-bed reactor packed with silica gel pellets (approximately 3mm by 5 mm in size). Adsorption studies were conducted by passing humid air (RH > 90%) containing 50 ppm_v of methanol through the reactor in the dark. The residence time through the silica gel was approximately 4.3s. To assess the simultaneous adsorption and destruction efficiency of the silica gels, the same experiment was performed in the presence of UV light with a peak wavelength of 365 nm.

Silica gels (doped with 12% titanium dioxide) were made with average pore sizes of 270Å, 120 Å, and 45 Å. These gels were tested in the reactor for their adsorption and adsorption/destruction capabilities. The results of these tests can be seen in Fig. 10. As expected from previous batch studies, the gel with the largest pore size adsorbed the least amount of methanol while the gel with the smallest pore size adsorbed the greatest amount. The 45 Å gel reached exhaustion after about 800 minutes, while the 120 Å and 270 Å gels reached exhaustion after 570 and 330 minutes, respectively. In the presence of UV light, methanol was adsorbed onto the silica gel and simultaneously destroyed via oxidation catalyzed by the titanium dioxide and UV light. The amount of removal via adsorption and destruction was dependent on the pore size of the gel, with the 45 Å gel removing the greatest amount of methanol (between 93 and 97% of the influent concentration after the system reached steady state).

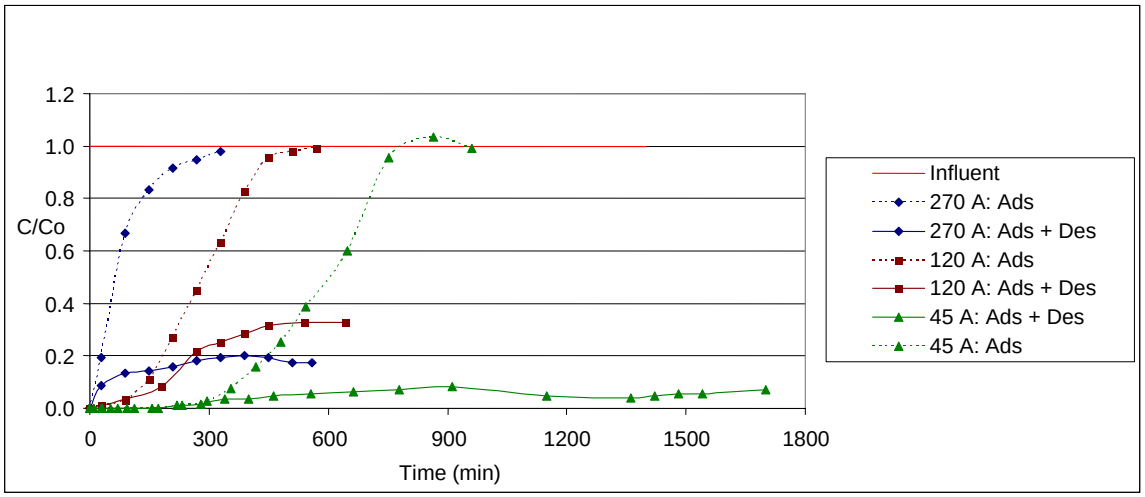


Fig. 10. Breakthrough Curves for Silica Gels with Various Pore Sizes

The adsorption/destruction curve using the 45 Å gel was repeated with a longer sampling time to assess the potential for the long-term destruction of methanol. Fig. 11 shows the results from the first experiment (labeled “45A: Ads + Des” in Fig.1) as well as a second experiment, which lasted four days. This second test shows that the system does indeed reach steady state, oxidizing 85-90% of the methanol entering the system.

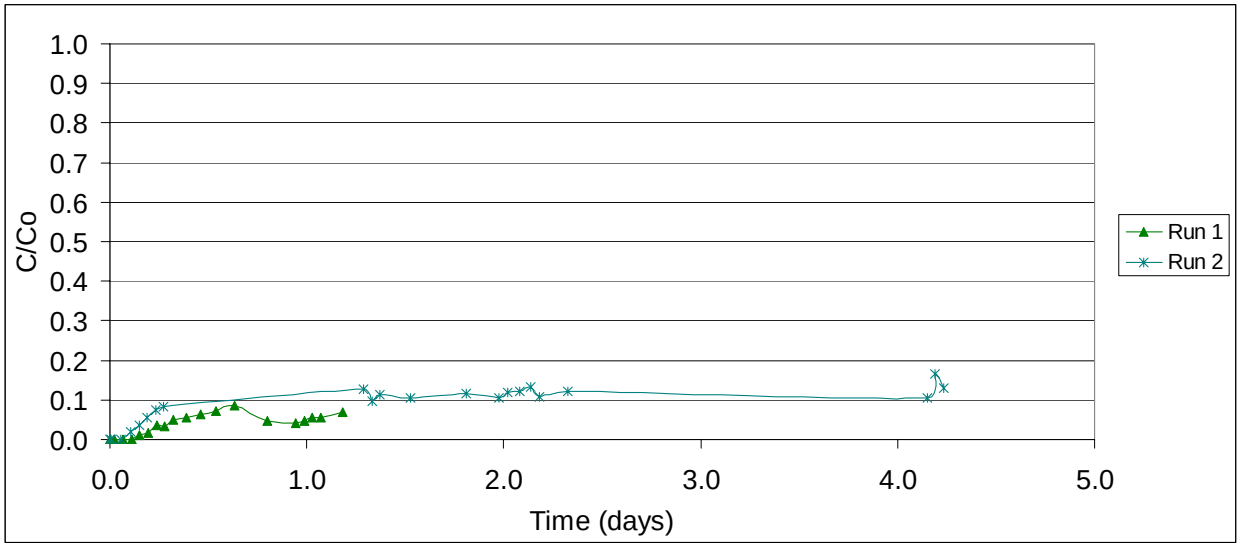


Fig. 11 Breakthrough Curves for 45 Å gels in the Presence of UV Light

Adsorption and adsorption/destruction tests were also conducted using a shorter residence time (2.1 s). The 45 Å gel reached exhaustion after about 550 minutes when adsorption was the only removal mechanism. In the presence of UV light, the 45 Å gel showed 65% methanol removal after 345 minutes, when the system appeared to reach steady state.

6. Reevaluation of Silica Gel Synthesis

The synthesis protocol of the silica gels used thus far involved an aging process that takes four days (two days at room temperature and two days at 65 degrees C). Since a four-day aging process is inconvenient during full-scale production, gels were synthesized with reduced aging times and tested for BET surface area, total pore volume, average pore size, and destruction efficiency. As seen in Table 4, the various aging times did not have a large effect on the physical properties of the gel. The methanol destruction ability of each gel was tested by passing methanol-laden air (50 ppm_v) through the fixed-bed reactor in the presence of UV light. As seen in Fig. 12, the destruction efficiency of each gel was similar. Therefore, these alternative synthesis strategies are all viable.

Table 4 The Effect of Various Aging Times on Silica Gel Properties.

Room Temp (days)	65C (days)	SSA (m^2/g)	Pore V (cc/g)	Pore Size (Å)
0	1	477	0.61	51
1	1	536	0.62	46
0	2	503	0.52	41
0	3	587	0.59	44
2	2	488	0.58	47

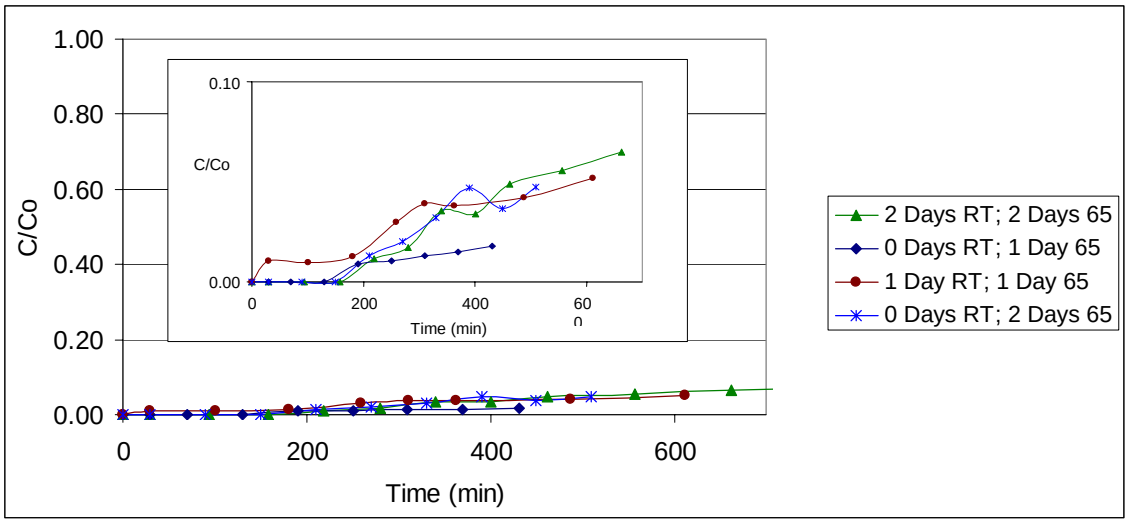


Fig. 12. Destruction Efficiency of Silica Gels Aged at Various Times

7. Methanol Destruction via Photolysis or Ozone

In order to rule out methanol destruction via photolysis or oxidation by ozone, which can be created by UV light at 254 nm, experiments were conducted whereby humid air with a methanol concentration of 40 ppm_v was passed through an empty reactor in the presence of UV light. UV bulbs with peak wavelengths of 365 nm, 312 nm, and 254 nm were used. Fig. 13 shows that no methanol was destroyed in an empty reactor.

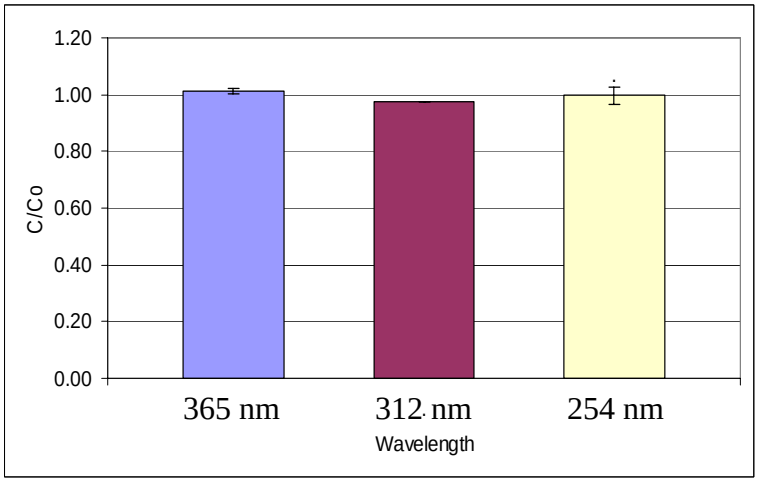


Fig. 13 Methanol Concentration after Exposure to UV Light in a High Humidity Environment

8. LCA and Biological Degradation Studies

Connections at the Luke, MD mill were made to introduce them to the LCA portion of the project. A detailed list of questions was provided that if answered fully, will provide valuable information to assist with the LCA comparison of their business as usual approach (i.e., incineration) vs. the technologies proposed herein. The microbial column apparatus was set up.

FUTURE STUDIES

During the next quarter, the effects of titanium dioxide loading in silica gels will be studied to optimize UV penetration through the gel and methanol destruction. UV bulbs with peak wavelengths of 312 nm and 254 nm will be used during destruction experiments to test the effect of UV wavelength on methanol destruction. The production protocol of the silica gels will be further modified to allow easier full-scale production of TEOS gels. In addition, gels will be synthesized using sodium silicate as the precursor since this material is less costly than TEOS. Both the sodium silicate and TEOS gels will be analyzed for BET surface area, total pore volume, average pore size, and methanol destruction ability.

The optimization of the PVI method for coating activated carbon will continue. Similarly, degradation rates of methanol via a biofilm will be explored.

References:

Kim, Jinsoo. Song, Ki Chang. and Pratsinis, Sotiris E. The effect of hydrolysis temperature on the synthesis of bimodally nanostructured porous titania. Journal of Nanoparticle Research 2:419-424,2000

Patents: None filed

Publications/Presentations:

Mazyck, D.W., Wu, C.Y., Lindner, AS., Sheahan, R., and Jain, A. *TiO_2-coated carbon for the removal of VOCs*. TAPPI Paper Summit, 2004.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Comments
1	Development of Materials		
1.1	Literature Review	8/31/03	Review journals and patents
1.2	Assess Commercial Products	9/30/03	Characterize pros and cons
1.3	Tailor Products with Wood Biomass	11/31/03	Optimization for application
1.4	Assess silica as a sorbent	9/30/03	Characterize pros and cons
1.4	Optimize Coating Strategy	1/31/04	Focus on sol gel

ID Number	Task / Milestone Description	Planned Completion	Comments
1.5	Quantify Regeneration Efficiency	3/31/05	Performance testing
2	Pilot Design and Testing	9/30/03	
2.1	Site Visits	10/31/03	Mill assessments
2.2	Design System	12/31/03	Schematics/Bill of Materials
2.3	Construct and Evaluate Bench Apparatus	3/31/04	For prototype research
2.4	Construct Pilot Plant	12/31/04	For field site installation
2.5	Evaluate Pilot Plant	3/31/05	Shakedown tests
3	Field Tests	2/28/06	
3.1	Data Collection	2/28/06	Performance characterization
3.2	Assess bio/silica/carbon synergies	11/31/05	
3.3	Modify Pilot Plant	12/31/05	If necessary
4	Life Cycle Analyses	3/31/06	
4.1	Environmental	3/31/06	
4.2	Energy	3/31/06	
4.3	Economic	3/31/06	

Approved Budget Data:

Phase / Budget Period			DOE Amount	Cost Share	Total
	From	To			
Year 1	4/03	3/04	434,629	156,643	591,272
Year 2	4/04	3/05	650,617	167,574	818,191
Year 3	4/05	3/06	553,503	143,744	697,247
Year 4					
Year 5					
		Totals	1,638,749	467,961	2,106,710

Second Project Year Spending Plan:

	YEAR 2				
	Feb-Mar 2004	2ndQ 2004	3rdQ 2004	4thQ 2004	TOTAL 2004
UF Personnel					
Faculty	3,440	9,855	6,375	4,170	23,840
Graduate students	12,180	34,900	22,585	14,770	84,435
Fringe	900	2,580	1,670	1,096	6,246
TOTAL LABOR & FRINGE	16,520	47,335	30,630	20,036	114,521
Supplies	1,645	4,710	3,045	1,990	11,390
Travel	1,970	5,650	3,655	2,390	13,665
NCASI	19,715	56,475	36,545	23,900	136,635
MSI	54,520	156,200	101,075	66,100	377,895
Other direct costs (publications, analysis, tuition)	4,180	11,980	7,755	5,070	28,895
TOTAL DIRECT COSTS	98,550	282,350	182,705	119,486	683,001
INDIRECT COSTS	9,653	27,656	17,896	11,704	66,909
TOTAL DIRECT & INDIRECT	108,203	310,006	200,601	131,190	750,000

Index of HQ CPS and Award CID Numbers

Index of HQ CPS and Award CID Numbers