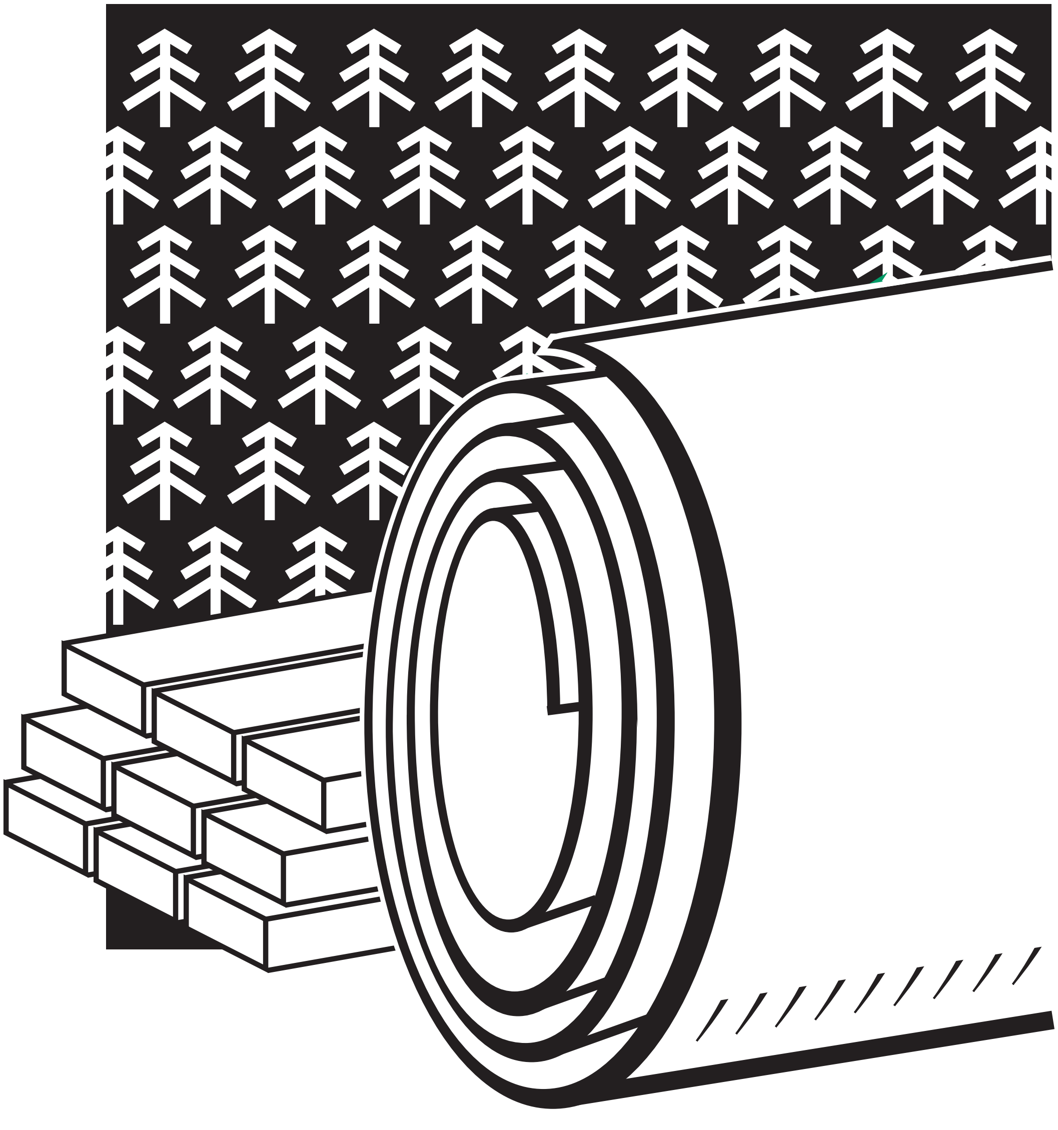
Forest Products Industry of the Future

Quarterly Status Reports

As of September 30, 2008



U.S. DEPARTMENT OF ENERGY

02-GA50113-09

Forest Products

Industry of the Future

Quarterly Status Reports

As of September 30, 2008

Contacts

HQ Program Managers

Bhima Sastri	202-586-2561	bhima.sastri@ee.doe.gov

Field Office Project Managers

Gibson Asuquo	303-275-4910	Gibson.Asuquo@go.doe.gov

Other

Tim Ramsey	303-275-4933	tim.ramsey@go.doe.gov
Elmer Fleischman	208-526-9023	Elmer.Fleischman@inl.gov

Forest Products Projects

Highly Energy Efficient Directed Green Liquor Utilization (D-GLU) Pulping

North Carolina State University

GO14308

QUARTERLY PROGRESS REPORT

Project Title: HIGHLY ENERGY EFFICIENT D-GLU (DIRECTED GREEN LIQUOR UTILIZATION) PULPING

Covering Period: August 01, 2008 through October 31, 2008

Date of Report: October 14, 2008

Recipient: North Carolina State University (NCSU)

Award Number: DE-FC36-04GO14308

Subcontractors: Georgia Institute of Technology (GIT), Evergreen Pulp, Inc.

Other Partners: N/A

Contact: Lucian A. Lucia, 919.515.7707 (W), 919.515.6302 (F) lucian.lucia@NCSU.edu

Project Team: Dimitris Argyropoulos (NCSU), Sujit Banerjee (GIT), Andrew Kulchin (Evergreen Pulp, Inc.), Gibson Asuquo (US DOE)

Upload Site: https://www.eere-pmc.energy.gov/SubmitReports.aspx

Project Update: The mill trial has been delayed because of unforeseen market forces. A firm date of December 2008 had been set for the trial, but we are in limbo until (1) the pulp markets recover, and (2) the mill re-opens; meanwhile, we have been continuing to provide mill support by CONTINUING the work in our laboratories.

STATUS AS OF 14 OCTOBER 2008

EVERGREEN PULP INC.

DATE: October 7, 2008
TO: Lucian Lucia
FROM: Andrew Kulchin
SUBJECT: D-GLU Trial at Evergreen Pulp Update 20081007

The piping contractor has one week of work to complete and Evergreen Pulp has a few days of instrumentation connections to make. The VP of Manufacturing, Jim Lund has committed to completing the D-GLU installation in December 2008. Recent cash and credit flow issues have lead to some extreme business decisions and raw material procurement problems. The mill is expecting to shutdown due to low chip inventories for the last two weeks of October. Start-up is expected on November 1st. I am still hopeful that the D-GLU installation will be completed in December 2008.

MILESTONE 3: Answers to the possibility of significantly altering green liquor recausticization based on Task 5

MILESTONE 5: Complete engineering studies on implementing D-GLU at hardwood and softwood mills

In this quarter we continued the study of the impact of liquor from the upper cooking zone (also referred to as spent green liquor) on recausticizing and began research of the impact of green liquor impregnation on TCF bleaching of low kappa number pulp. A rough outline for the mill trial was agreed upon and is included in this report.

By replacing white liquor on a AA basis with green liquor at a green liquor addition of 0.75 m3/O.D. ton of wood pulped, there is expected to be a 3% increase in the evaporation load based on steady state modeling. The objective of the recausticizing work was to determine the impact of bringing some of the liquor extracted from the pre-impregnation stage back to the slaker rather than sending it through the evaporation plant and recovery boiler. The amount would be 4-5% of the green liquor flow to the slaker. There were three questions we set out to find at least preliminary answers to:

- Did the liquor from the upper cooking zone impact the recausticizing reaction?
- If so, could the part of the organics impacting the recausticizing reaction be filtered out?
- What fraction of the organics would go with the lime mud and what fraction would go with the white liquor?

The bleaching work is in response to the mill’s switch to fully bleached chemical pulp with a TCF bleaching sequence (bleaching sequence $O(P_{soak})QP(PO)$). The lab studies are designed to understand the impact of green liquor impregnation on cooking to low kappa number (target 13) and subsequent bleaching.

The bleaching work is under way and will be reported on in the next quarterly report. The recausticizing work is reported here as is mill trial plan.

Comparison of recausticizing different green liquors

In the previous quarter it was reported that recausticizing of liquor from the upper cooking zone to around 83% recausticizing efficiency requires 1.75 times the stoichiometric amount of calcium hydroxide or 2.25 times of stoichiometric amount of calcium oxide. Causticizing efficiency is defined as:

$$\frac{OH^{-}{}_{WL} - OH^{-}{}_{GL}}{OH^{-}{}_{WL} - OH^{-}{}_{GL} + CO_{3}^{2-}{}_{WL}} \times 100$$

The experimental work was done to understand why over-liming is required. The filtration of high molecular weight organics from the extracted liquor was evaluated. We also ran one experiment with a mixture of liquor extracted from the upper cooking zone (7.4% by volume) and mill green liquor (92.6% by volume).

Green liquor from the mill was recausticized following the same procedure as stated in the previous report. This was done to confirm that good causticizing efficiency could be obtained. Figure 1 shows the recausticizing efficiency vs. stoichiometric ratio of added calcium hydroxide for recausticizing reactions carried out at 90-95 °C for 90 minutes. A recausticizing efficiency of 80% is achieved for the mill green liquor at a stoichiometric ratio of 1, compared to the ratio of 1.75 needed to reach the same recausticizing efficiency for the extracted liquor from pre-impregnation.

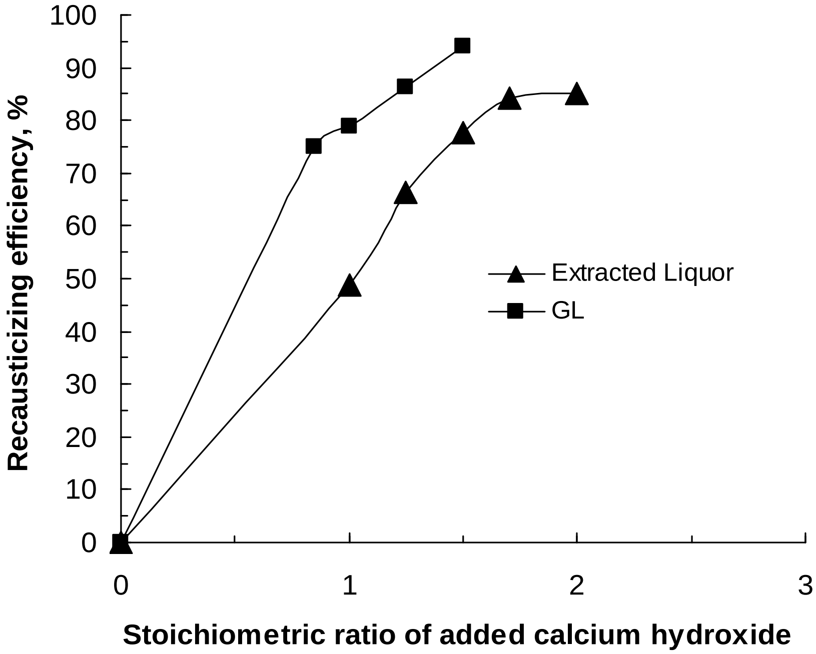


Figure 1. Change of recausticizing efficiency against stoichiometric ratio of added calcium hydroxide.

One run with a mix of liquor extracted from the upper cook (7.4% by volume) and mill green liquor (92.6% by volume) was made. The calcium addition as calcium hydroxide was 1.25 the molar ratio needed to convert 100% of the carbonate. A recausticizing efficiency of 81% and a causticity of 84.6% were obtained indicating that the mill might be able to recausticize a mixture of up to 7% by volume of upper extract liquor in green liquor without significant over-liming. Before considering this as an option, we need to see the results of the mill trial with green liquor impregnation and then determine the impact this approach would have on pulping as discussed briefly below.

Additional recausticizing runs were made with 100% liquor from the upper cook to better understand the role of the organics and the ability to separate the organics from the spent green liquor to minimize the impact on recausticizing and pulping.

Distribution and effect of dissolved organics on recausticizing

Two mechanisms were thought to possibly play a role in the requirement of excess lime to reach the desired recausticizing efficiency. The first was that organics in the extracted liquor bind calcium; the second was that the organics inhibit pore diffusion of the carbonate ions from the green liquor into the calcium hydroxide particles. Based on studies of calcium in pulping and evaporation, we know that black liquor organics will bind calcium and that the amount of calcium bound depends on the temperature profile of the cook and the amount of carbonate in the liquor [1-4].

To test the hypothesis that organics were binding the excess calcium, the soluble calcium content was measured in the liquor from recausticizing experiments of various lengths, Table I. To measure the soluble calcium the supernatant was centrifuged at 10,000 rpm for 30 minutes to remove any resulting precipitates, and the supernatant was filtered through a 0.2 µm filtering disc. The filtrate was then digested by using nitric acid and hydrochloric acid. The solution was finally analyzed with ICP. The soluble calcium increases with time, but it is a small amount compared to the total amount of calcium added as calcium hydroxide. For these experiments, the amount of calcium hydroxide added was 1.25 the stoichiometric amount required which for the spent green liquor translates to 40.32 g Ca/l. The highest value for soluble calcium is just under 90 ppm or $90x10^{-6}$ g Ca/l (.0002%). Based on these results, organics do not bind sufficient calcium to make it unavailable for recausticizing.

Table I. Soluble calcium in recausticized liquor and carbon content of lime mud

Recausticizing time, min	Soluble calcium, ppm	Lime mud carbon analysis		
		Total carbon, %	Carbonate C, %	Organic carbon, %
0	3.5			
6	33.5	8.25	70.1	29.9
12	28.4	8.6	70.3	29.7
24	24.8	8.45	73.3	26.7
44	27.1	9.07	70.2	29.8
58	24.6	8.7	74.6	25.4
90	88.6	8.7	76.4	23.6

During slaking, solid calcium hydroxide reacts with carbonate ions from the green liquor to form calcium carbonate (Figure 2). We hypothesize that the organics in the spent green liquor are inhibiting the diffusion of carbonate and hydroxide anions in the pores of the solid calcium particles.

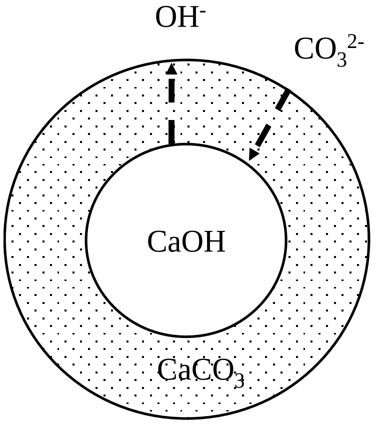


Figure 2. Illustration of shrinking core in recausticizing reactions.

Because black liquor organics are soluble in alkali, we expected the majority of the organics to return to the digester with the white liquor, but we analyzed the lime mud fraction from the runs in Table I to determine how much of the organics might be removed with the lime mud. Analysis of the spent green liquor, Table II, showed that there is about 30.6 g of organics/liter of spent green liquor (density 1,113 g/l). If we consider the experiment run for 58 minutes in Table I, the organic carbon in the unwashed lime mud is only 2.0 g/l, representing 6.5% of the total organics. Based on a filtration experiment using lime mud, washing will removed more of these organics so the actual fraction would be less than 6.5%. From this we confirmed that the majority of the organics will remain soluble and therefore return to the digester with the white liquor. This is not desirable as the dissolved organics will consume pulping chemical. Additionally, we have concluded that lime mud cannot be effectively used to filter the organics from the extracted liquor.

Effect of membrane filtration on recausticizing

Membranes can be used to remove organics from pulping liquors [5-7]. An ultrafiltration membrane (3000 MW cut-off) was used to remove the higher molecular weight fraction of the organics from the liquor extracted from the upper cook. This resulted in removal of 34% of the organics, Table II. The filtrate was then causticized for comparison to the unfiltered spent impregnation liquor. A 1.25 stoichiometric ratio of calcium hydroxide was used in both cases. A significant improvement in the recausticizing efficiency was achieved, 75.8% vs. 69.5%, but a full increase in causticizing efficiency was not achieved. Additionally, the filtered solution would still have a significant fraction of the organics which would return to the digester.

Table II. Recausticizing of spent impregnated green liquor and its filtered counterpart

	Spent GL	Filtered spent GL
Solids content, %	15.2	15.6
Recausticizing efficiency	69.53	75.83
Organic content, %	18.1	11.6
Soluble calcium recausticizing, ppm	73.9	39.3

Other recausticizing conditions are the same as mentioned above

Conclusions regarding recycling upper extract liquor

Replacing white liquor with green liquor in impregnation on a AA basis (at 0.75 m^3/O.D. ton pulp) will result in a 3% increase in the weak black liquor to the evaporators if the liquor to wood ratio is kept constant in the digester. This is because green liquor does not replace white liquor on a 1:1 basis and therefore, less black liquor is recycled to the digester. Recycling a portion of the liquor extracted from the upper cooking zone would allow the mill to keep the evaporative loading constant, but it would also result in organics in the recausticized white liquor because there is no simple way to remove the organics. We have a better understanding of the role of the behavior of the organics during recausticizing and while one run indicates that it may be possible to add a fraction of upper extract liquor (7% or less by volume) more work would need to be done if the mill saw value in such an approach after the mill trial. In general though, this approach does not look promising because of the expected negative impact on chemical consumption during pulping and the lost heat to the recovery boiler as organics.

Generation of low kappa pulp with green liquor impregnation

Lo-solids cooking is being simulated in the laboratory using two MK digesters. The lab scale pulping has been carried out to prepare low kappa number pulp for the TCF bleaching experiments. As the first step of the study, three cooks with 100% white liquor impregnation have been made to serve as control, and the pulping conditions and cook results are presented in Tables III and IV respectively.

Table III. Conditions for Lab Cooks with 100% WL Impregnation

Cook ID		1	2	3
Impregnation/Upper Cook				
Temp. start	^{o}C	25	25	25
Temp., final	^{o}C	135	135	135
Total L:W		4	4	4
Total H-Factor		23.2	23.2	23.2
Water in chips	L	0.89	0.89	0.89
White liquor	L	1.265	1.238	1.238
Green liquor	L	0	0	0
Liquor make-up	L	1.845	1.872	1.872
AA (white liquor)	%	12.5	12.5%	12.5%
AA (green liquor)	%	0	0	0
UC extraction	L	2	2	2

Lower Cook				
Temp. start	°C	135	135	135
Temp., final	°C	165	165	165
L:W		4	4	4
Total H-Factor		2023	2023	2019
White liquor	L	1.9	2.0	2.0
Black Liquor	L	0	0	0
AA, total	%	18.4	20.0	22.0
TTA	%	24.0	25.5	27.9

Table IV. Results of Lab Cooks with 100% WL Impregnation

Cook ID		1	2	3
Screened yield	%	41.34	41.68	42.17
Reject	%	0.12	0.08	0.50
Total Yield	%	41.46	41.76	42.67
Kappa		14.5	13.4	16.0
Residual alkali as Na_2O				
Impregnation NaOH	g/l	7.3	8.0	7.6
Lower cook NaOH	g/l	26.9	23.5	24.1

The Kappa from the three pulps was higher than the target of 13. The three pulps were mixed and bleached with the TCF bleaching sequence $O(P_{soak})QP(PO)$ at the conditions prescribed by the mill. The final pulp brightness was 78% (ISO), below the target of 87% brightness. More pulp is currently being generated using a higher H-factor to obtain the target kappa. This pulp will then be bleached and the PO stage will be optimized with the expectation of reaching the target 87% brightness. The next step after the control is achieved will be to determine the bleachability of pulp generated using a green liquor charge of 0.75 m^3 GL/ton of O.D. wood in the impregnation stage.

Outline for Mill Trial Plan

While the details of the mill trial plan are subject to the operating constraints of the day, some guiding principals were agreed upon. The target green liquor application for the upper cook is 0.75 m^3/ton O.D. wood. This represents a green liquor flow of 169 gpm at current pulp production. The mill will step up to this level over about 6 days and then remain at that level for a few days as the mill capacity allows. An example of how the green liquor flow might be stepped up is illustrated in Table V. It was also agreed that the trial should be started at the end of a bleached pulp run so that it could be continued into a brown pulp run if the trial is going well. That would provide some production data to the mill regarding the impact of green liquor on both grades.

Table V. Example of how the green liquor flow might be increased over multiple days to the final target of 169 gpm.

Day	1	2	3	4	5	6
GL flow gpm	25	50	75	105	135	169

The mill is lime capacity limited and therefore has white liquor with a low causticity. The plan is to keep the lime flow constant during the trial and in this way allow the causticity to increase between 80 and 85%. In this way the mill will offset some of the extra evaporation load to the evaporators as a higher dosage of green liquor is needed when compared to white liquor to achieve the desired alkali charge.

ID TASK NO. 2: Addressing the necessary research tasks to address mill implementation requirements at Evergreen Pulp, Inc.

ID TASK NO. 3: Green liquor (GL) laboratory pulping studies associated with Task 2

Experimental

Because the focus of this work was pulp production, the chips employed were classified and used as they would be in the Evergreen Pulp, Inc., mill situation. In the laboratory, the chips were screened and the over and fines were removed before any tests.

The moisture was measured using the TAPPI standard method after the chips were in storage for at least a week in polyethylene plastic bag.

The liquids employed in the penetration tests were cooking liquors. One of them was conventional cooking liquor for pulp production (white liquor) and other one was a modified cooking liquor (mix between white and green liquor); both were produced in the laboratory and diluted in water to adjust the concentration.

The concentrations were maintained at an average level that is seen in actual mill cooking environments during the impregnation phase for softwood. Also, a laboratory green liquor was used in laboratorial impregnation tests. This green liquor produced in laboratory conditions was mixed with white liquor to form the "modified liquor."

The liquor concentrations are shown in Table VI.

Table VI: Liquor concentration used in penetration tests

Liquor	**NaOH, mol/L**	**Na2S, mol/L**	**Na2CO3, mol/L**	**Total Na, g/L**
Conventional	0.5645	0.1048	0	0.386
Modified	0.6620	0.1757	0.2161	0.578

The tests were performed at 50^oC, 70^oC, and at 90^oC.

The alkali concentration was supposed to be constant because the liquor/wood was very high: 700mL liquor/20g wood chips. The procedure to measure the quantity of liquor that penetrated in chips was gravimetric with 0.01g accuracy. The chips were placed in a perforated plastic bottle (55mm in diameter x 85mm tall) with 3 stainless steel spheres having 1 cm diameter each. This device with equivalent to 20g o.d. (oven-dried) chips immersed in a 1000mL capacity beaker with 700 mL liquor that was immersed previously in a bath with an adjusted temperature where it was maintained during the test. Every five minutes we determined the weight. The beaker was then removed from the bath, dried externally, and the weight was measured with the bottle of chips suspended, but immersed. The weight of this with the chips that were not suspended was also determined. It was therefore possible to determine an accurate amount of liquor penetration into the chips without any need to dry it. The difference of total weight between consecutives measures of the beaker with liquor and device with chips unsuspended was attributed to evaporation. The difference of weight in the suspended chips after discounting the amount attributed to evaporation was the amount of liquor that penetrated in chips.

This measurement was made every five minutes until 180min. of treatment.

After all the tests were calculated, the average penetration and penetration rate by grams per 100 grams of sample of wood per minute were obtained. The experimental design was randomized and was made at minimum of two repetitions for every treatment.

Data analysis

Table VII shows the results for the screened chips. The chips classified over 25.4 mm were not used because they were considered oversized for the specific mill use, while less than 9.6 mm were also not used because they were considered fines.

Table VII: Chips classification

Screen opening, mm	Quantity, %	Situation for use
25.4	1.59	rejected
23.0	42.92	accept
15.0	20.38	accept
9.6	27.16	accept
Fines	8.95	reject

The chips classification show a little more fines then expected in most normal situations. But only accept chips as shown in Table VII were used.

The chips moisture average was measured after it had been classified and stored in a plastic bag for at least a week.

The effect of 50°C on average absorption rate and total average absorption for conventional and modified liquors are presented in Figures 3 to 7.

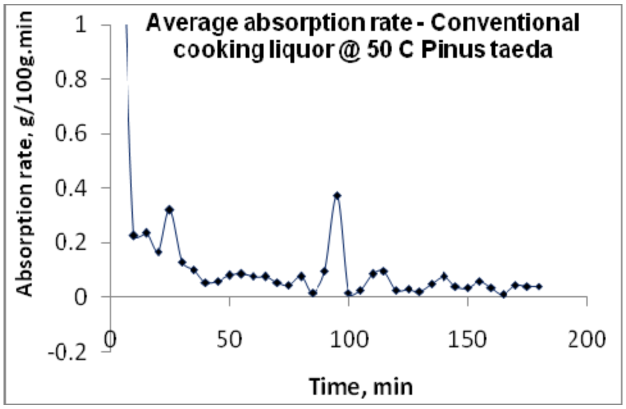


Figure 3 – Absorption rate average of conventional cooking liquor by *Pinus taeda* chips at 50°C.

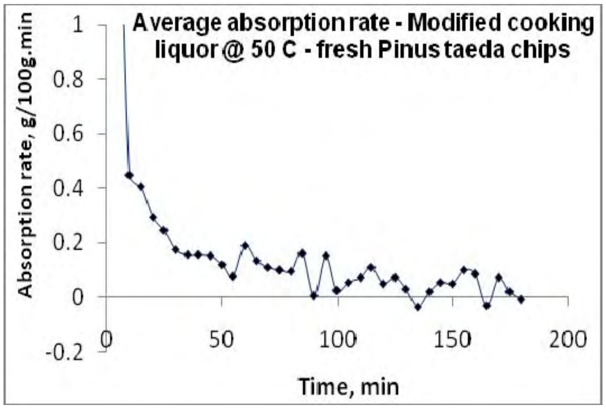


Figure 4– Absorption rate average of modified cooking liquor by *Pinus taeda* chips at 50°C.

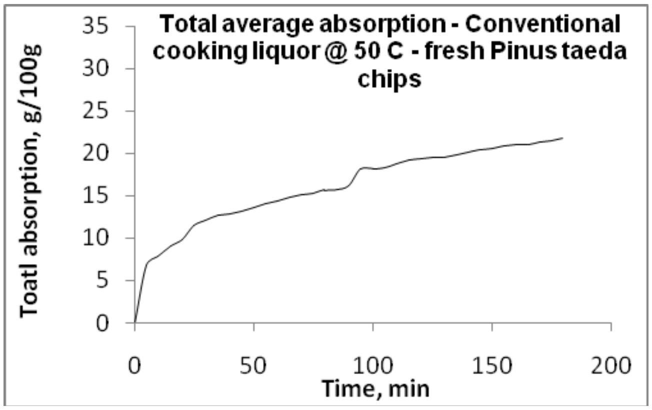


Figure 5 – Total average absorption of conventional cooking liquor by *Pinus taeda* chips at 50^{o}C.

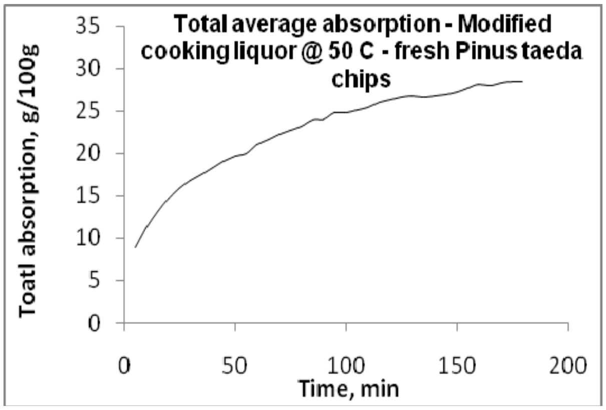


Figure 6 – Total average absorption of modified cooking liquor by *Pinus taeda* chips at 50^{o}C.

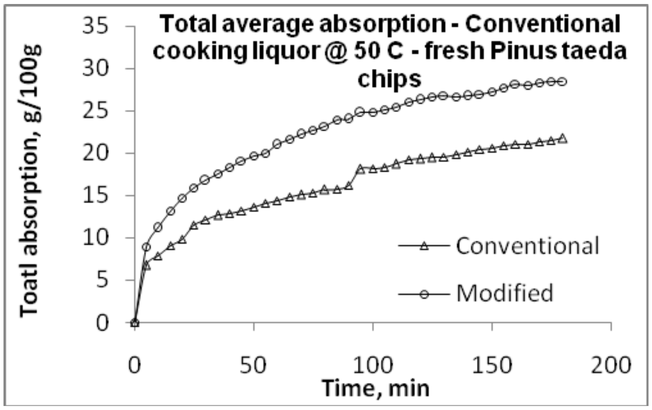


Figure 7 – Total average absorption of conventional and modified cooking liquor by *Pinus taeda* chips at 50^{o}C.

The results demonstrate that modified cooking liquor displays faster penetration compared to conventional cooking liquors at 50^{o}C. It is also possible to verify that close to 95min. at 50^{o}C the absorption rate varies a lot mainly in the conventional cooking liquor system. This variation can likely be attributed to lignin chemical reactions.

The effect of temperature of 70^{o}C on average absorption rate and total average absorption of conventional and modified liquors are presented in Figures 8 to 12.

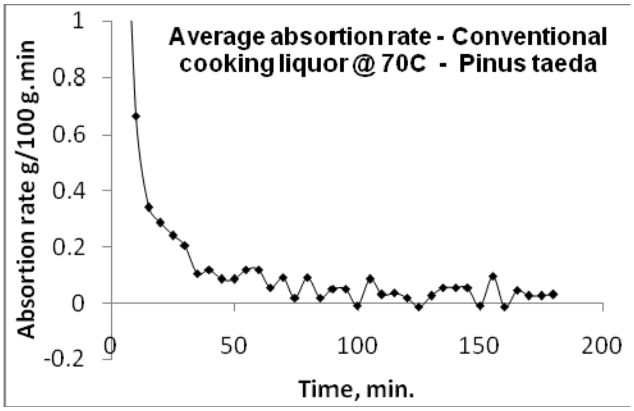


Figure 8 – Absorption rate average of conventional cooking liquor by *Pinus taeda* chips at 70^{o}C.

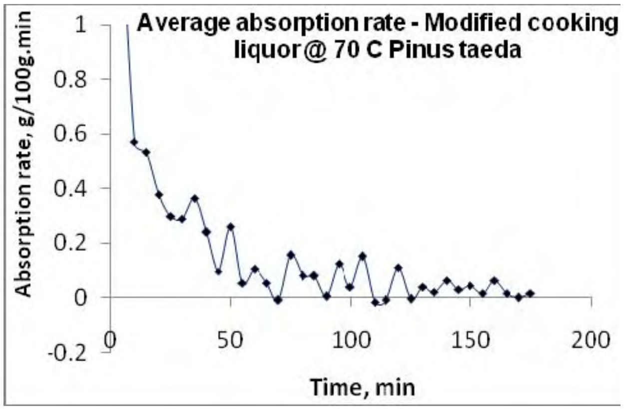


Figure 9– Absorption rate average of modified cooking liquor by *Pinus taeda* chips at 70^{o}C.

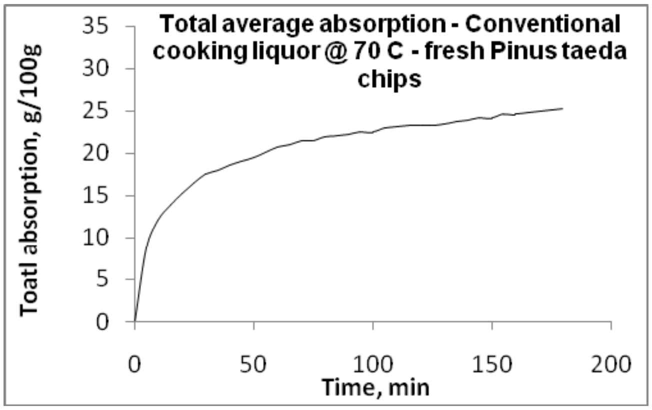


Figure 10 – Total average absorption of conventional cooking liquor by *Pinus taeda* chips at 70^{o}C.

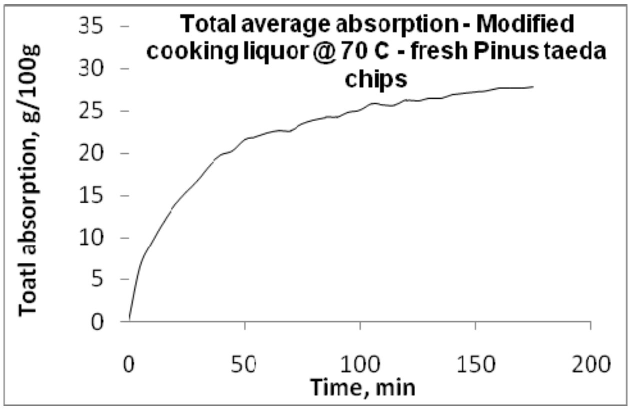


Figure 11 – Total average absorption of modified cooking liquor by *Pinus taeda* chips at 70^{o}C.

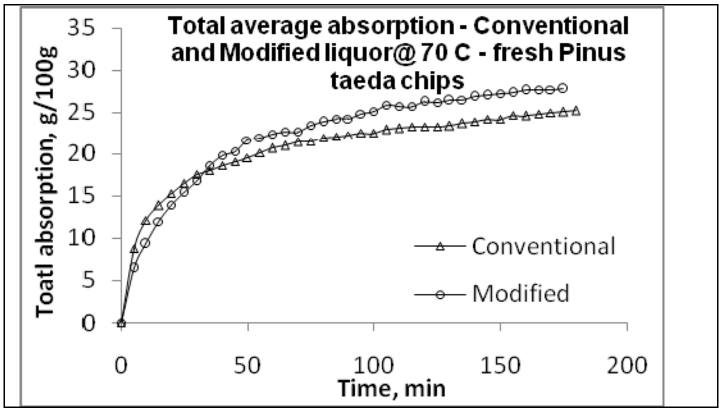


Figure 12 – Total average absorption of conventional and modified cooking liquor by *Pinus taeda* chips at 70^{o}C.

The results for penetration of liquor in *Pinus taeda* chips at 70°C show the same tendency at 50°C but the effect of modified liquor compared with conventional liquor is weaker. The oscillation in the total absorption is more visible in the modified liquor curve (Figure 11) compared to the conventional liquor curve (Figure 10) which suggests that more reactions are taking place. The oscillation effect is probably not perceptible with a large amount of chips because its effect is dissipated amongst them.

It is possible to demonstrate, as expected, that with an increase in liquor temperature, that the penetration is faster in conventional cooking liquor as well as in modified cooking liquor, but chemicals reactions and dissolution of wood material take place at the same time[8] that affect the swelling and allow more accessibility of chemicals into the wood structure. This effect can be verified, in that case, in the absorption rate which strikes an average balance between absorption liquor and material dissolution.

The ionic strength associated with modified liquors is higher compared with conventional cooking liquors which have less sodium. It probable affects the chip swelling and allows the modified cooking liquor to penetrate faster than conventional cooking liquor at lower temperatures (50°C and 70°C). Additionally, a surface tension decrease when the temperature increases helps the both liquors penetration.

The effect of temperature of 90°C on average absorption rate and total average absorption of conventional and modified liquors are presented in Figures 13 to 17.

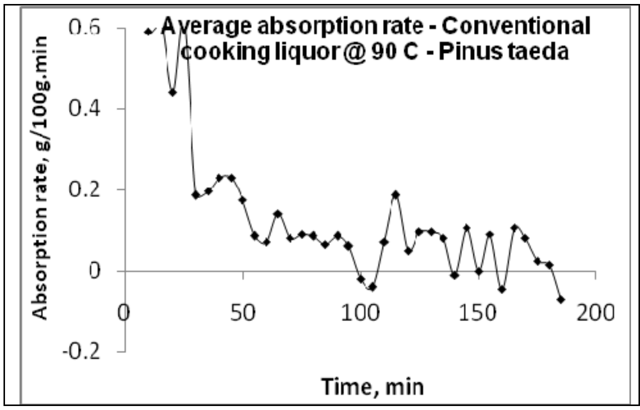


Figure 13 – Absorption rate average of conventional cooking liquor by *Pinus taeda* chips at 90°C.

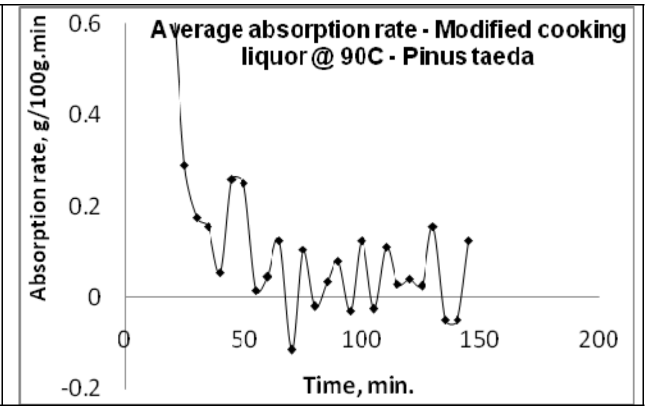


Figure 14– Absorption rate average of modified cooking liquor by *Pinus taeda* chips at 90°C.

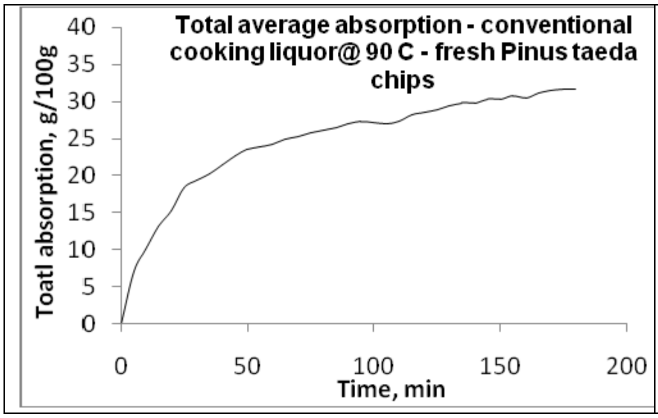


Figure 15 – Total average absorption of conventional cooking liquor by *Pinus taeda* chips at 90°C.

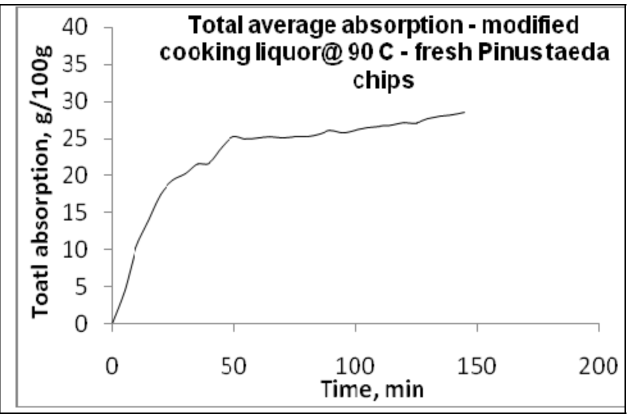


Figure 16 – Total average absorption of modified cooking liquor by *Pinus taeda* chips at 90°C.

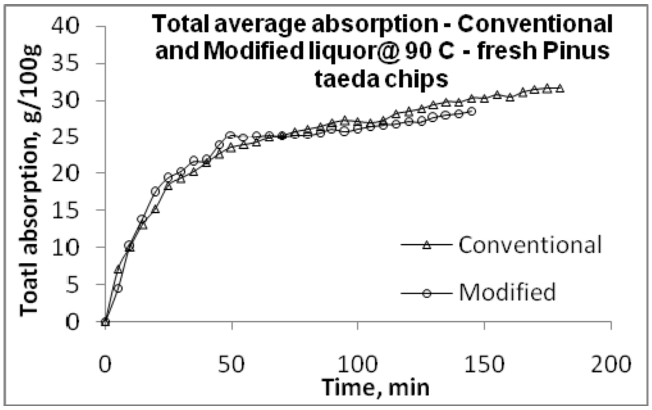


Figure 17 – Total average absorption of conventional and modified cooking liquor by *Pinus taeda* chips at 90°C.

The results for penetration of liquor in *Pinus taeda* chips at 90°C show that the effect of modified liquor compared with conventional liquor is small. Yet, the absorption rate is higher in the first 50min. compared with conventional cooking liquor which affects the average total absorption. Around 100min. for the conventional cooking liquor (Figure 13) and around 70min. for the modified cooking liquor (Figure 14), the absorption rate shows a negative value that could suggest a loss of woody material possibly as a result of chemical reactions.

When the liquor temperature increases, the surface tension decreases and helps liquor penetration. However the results show that the temperature effect is different for conventional and modified liquors. The total liquor absorption varies between conventional and modified liquor when the temperature increases from 50°C (Figure 7) and 70°C (Figure 12) to 90°C (Figure 17). When the temperature reaches 90°C, and if maintained more than 115min., the amount of liquor absorption is superior if conventional cooking liquor is used compared to modified liquor. On the other hand, if the temperature is not too high (50 or 70°C), the total absorption is superior if modified liquor used is compared with conventional cooking liquors. **It shows the potential for the use of modified liquor (green liquor) during the first part of kraft cooking or for pretreatment for enzymatic hydrolysis.**

The Figure 18 and 19 present the effect of different temperatures on the absorption rate of conventional and modified cooking liquor as a function of penetration test time.

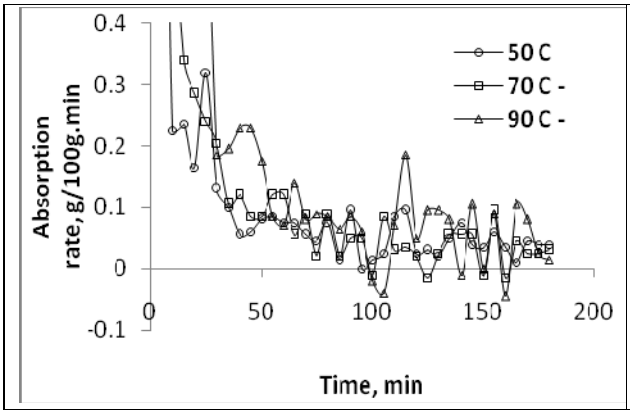


Figure 18 – Average absorption rate of conventional cooking liquor by *Pinus taeda* chips at 50, 70 and 90°C.

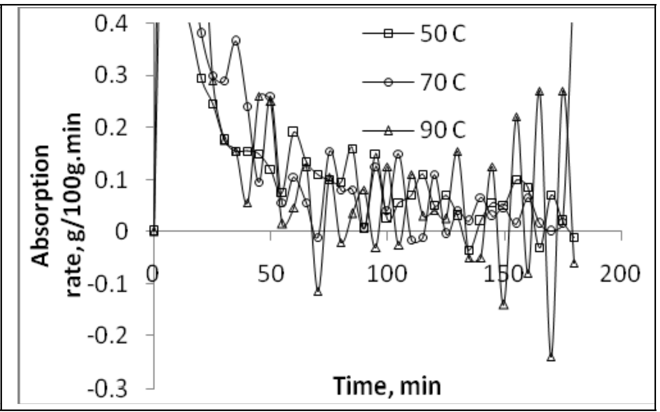


Figure 19 – Average absorption rate of modified cooking liquor by *Pinus taeda* chips at 50, 70 and 90°C.

It can be verified that in both cases (conventional and modified cooking liquor), when the temperature increases the absorption rate variation also increases. This effect could be attributed to surface tension as well as fast chemical reactions that take place; it reflects possibly more accessibility for liquor that cause oscillations in absorption rate along time. This behavior is more evident in modified cooking liquor at 90°C (Figure 19) mainly when negative values are obtained.

It is known that deacetylation is a relatively fast reaction[9] that occurs at the beginning of alkali-wood contact and affects accessibility and physical structure. The behavior shown in this work suggests a dissolution of wood material, and at the same time swelling cycles that allow absorption of more conventional cooking liquor as well as modified cooking liquor. This kind of behavior is more evident at higher temperature.

Figures 20 and 21 show our tests at 70°C. Figure 20 is an overview of an actual test in progress and Figure 21 illustrates matter leaving the chips. The matter is probably extractives and reaction products.

Figure 20- Overview of *Pinus taeda* chips penetration test with modified cooking liquor at 70°C.

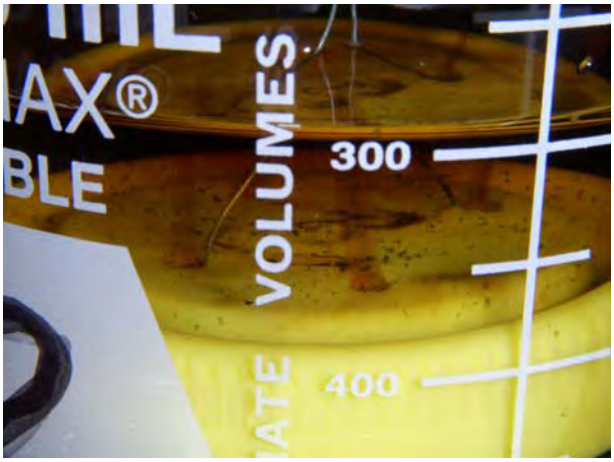


Figure 21- View of material going out from *Pinus taeda* basket chips after 60min. of treatment with modified cooking liquor at 70°C.

We therefore reached the following conclusions:

- The technique developed to evaluate chip liquor penetration displays accuracy and a great potential. It allows us to evaluate chips or wood penetration directly and include the swelling effect.
- Employing complementary tests with this technique can evaluate impregnation and chemical kinetics as well.
- The absorption rate of liquor is larger at the beginning of the process and declines with time despite liquor employed and temperature increases.
- The penetration rate in variable with time, but highest at the beginning.
- In the wood chip, the absorption rate is not linear, but displays a cyclic variation with time. This variation depends on temperature and liquor employed. The variability increases with temperature.
- Pressure is an important parameter that needs to be evaluated for its effect on penetration: it can be possible be evaluated using this technique.

References

1. Hartler, N.; Libert, J. The behavior of certain inorganic ions in the wood/white liquor system. Svensk Papperstidn. 12: 454-457 (1973).
2. Lundqvist, F.; Olm, L.; Tormund, D. Effects of carbonate on delignification of birch wood in kraft cooking. Nordic Pulp Pap. Res. J. 21(3): 290-296 (2006).
3. Lansdell, G.; Frederick, W.J.; Schmidl, W. An investigation of the accelerated $CaCO_3$ fouling in evaporators processing black liquor from displacement batch kraft pulping. AIChE Spring Meeting. Paper No. 23c (2000).
4. Frederick, W.J. Jr.; Grace, T.M., *A study of evaporator scaling: Calcium carbonate scales*, in *Proj. 3234 (3)*, Institute of Paper Chemistry. p. 141 pp. (1977).
5. Forss, K.G. Finnish plywood, particleboard and fiberboard made with a lignin-base adhesive. Forest Prod. J. 29(7): 39-43 (1979).
6. Wallberg, O.; Jönsson, A.-S.; Wimmerstedt, R. Fractionation and concentration of kraft black liquor lignin with ultrafiltration. Desalination 154: 187-199 (2003).
7. Keyoumu, A.; Sjödahl, R.; Henriksson, G.; Ek, M.; Gellerstedt, G.; Lindström, M.E. Continuous nano- and ultra-filtration of kraft pulping black liquor with ceramic filters A method for lowering the load on the recovery boiler while generating valuable side-products. Ind. Crops Prod. 20: 143-150 (2004).
8. Inalbon, M.C.; Mocchiutti, P.; Zanuttini, M. The deacetylation reaction in eucalyptus wood. Kinetics and effects on the effective diffusion. In print, Bioresource Technology, 2008.
9. Maattanen, Marjo and Tikka, Panu. Penetration of water and black liquor into overthick and treated wood chips PAPERI JA PUU - PAPER AND TIMBER **V.** 90 **(**2) **:** 34-39. FEB 2008

Patents:

We anticipate allowing the consortium to handle all Intellectual Property issues.

Publications:

N/A

Presentations:

N/A

MILESTONE STATUS TABLE:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments (1/31/2007)
1	Organization of pulping project mill consortium and agenda for implementation over four years	01/01/05	Currently pursuing: have interest from Aracruz, Stora-Enso, Botnia, Georgia Pacific, Suzano	We are currently assembling the consortium of companies for mill implementation beyond Evergreen Pulp
2	Addressing the necessary research tasks to address mill implementation requirements at Evergreen Pulp, Inc.	08/15/05	04/01/2006	This is nearly complete
3	Green liquor (GL) laboratory pulping studies associated with Task 2	12/01/05	04/15/2006	Baseline work has been completed to satisfaction of mill
4	Fundamental and applied determination of handling green liquor impregnation and liquor flows; work in coordination with Milestone 1 to eliminate any problems in mill; have supporting engineering design	06/30/06	01/31/2008	We are nearing completion of this with work on site and with the support of the University of Viçosa (Prof. Gomide) – will be done by end of this month
5	Mill trial	07/01/06		DELAYED
6	Applied and fundamental studies for the pulping catalyst including role, fate, impact on pulp properties, impact on recovery, exploration for alternative organics	12/31/07		These tasks are part of phase 2 in our GL pulping project
7	Selection of mill(s) that has conducted the appropriate mill studies for additive-enhanced GL pulping	04/01/08		Evergreen Pulp has expressed interest in this task as of 4/01/07

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments (1/31/2007)
8	Exploration of mill specific issues related to odor, environmental issues, solid impacts, and corrosion for Milestone 4	06/30/08		Student work recently performed and to be included in the second report indicates that the emissions are negligible.
9	Final Engineering report and lab work supporting mill trials for additive-enhanced GL impregnation	12/31/09		
10	Mill trial at selected sites based on engineering criteria developed with mill	09/30/09		
11	Final report for the industry and DOE	12/31/09		

MILESTONES:				
1	**MILESTONE 1: Answers to feasibility and planning of GL pulping process (pulp properties, secondary effects on mill) in target mill**	01/15/06	04/15/2006	We have addressed this as well as we will do at this point
2	**MILESTONE 2: Answers to the question of how the build up of scale in the pulp mill and downstream occurs**	12/31/06	01/31/2007	This milestone is not critical at this point – our work does not point to it being a “show stopper”
3	**MILESTONE 3: Answers to the possibility of significantly altering green liquor recausticization based on Task 5**	06/01/07		This is potentially a new avenue for used GL to be recycled – currently not a high priority
4	**MILESTONE 4: Answers to the economic use and application of additive-enhance GL pulping**	02/01/08		Once the mill trial is completed, this will be the second major phase of the project
5	**MILESTONE 5: Complete engineering studies on implementing D-GLU at hardwood and softwood mills**	03/31/07		We are currently working with Evergreen Pulp & the University of Viçosa to finalize this engineering work; this will be on-going work in the consortium for other companies
6	**MILESTONE 6: Demonstrate 15% energy savings at mill trials of D-GLU pulping technology**	07/01/07		This will be documented at Evergreen Pulp by June 2008

Budget as of 10/14/2008

Quarter	Estimated Federal Share of Outlays	Actual Federal Share of Outlays	Estimated Recipient Share of Outlays	Actual Recipient Share of Outlays	Cumulative
3Q04	-	-		-	-
4Q04	-	-		-	-
1Q05	750.41	750.41	5,935.00	5,935.00	6,685.41
2Q05	37,713.92	37,713.92	5,920.00	5,920.00	43,633.92
3Q05	168,540.18	168,540.18	1,419.36	1,419.36	169,959.54
4Q05	86,152.73	86,152.73	16,785.42	16,785.42	102,938.15
1Q06	124,301.84	124,301.84	1,891.88	1,891.88	126,193.72
2Q06	26,988.22	26,988.22	41,579.51	41,579.51	68,567.73
3Q06	54,328.09	54,328.09	5,150.46	6,529.21	60,857.30
4Q06	89,397.43	89,397.43	19,686.96	21,085.29	110,482.72
1Q07	134,927.75	134,927.75	5,171.16	6,530.59	141,458.34
2Q07	78,286	78,285.65	6,528	6,528.28	84,813.93
3Q07	80,090	80,090.24	6,885	6,884.61	86,974.85
4Q07	156,797	156,796.62	6,907	6,907.29	163,703.91
1Q08	85,710	85,709.83	6,747	6,746.73	92,456.56
2Q08	48,508	48,508.34	119,364	119,364.47	167,872.81
3Q08	55,946	55,946.49	7,623	7,623.93	63,570.42
4Q08	99,729		7,604		-
1Q09	150,000		7,000		
2Q09	1,340,000		1,347,000		
3Q09	-		-		
4Q09	-		-		
1Q10	-		-		
2Q10	-		-		
3Q10	-		-		
4Q10	-		-		
	2,818,166	1,228,437.74	1,619,198	261,731.57	1,490,169.31
				includes Evergreen Pulp	

Development of Screenable Wax Coatings and Water-Based Pressure Sensitive Adhesives

University of Minnesota

GO14309

DOE F 4600.3A
(03-94)

U.S. Department of Energy

OMB Control No.
1910-0400

Milestone Log

OMB Burden Disclosure Statement

Program/Project Title: Development of Screenable Wax Coatings and Water-Based Pressure Sensitive Adhesives

Program/Project ID No.: DE-FC36-04GO14309

ID No.	Description	Planned Completion Date	Actual Completion Date	Comments As of 09/30/08
1	**Formulation of benign label grade water-based pressure sensitive adhesives (PSA).**	10/06	10/06 *Refinements Ongoing	* A new approach for monitoring the movement of surfactant was published this quarter, Xu, G. H., Jinping Dong, J., Severtson, S. J., Houtman, C. J., Gwin, L. E. Characterizing the Distribution of Nonylphenol Ethoxylate Surfactants in Water-based Pressure-Sensitive Adhesive Films using Atomic-Force and Confocal Raman Microscopy, *Journal of Physical Chemistry B*, 112(38), 11707-11914, 2008. This method will allow us to now monitor the movement of surfactant to the surface of a film where it impacts the recycling behavior. Future studies will examine the movement of both emulsifiers, as well as wetting agents.
2	**Demonstrate screening of water-based PSAs at pilot scale.**	10/06	10/06 *Refinements Ongoing	* We continue to use Government certification testing at USDA FPL (a project partner) as a tool to promote new technologies. Several certifications were issued this quarter for commercial products from Franklin International, and we have started to examine the possibility of certification documentation issues for several H.B. Fuller products.
3	**Demonstrate benign coatings with the same performance as existing formulations**	11/09		Given our current findings and feedback from those who are attempting to market this technology, an important requirement is the need for products to be green overall (e.g., compostable). It is believed that this can be accomplished through relatively minor modifications to the backbone of the adhesive polymer, which we intend to pursue.
4	**Development of new screenable commercial PS labels**.	11/09		Currently, there is tremendous interest in "green" products. However, the definition is unclear. We are currently designing tests to gauge the compostability of products to determine if recycling compatible (i.e., screenable) is consistent with a product being compostable.
5	**Development of benign coating products.**	11/09		

Budget Data (06/30/08): The actual spending should reflect the money actually spent on the project in the corresponding periods.

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**
4Q04	10/1/04	12/31/04	112,872	94,000	35,853	29,140	123,140
1Q05	1/1/05	3/31/05	104,308	98,494	35,854	34,473	256,107
2Q05	4/1/05	6/30/05	50,942	76,506	35,853	41,600	374,213
3Q05	7/1/05	9/30/05	51,090		35,854	48,201	422,414
4Q05	10/1/05	12/31/05	65,796		29,561	28,361	450,775
1Q06	1/1/06	3/31/06	65,800	225,000	29,560	30,374	706,149
2Q06	4/1/06	6/30/06	65,796		29,561	29,784	765,301
3Q06	7/1/06	9/30/06	65,800		29,560	29,368	848,772
4Q06	10/1/06	12/31/06	62,686	60,000	23,670	23,471	931,034
1Q07	1/1/07	3/31/07	49,349	58,880	23,669	23,382	1,044,636
2Q07	4/1/07	6/30/07	52,688	90,246	23,670	23,356	1,149,458
3Q07	7/1/07	9/30/07	45,999	90,000	23,667	14,822	
4Q07	10/1/07	11/30/07			23,667		
Totals			**793,126***	**793,126**	**356,332***	**356,332**	**1,149,458**

* Values for the approved 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	10/04	10/05	319,212	143,414	462,626			
Year 2	10/05	10/06	263,183	118,242	381,424			
Year 3	10/06	10/07	210,731	94,676	305,407			
Totals			793,126	356,332	1,149,458			

QUARTERLY PROGRESS REPORT

Project Title: Development of Screenable Wax Coatings and Water-Based Pressure Sensitive Adhesives

Covering Period: July 1st, 2008 through September 30th, 2008

Date of Report: October 31st, 2008

Recipient: Department of Bioproducts and Biosystems Engineering, University of Minnesota, 2004 Folwell Avenue, St. Paul, MN 55108

Award Number: DE-FC36-04GO14309

Subcontractor: United States Department of Agriculture Forest Service, Forest Products Laboratory

Other Partners: Boise Cascade Corp., Franklin International, The International Group, Inc.

Contact: Steven J. Severtson, (612) 625-5265, sever018@umn.edu

Project Objective: The project objective is the design of new water-based pressure sensitive adhesive (PSA) products and wax coatings that are engineered for enhanced removal during the processing of recycled fiber. Research includes the formulation, characterization, and performance measurements of new screenable PSAs and wax treatments, testing of modified paper and board substrates and the design of test methods to characterize the inhibition of adhesive fragmentation and wax comminution and relative removal efficiencies of developed formulations.

Background: The presence of PSAs and wax coatings in recycled paper creates a number of problems for the recycling process including lost production and diminished product quality. This project will focus on the design of adhesives and coatings that are more effectively removed from the papermaking process during furnish screening. These new materials should possess properties that enhance removal without impacting performance.

Work will include the identification of properties that control adhesive fragmentation and coating comminution and use of this information to design new formulations optimized for both removal and product performance. Through an iterative process where the surface and bulk mechanical properties of materials are characterized and compared against repulping behavior and screening removal efficiencies, the properties controlling fragmentation and comminution will be identified. Products will then be reformulated to manipulate these properties and produce commercially feasible, screenable products. In addition to the development of new adhesives and wax coatings, the role of the paper substrates in determining removal efficiencies will be investigated. Treatments such as strength resins, pigment coatings, sizing agents and others will be used to modify the wet and dry strength of paper, interfacial properties and PSA/coating-paper adhesion. The influence of the modifications on the adhesive fragmentation and coating comminution will be determined from monitoring the particle size and morphology during repulping operations and by measuring screening removal efficiencies. It is expected that the results of this work will identify combinations of paper and PSA or board and wax treatments that provide for significant screening removal efficiencies of the adhesive or coating layer.

Status: A summary of results obtained during the reporting period by the University of Minnesota and its partners are as follows:

- Conference calls were held on July 15, August 21 and September 4 between L. Gwin (Franklin International) and S. Severtson (UM). These meetings are used to make research plans, clarify and review information conveyed via emails and phone calls and will often involve other participants from Franklin International and/or the University of Minnesota.

- Publications published during this quarter,

  - Xu, G. H., Jinping Dong, J., Severtson, S. J., Houtman, C. J., Gwin, L. E. Characterizing the Distribution of Nonylphenol Ethoxylate Surfactants in Water-based Pressure-Sensitive Adhesive Films using Atomic-Force and Confocal Raman Microscopy, *Journal of Physical Chemistry B*, 112(38), 11707-11914, 2008.

- As discussed in the last quarterly report, emulsifiers in water-based PSAs influence and often govern the extent to which an adhesive film fragments. This effect involves the movement of surfactant to the film interface where it contacts the attached paper facestock. Thus, selecting surfactants to maximize the recycling compatibility requires an understanding of the transport and fate of surfactants in adhesive films. We have developed a method using confocal Raman microscopy (CRM) and combination with atomic force microscopy (AFM). We have also successfully applied an exponential decay model to fit the distribution data. These methods will be used to examine the relationship between surfactant structure and their distribution behavior.

- Surfactant distributions in model pressure-sensitive adhesive (PSA) films were investigated using these methods. The PSAs are water-based acrylics synthesized with *n*-butyl acrylate, vinyl acetate and methacrylic acid and two commercially available surfactants, disodium (nonylphenoxypolyethoxy)ethyl sulfosuccinate (anionic) and nonylphenoxypoly(ethyleneoxy) ethanol (nonionic). The ratio of these surfactants was varied, while the total surfactant content was held constant. AFM images demonstrate the tendency of anionic surfactant to accumulate at the film surfaces and retards latex particle coalescence. CRM confirms that the more hydrophilic surfactant tends to migrate to the film interfaces. This is consistent with its greater water solubility, which causes it to be transported by convective flow during the film coalescence process. The behavior of the more hydrophobic surfactant is consistent with its greater compatibility with the polymer, showing little enrichment at film interfaces, and interestingly, little lateral variability in concentration measurements made via CRM.

- Both CRM and AFM were used to examine the movement of surfactant under various temperature and humidity conditions. It appears that moisture levels have a significant impact on the z-directional movement of the surfactants, and this effect is enhanced via cycling. It also appears that temperature impacts the movement of surfactant. These results indicate that the storage of the PSAs can have a strong impact on their recycling behavior. We expect to submit a manuscript on this topic to a scientific journal next quarter.

- As discussed, a series of polymer latexes were synthesized via seeded-emulsion copolymerization of butyl acrylate with small amounts of acrylic acid (AA) and vinyl acetate (VA). The synthesized particles had similar particle sizes and were prepared under identical conditions, which allowed us to separate various parameters such as particle size and gel content. The samples were characterized via gel permeation chromatography (GPC) and AFM to give gel content, molecular weight, particle size, as well as surface morphology. The variables under investigation in this work included type and amount of surfactants, crosslinking density of the polymer and effect of chain transfer agent. The properties of the various members of this series provided interesting results. Although the expected underlying trend remained: as the shear strength increased, the peel and tack of the films decreased accordingly.

- The interaction of these PSAs with moisture is being tested as well as the recycling behavior. A more fundamental understanding of what controls the loss of strength in polymer films when exposed to moisture would provide greater flexibility in designing recycling compatible formulations. These systems will also be characterized using CRM and AFM and the results will be used to model the movement of surfactants and thus their impact on recycling behavior.

- A series of diblock copolymers containing one block with lower glass transition temperature and the other block containing sulphonated repeat units were synthesized and characterized with various techniques. The molecular parameters for the diblock polymer include the length of each block and their relative length and degree of esterification. The synthesis involved the polymerization of PnBA (or PEXA) followed by the polymerization of HEA or HEMA as the second block. The hydroxyl groups were converted to sulphonated groups via an esterification reaction. These block polymers had narrow molecular weight distributions, owning to the controlled polymerization technique being used. These block copolymers were characterized via a number of techniques including transmission electron microscopy (TEM), GPC, and nuclear magnetic resonance spectroscopy (NMR).

Plans for Next Quarter:

A trip is planned to Franklin International in early October to discuss strategies for marketing new technologies. PSAs will be produced with new surfactants, which will hopefully limit migration to film surfaces. This will allow better control over recycling behavior of PSA films and greater stability of this property. Also, efforts will be initiated to synthesize PSAs, which are both recycling compatible and environmentally benign.

Biological Air Emissions Control for an Energy Efficient Forest Products Industry of the Future

Texas A&M

GO14310

QUARTERLY PROGRESS REPORT

Project Title: **Biological Air Emissions Control for an Energy Efficient Forest Products Industry of the Future**

Covering Period: **July 1, 2008 through September 30, 2008**

Date of Report: **November 10, 2008**

Recipient:
South Texas Environmental Institute
Texas A&M University-Kingsville
Department of Environmental Engineering, MSC 213
Kingsville, Texas 78363

Award Number: **DE-FC36-04GO14310**

Subcontractors:
Bio•Reaction Industries LLC
18500 SW Teton Avenue
Tualatin, OR 97062

Other Partners:
Stimson Lumber Company
Forest Grove, OR

Contacts:
Dr. Kim Jones
Department of Environmental Engineering
Texas A&M University-Kingsville
Kingsville, TX 78363
(361) 592-21897

Dr. James Boswell
Bio•Reaction Industries LLC
18500 SW Teton Avenue
Tualatin, OR 97062
(936) 597-7711

Project Team:
Gibson Asuquo
U.S. Dept of Energy
Golden Field Office
Golden, CO 80401
(303) 275-4910

Tim Ramsey
Project Monitor
US DOE Golden Field Office
Golden, CO 80401
(303) 275-4933

Project Objectives

The gaseous emissions from the hardboard mill presses at lumber plants such as that of the Stimson Lumber Company contain both volatile and condensable organic compounds (VOC and COC, respectively), as well as fine wood and other very small particulate material. In applying bio-oxidation technology to these emissions Texas A&M University-Kingsville (TAMUK) and BioReaction (BRI) evaluated the potential of this equipment to resolve two (2) control issues which are critical to the industry:

- First, the hazardous air pollutant (HAP) emissions (primarily methanol and formaldehyde) and
- Second, the fine particulate and COC from the press exhaust which contribute to visual emissions (opacity) from the stack.

In a field test in 2006, the biological treatment technology met the HAP and COC control project objectives and demonstrated significantly lower energy use (than regenerative thermal oxidizers (RTOs) or regenerative catalytic oxidizers (RCOs), lower water use (than conventional scrubbers) all the while being less costly than either for maintenance. The project was continued into 2007-2008 to assist the commercial partner in reducing unit size and footprint and cost, through added optimization of water recycle and improved biofilm activity, and demonstration of opacity removal capabilities.

Q4 FY2008 Status

The pilot opacity removal field test of the biofiltration technology at the Stimson Lumber Forest Products plant in Gaston, Oregon was completed in August of 2008. The unit deployed included both a biotrickling unit and a biofiltration section. The Wager 6500 opacity meter was successfully installed for measurement of the emissions opacity from the hardboard press vents at the Stimson plant for a pilot test designed to treat approximately 1,000 acfm of emissions. The opacity measurements were collected and compared to visual measurements based on EPA Method 9. Inlet opacity exhibited cyclic loading as expected based the operation of the press vent system. Biofiltration outlet opacity exhibited significant reductions which were further optimized with trickling water recycle rates modifications and air volume throughput variations which further improved opacity and VOC reduction in the outlet stream. The unit was successful enough to confirm a decision by Stimson Lumber to install a field scale Biological Treatment unit including a larger bioscrubbing section and a biofiltration unit as a digester (constructed by Tri-Mer Inc.) to further eliminate VOCs in the outlet gas and liquid phases.

The relationship between measured opacity and VOC emissions removal was evaluated using an RAE Systems organic analyzer and checked by GC-FID. Canister air samples were also measured for VOCs using GC-MS analysis. The removal rates, removal efficiencies and opacity reductions during these experiments are being analyzed to confirm optimal conditions and developed into several refereed journal articles for additional peer review.

.Dr. James Boswell and Dr. Kim Jones of the project team developed and completed a presentation to chemical industry groups on the biofiltration technology at the Texas

Chemical Council's annual meeting on June 12, 2008 in Galveston, Texas. The technology was presented at a session highlighting energy saving technologies for industry.

Private Partner Commercialization Progress

In December of 2007 a 160,000acfm unit was completed in the wood products industry. Start-up was conducted in March and the unit is in full operation controlling the VOC and HAP emissions from an oriented strand board (OSB) press. In addition a 50,000 acfm unit was installed and is in operation on a plywood mill in Oregon. Design and/or construction activities continue on an additional nine (9) bio-oxidation systems in the wood products industry. These units will all start-up by approximately October, 2008. Using bio-oxidation systems (instead of RTOs) in the 11 units that have been or will be started-up this year (2008) will annually save an estimated **7,000,000 therms of natural gas; $70,000,000;** and eliminate the emissions of **80,000 tons of CO_2; and more than 500 tons of NOx**.

Bio•Reaction continued pilot evaluations with a major automobile manufacturer for a biological air treatment system. The pilot applications in the auto industry are being conducted to determine the use on specific paint emission streams that use predominately water soluble solvents. In addition odor removal applications are being assessed for HVAC plant air systems. Also Bio•Reaction is working with a Chinese company on the design and installation of two bio-oxidation units for HAP and odor control in China; and is partnering with a European company for applications in Europe.

Q1 FY2009 Plans

This project received a no-cost extension until February of 2009 to complete the final publications, reports and commercialization updates.

Patents: None this Quarter

Publications/Presentations

Ramirez, D., Chavan, V., Santos, S., Jones, K. (2008) Relative Humidity and Temperature Effect on Solid Phase Micro Extraction for the Monitoring of Volatile Organic Compounds, presented at the 101st Annual Meeting of the Air & Waste Management Association, June 24-27, Portland, OR.

Jones, K., Khilnani, M., Karre, A., Santos, S., Paca, J. (2007) FT-IR Characterization of Biofilms formed on Engineered Biofiltration Media Treating Volatile Organic Emissions for the Forest Products Industry, in *Biotechniques for Air Pollution Control*, Kennes, C. and Veiga, M., eds. Universidade da Coruña, ISBN 978-84-9749-258-4.

Santos, S., Jones, K., Abdul, R., Boswell, J., Paca, J. (2007) Treatment of Wet Process Hardboard Plant VOC Emissions by a Pilot Scale Biological System, *Biochemical Engineering Journal*, v37, n3: 261-270.

Jones, K. (2007) Saving Energy, Saving Earth, *FDM Asia*, v19, n3, April 2007.

Santos, S., Jones, K., Baliwala, L., Abdul, R., Boswell, J. and Cochran, J. (2006) Treatment of Wet Process Hardboard Plant Emissions by a Pilot Scale Biological System, published in the Proceedings of the 2006 USC-TRG Conference on Biofiltration for Air Pollution Control, Long Beach, California, October 18-20.

Jones, K., Santos, S., Baliwala, L., Boswell, J. and Paca, J. (2006) Biological air emissions control for α-pinene and formaldehyde for a forest product industry application with a coupled biotrickling filter and biofilter system, in Proceedings of 17th International Congress of Chemical and Process Engineering CHISA 2006, Prague, Czech Republic, 27–31 August 2006.

Santos, S., Jones, K., and Boswell, J. (2005) Biological Treatment of Air Emissions for Forest Product Industry Applications, presented at the NSF sponsored CREST-RESSACA Conference on Emerging Technologies for a Sustainable Environment, October 20-21, South Padre Island, Texas.

Milestone Status Table:

ID	Tasks/Milestones				
No.		Planned Completion	Actual Completion	Comments	
1.	Bench Scale and Field Scale Unit Design	12/31/04	12/31/04		
2.	Field Pilot Unit Construction	6/30/05	8/15/05		
3.	Field Pilot Unit Startup	7/31/05	8/15/05		
4.	Preliminary Pilot Scale Testing and Field Testing Plan Development	10/1/05	8/15/05		
5.	Optimization of Biotrickling Filter	12/31/05	3/15/06	Field unit 1	
6.	Optimization of Biofilter Section	12/31/05	3/15/06	Field unit 1	
7.	Develop process models	2/28/06	8/31/08		
8.	Optimize water reuse	2/28/06	8/31/08		
9.	Characterize biofilms	2/28/06	8/31/08		
10.	BF Tech Product marketing	8/31/08		Ongoing	
11.	Final Report Phase I Publication	9/1/06	11/1/07	Published BCEJ	
12.	Optimization of Bench BTF	8/31/08	12/31/08		
13.	Optimization of Bench BF	8/31/08	12/31/08		
14.	Final Report Phase II Publication	9/1/08	12/31/08		

Budget Data:

Texas A&M University – Kingsville
Award DE-FC36-04GO14310
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		Note 1		Note 1		
3Q04	9/1/04	9/30/04	0	0	0	0	
4Q04	10/1/04	12/31/04	4,642	4,642	2,000	2,000	
1Q05	1/1/05	3/31/05	3,922	3,922	3,500	3,500	
2Q05	4/1/05	6/30/05	18,955	18,955	15,000	15,000	
3Q05	7/31/05	9/30/05	25,649	25,649	20,000	20,000	
4Q05	10/1/05	12/31/05	26,670	26,670	57,265	57,265	
1Q06	1/1/06	3/31/06	94,944	94,944	57,981	57,981	
2Q06	4/1/06	6/30/06	15,892	15,892			
3Q06	7/31/06	9/30/06	1,983	1,983			
4Q06	10/1/06	12/31/06	16,497	16,497			
1Q07	1/1/07	3/31/07	14,988	14,988			
2Q07	4/1/07	6/30/07	13,611	13,611			
3Q07	7/1/07	9/30/07	11,232	11,232			
4Q07	10/1/07	12/31/07	10,017	10,017			
1Q08	1/1/08	3/31/08	9,511	9,511	3,500	3,500	
2Q08	4/1/08	6/30/08	8,622	8,622	8,500	8,500	
3Q08	7/1/08	9/30/08	34,645	34,645	10,000	10,000	
4Q08	10/1/08	12/31/08	30,920				
1Q09	1/1/09	2/28/09					
Totals			**342,700**	**311,780**	**177,746**	**177,746**	

Federal Share = $192,729 (9/1/04-8/31/06) + $149,971(9/1/06-8/31/08)
* Update quarterly
**Estimated for 2006
General Note: DOE Laboratory partner spending should not be included in the above table. If a DOE Laboratory is a partner, report their spending and spend plan information in the table below (use separate tables if multiple DOE Laboratories are involved).
General Note: The information in this table should be consistent with the information provided in section 10 of the quarterly financial status reports (SF269 or SF269A).
Note 1: Leave blank. Only the actual DOE/Cost Share amounts spent through 6/30/04 are needed.
Note 2: Amount for this quarter and subsequent quarters should be updated as necessary on a quarterly basis. Estimates need to be provided for the entire project. If spending for a given quarter is different than estimated, then the remaining quarter's estimates should be updated to account for the difference. Total DOE and Cost Share amounts should be the same as the Award amount.

Integration of the Mini-Sulfide Sulfite Anthraquinone (MSS-AQ) Pulping Process and Black Liquor Gasification in a Pulp Mill

North Carolina State University

GO16041

Recovery of Sulfur from Simulated Black Liquor Gasification Product Gas - Quarterly Progress Report (July – September, 2008)

RTI conducted a series of tests to determine the technical feasibility of recovering sulfur from a simulated synthesis gas mixture that would be produced by gasification of black liquor. In this sulfur recovery process, the sulfur present in the synthesis gas as H_2S is removed by a regenerable sorbent. During regeneration, the sulfur is removed from the sorbent as SO_2, which is recycled to the MS-AQ pulping process. The sorbent used in this series of tests was RVS-1, which was developed at DOE's National Energy Technology Laboratory to remove H_2S from coal-derived synthesis gas and is commercially available from Sud-Chemie.

The testing was conducted in RTI's high pressure, high temperature sorbent test system, shown in Figure 1. This system included a 2-inch internal diameter quartz fixed-bed reactor equipped with a porous quartz distributor. The quartz reactor was housed within a 4-inch stainless steel pressure vessel. The stainless steel pressure vessel was heated externally by a 3-zone electric furnace. The effluent H_2S concentration from the sorbent bed was monitored with a gas chromatograph equipped with a sulfur chemiluminesence detector.

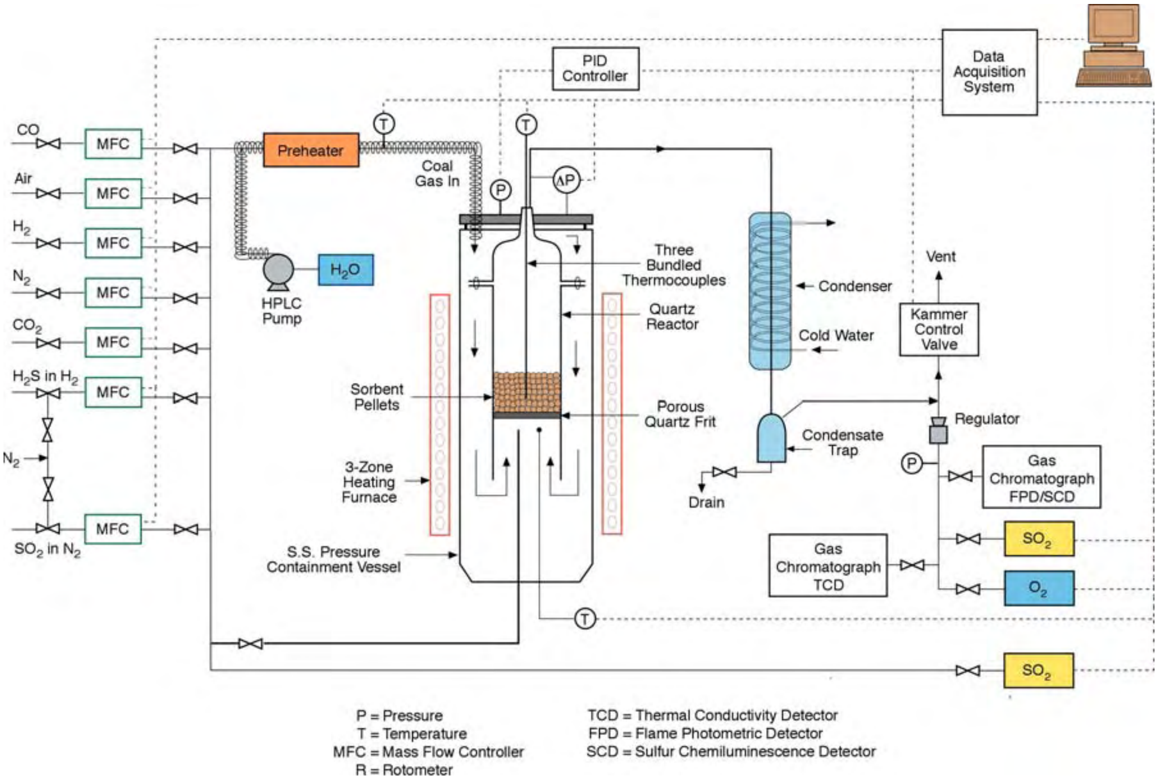


Figure 1. RTI's High Temperature High Pressure Sorbent Test System.

A series of five parametric tests were conducted to demonstrate sulfur removal performance of RVS-1 over a defined window of simulated synthesis gas compositions. The details of the synthesis gas compositions used during these tests are provided in

Table 1. The test consisted of exposing the sorbent to the appropriate synthesis gas mixture until the effluent H_2S concentration exceeded 5,000 ppmv. The synthesis gas was purged from the reactor and the sorbent regenerated with a mixture of 2 vol% O_2 in N_2. During both the sulfur removal and regeneration, the effluent sulfur concentration in the effluent gas was monitored. A new batch of sorbent was used for each test.

Table 1. Test Conditions for Black Liquor Gasification Product Gas Treatment

Component	Volume % Test 1		Volume % Test 2		Volume % Test 3		Volume % Test 4		Volume % Test 5	
	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
H_2O	40	--------	30	-------	20	-------	10	-------	5	-------
H_2S	6	10	7	10	8	10	9	10	9.5	10
H_2	31.2	52	36.4	52	41.6	52	46.8	52	49.4	52
CH_4	3	5	3.5	5	4	5	4.5	5	4.75	5
CO_2	18	30	21	30	24	30	27	30	28.5	30
CO	1.8	3	2.1	3	2.4	3	2.7	3	2.85	3
	100	100	100	100	100	100	100	100	100	100

A typical breakthrough curve showing the H_2S content of the treated gas is shown in Figure 2.

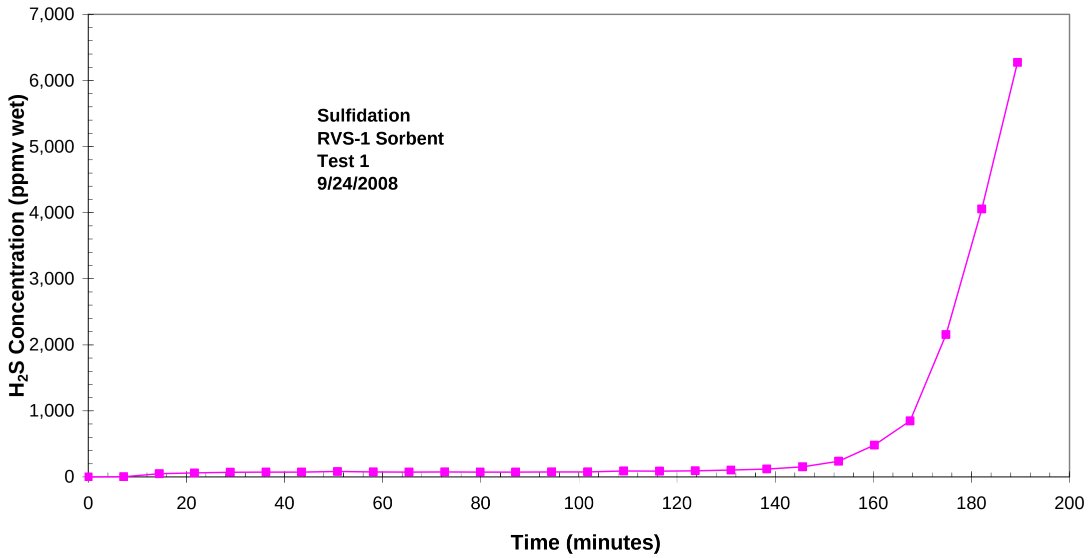


Figure 2. H_2S concentration (wet basis) at sorbent bed exit as a function of sulfidation time for Test 1.

The breakthrough data, shown in Figure 2, were used to calculate the sulfur capacity of the sorbent. Under the testing conditions used, the sorbent capacity was between 18 and 20 wt%. The sorbent was able to reduce the H_2S concentration from between 6 and 10 vol% to below 100 ppmv, which represents > 99% H_2S removal. Data from the regeneration of these sorbents demonstrated that sulfur recovery as SO_2 was between 60 and 80% of the sulfur loaded on to the sorbent. Previous testing with this sorbent has demonstrated that a few cycles are necessary to achieve consistent reproducible performance between subsequent sulfur removal and regeneration cycles. Thus the sulfur recovery for the first cycle observed during this testing may be lower than would be observed after completing between 3 and 5 cycles.

These results demonstrate that the regenerable desulfurization sorbent, RVS-1, can remove > 99% of the sulfur in a synthesis gas stream generated by black liquor gasification and that this sulfur can subsequently be recovered as SO_2.

Direct Causticization for Black Liquor Gasification in a Circulating Fluidized Bed

IPST at Georgia Tech

GO16042

The PI was on leave last quarter and was not able to submit a status report for the period ending September 2008.

Fibrous Fillers to Manufacture Ultra High Ash / Performance Paper

G.R. International

ID14439

QUARTERLY PROGRESS REPORT

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

Covering Period: July 1st through September 30th, 2008

Date of Report: October 31st, 2008

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

Contact(s):
Vijay K. Mathur (Principle Investigator)
Phone: (253) 874-1067
Cell: (253) 951-1720
Lab: (253) 924-6070
Fax: (253) 925-5195
E-mail: griinc@hotmail.com

Project Team: Dr. Chen (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" (producing large quantities of fibrous fillers for commercial trials).

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 pilot scale. It is has also demonstrated their unique performance attributes in paper. Our current focus is 1) build a prototype plant for manufacturing of "Fibrous Fillers" on a commercial scale reactor, the application of "Fibrous Fillers" in paper (proof of concept), 2) to increase the fundamental knowledge of pigment manufacturing and 3) to run commercial paper machine trials. 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 – prototype plant.
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, 5,000 gallon reactor. The material produced from the full scale reactor is used for production scale paper machine trials. These trials are conducted with our industry partners like Grays Harbor Paper Company and Weyerhaeuser Company.

Focus For FY 05, FY06, FY07, and FY08: Validation of Technology on a Commercial Scale

- GRI’s primary focus is to operate a prototype plant for production of fibrous fillers and conduct commercial scale paper trials followed by market evaluation.

- GRI is also working with the University of Washington to study the mechanism of pulp and fibrous filler interaction.

- GRI is also scaling up the production of low-cost, energy efficient engineered filler modifications from our already patented S-PCC (Tech-2), SMP (Tech-4), SNF (Tech-8), SMP-LDD (Tech-6) and SMF (Tech-7).

Key Accomplishments:

TASK I (GRI): Optimization of Manufacture of Silicate Nano-Fibers (SNF) and Silicate Macro-Particle (SMP).

Task I-3.15: Prototype plant construction.

GRI has completed the building and startup of a full-scale prototype plant to produce fibrous/engineered fillers including Tech-2 (S-PCC), Tech-4 (SMP), Tech-6 (SMP-LDD), and Tech-7 SMF. The plant is located at Grays Harbor Paper Company (GHP) in Hoquiam, Washington.

Equipment List:

The following equipment has been purchased/leased for the startup the prototype plant.

Equipment List (Phase I):

1. Manual lime slaking system.
2. Lime screening system.
3. Manual silica slurry preparation system.
4. 5,000-gallon pressure reactor to produce Tech-2 (S-PCC), Tech-4 (SMP), Tech-6 (SMP-LDD) and Tech-7 (SMF).
5. Product screening system.
6. Liquid CO_2 supply system to produce low cost Super-PCC.
7. Pumps and motors.

Phase I construction is estimated to cost $1.0 million+.

These fibrous/engineered fillers will be pumped into a truck and then shipped to customers for commercial paper machine trials.

Budget and Funding:

Due to cost overruns, GRI has run into a shortage of funding. We have, therefore, cut back on buying new equipment, some automation, etc. The revised budget and current funding numbers are given below.

The current budget is as follows:

Budget:

Equipment	$301,429
Instrumentation	$57,824
Electrical	$62,362
Piping	$186,055
Mechanical	$95,021
Engineering	$57,820
Contingency	$20,000
Total	$780,511

Funding:

The following are GRI's current sources of funding:

DOE	$250,000
GRI & Partners	$300,000
GHP (In-kind)	$50,000
Total	$600,000

Shortfall:

We currently have ~$240,000 for accounts payable. We are currently trying to find additional funding. There is a possibility that GRI will have a shortage of funding to operate the plant in 2006 to manufacture Fibrous Filler (SMP-LDD or Tech-6) and Super PCC long enough to fully validate the techno-economic viability of the Fibrous Filler. GRI will require additional funding for FY 2006. GRI currently has a no-cost time extension from the DOE until April 2007.

Additional Equipment List for a Future Phase II Addition:

This prototype plant can be extended in Phase II to a full-scale automated plant. It will require additional equipment. This includes the following:

1. 10,000-gallon high-pressure reactor (600-800 psig) to produce SNF (Tech-8).
2. Heat exchanger to reduce energy consumption.
3. Lime and silica storage silos and bulk handling systems.
4. Automated lime handling and slaking system.

5. Compressor/blowers to take flue gas containing CO_2 from fuel boilers. An alternative will be a CO_2 separation system like amine absorption.
6. Product delivery system (piping from the plant to the paper machine).
7. Product storage tanks.

The prototype plant is located at Grays Harbor Paper Company.

Phase II is estimated to be an additional $2.5 million.

<u>Grays Harbor Paper (GHP) Contract:</u>

GRI received a letter of intent from GHP in May 2005. In December 2005, GHP signed an agreement with GRI for GRI to build the prototype plant at their site. The initial contract is for one year and if GRI's technology is proven to be technically feasible and economically viable, the contract can be extended for 5 years. In Phase I GRI was to supply up to 1000 tons/month of SPCC and 100 tons/month of Silicate Macro-Particles (SMP, SMP-LDD, and SMF) to GHP.

<u>Construction and Timeline:</u>

The construction started in the fourth quarter of 2005 and Phase I is now complete. The prototype plant produces SPCC (Tech-2), Tech-4 (SMP), Tech-6 (SMP-LDD) and Tech-7 (SMF). In Figures I-3.15-1 to I-3.15-7 below the various installed equipment is displayed. All the accompany equipment for making SPCC (Tech-2), Tech-4 (SMP), Tech-6 (SMP-LDD) and Tech-7 (SMF) is installed.

The steam system and the high pressure sealing system were completed in Q2 2006.

Figure I-3.15-1. Reactor for the prototype plant.

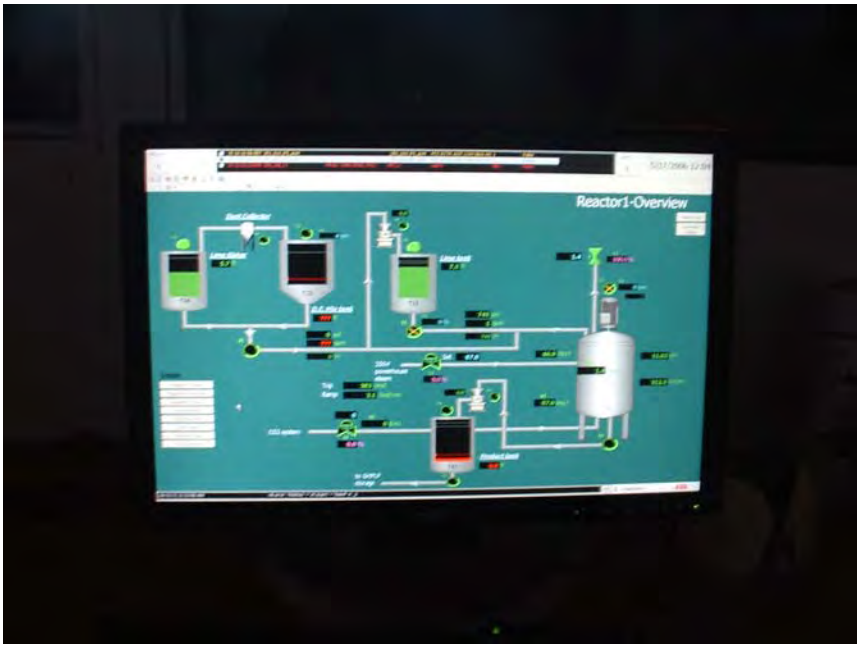


Figure I-3.15-2. Control screen for the ABB control system.

Figure I-3.15-3. Vibrating screen for lime preparation.

Figure I-3.15-4. DE mix tank and lime slaker with associated hoppers. Also pictured is the dust collection system for safe handling of lime and silica.

Figure I-3.15-5. Vibrating screen for product to remove reactor scale.

Figure I-3.15-6. Product storage tank and reject dumpster for the product screen.

Figure I-3.15-7. Reactor, lime slaker, DE mix tank and all associated pumps, piping, hoppers and crane structure.

Task I-3.20 & 21: Commercial production trials of calcium silicates for papermaking ({Tech-4} and/or SMF {Tech-7}).

See Task III-3.17 which described jointly the commercial pigment production and the associated commercial paper machine trial.

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

We have canceled the contract with LLNL.

We have retained, as an advisor, an expert on silicate chemistry, Dr. Della Roy of Pennsylvania State University.

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

Task III-3.17a: Pilot Paper Machine Trial using laboratory produced silicate "Fibrous Filler" (SMP {Tech-4} and/or SMF {Tech-7} and/or SNF {Tech-8}) and

Super Precipitated Calcium Carbonates (S-PCC) at University of Washington's Paper Lab.

Objective:

Using the laboratory reactor located at the Grays Harbor Paper mill site, lab quantities of SMF (Tech-7), SNF (Tech-8), Aragonite S-PCC (Tech-2A) and SMP (Tech-4) were produced. The SMF, SNF, S-PCC, and SMP produced were than utilized on a pilot paper machine at the University of Washington Paper Lab. This trial focused on GP Camas's xerocopy paper.

Approach:

The main focus of this trial was to optimize the addition of PCC, SMP, and SMF to reduce the basis weight and increase the ash of GP's xerocopy paper. Batches of SMP were produced in our 2 gallon laboratory reactor. SNF was also produced in the laboratory reactor. SMF was supplied from a residual batch of SMF from the 5,000 gallon reactor. The secondary focus of this trial is to replace GP's current furnish with SNF. The conditions for a typical batch of SMF, SMP, SNF, and S-PCC are displayed below in Table III-3.17-1 through 4.

Table III-3.17-1: The conditions for a typical SMF (Tech-7) batch in the 5,000 gallon prototype reactor.

Conditions	Typical SMF (Tech-7) Batch
Solids Concentration (#/gal)	0.35
Bulk Reaction Temperature (^{o}C)	200
Heating Up Time (min)	90
Bulk Reaction Time (min)	240

Table III-3.17-2: The conditions for a typical SMP (Tech-4) batch in the 2 gallon labratory reactor.

Conditions	Typical SMP (Tech-4) Batch
Solids Concentration (#/gal)	0.6
Bulk Reaction Temperature (^{o}C)	200
Heating Up Time (min)	75
Bulk Reaction Time (min)	180

Table III-3.17-3: The conditions for at typical SNF (Tech-8) batch in the 2 gallon laboratory reactor.

Conditions	Typical SNF (Tech-8) Batch
Solids Concentration (#/gal)	0.4
Bulk Reaction Temperature (^{o}C)	250
Heating Up Time (min)	150
Bulk Reaction Time (min)	120

Table III-3.17-4: The conditions for a typical S-PCC (Tech-2A) batch in the 2 gallon laboratory reactor.

Conditions	Typical SMF (Tech-7) Batch
Solids Concentration (#/gal)	0.6
Bulk Reaction Temperature (^{o}C)	200
Heating Up Time (min)	75
Bulk Reaction Time (min)	180

The design of this study will employ a statistical mixtures design. A geometrical representation or Part I is given in Fig.III-3.17-1. The test results will be analyzed using the optimum seeking computer programs.

Part I: Effect of pigments

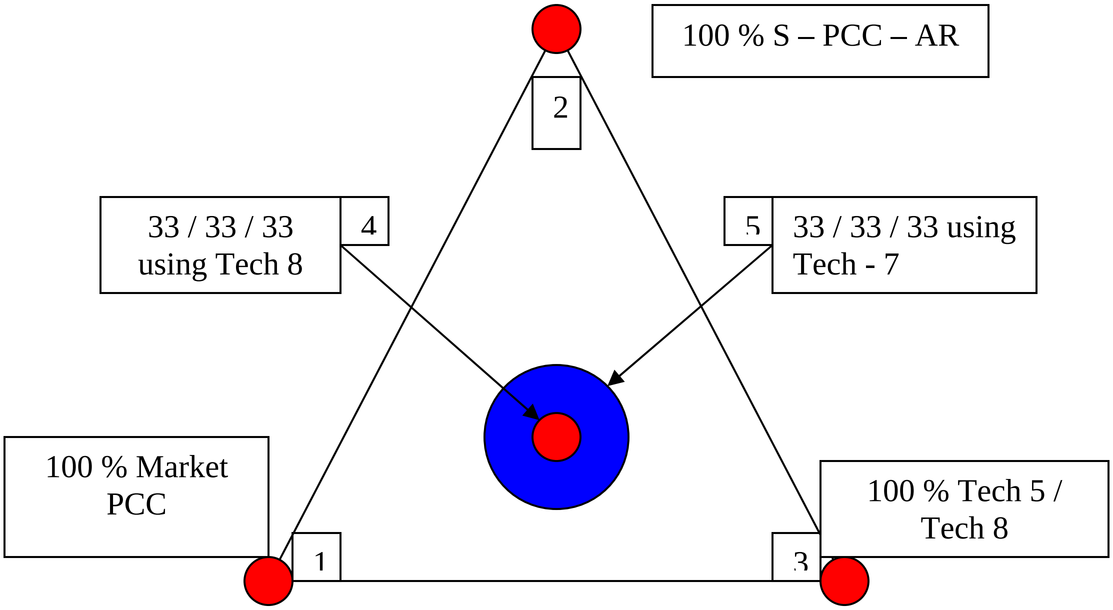


Figure III-3.17-1: Design of Pigments

Note that in addition to the above mentioned sheets, there will also be a no – filler sheet (i.e. pulp only) and a SNF only filled set of sheets.

Part II: Effect of increasing ash levels

Ash Levels

1. 18 %
2. 22 %
3. 26 %

Part III: Effect of reducing basis weight

Basis Weights

1. 20.5 #

2. 19.5 #

Method:
The pulp will be diluted to 0.6 % consistency. A measured amount of pulp will be placed in a beaker and the various chemicals and additives will be added in the same order and approximately same residence time as Camas's # 20 paper machine. The paper will be made according to TAPPI standards.

Pressing:	Constant Pressure Conditions
Drying:	Constant Drying Conditions
Calendaring:	Calendared to Constant Smoothness (Variable Pressures)

Results:

The paper samples taken from each condition and tested with TAPPI standard conditions and the data are in Table III-3.17A-1 in Appendix III-3.17A. Based on the results, 2 main mixtures were seen to offer improvements from this study. Both were 3 – Way blends. The first was made using Tech – 8. The second was made using Tech – 7. The conditions looked at had higher ash levels and lower basis weights

Wet End
GRI's silicates were found to offer improvements in both press solids and drying times, based on either ash increase or basis weight reduction. When the ash level was raised, but the basis weight kept constant, the drying time dropped 39.8 % and the press solids increased 18.5 %. When the basis weight was dropped, maintaining the ash level at the same time, the drying time decreased by 22.8 % and the press solids improved by 9.6 %.

Physical Properties
The ash level for both blends was 27 % greater than the PCC control.

The basis weight of the Tech – 8 blend was lower than the control by 6.3 %. The basis weight of the Tech – 7 blend was lower by 6.8 %.

The caliper for the Tech – 8 blend was higher by 3.9 %. The Tech – 7 blend's caliper was up by 2.9 %.

The bulk for both blends was higher (+11.4 % and 11.2 % respectively).

The smoothness of both blends was slightly higher (+ 7.6 % and 1.2 % respectively).

Strength Properties
The stiffness for both blends was higher in both directions. For the Tech – 8 blend, the MD stiffness improved by 36.3 % while the CD stiffness improved by 10.1 %. For the Tech – 7 blend, the MD stiffness was 25.8 % better and the CD stiffness was improved by 2.3 %.

The Tensile Index for the Tech – 8 blend was mixed. The MD tensile index was higher (+ 4.6 %), but the CD tensile index was lower (- 22.3 %). The tensile index for the Tech – 7 blend was higher in both directions (+ 7.0 % MD and + 9.7 % CD).

Optical Properties

Both blends had a higher brightness than the control (+ 0.3 points Tech – 8 and + 0.4 points Tech – 7).

Both blends lost opacity (- 2.9 points Tech – 8 and – 2.2 points Tech – 7).

Conclusions and Discussion:

GRI's product-containing sheets at lower basis weight and higher ash compared to market PCC sheets were:

- Able to dry faster
- Required less energy to dry
- Improved bulk and caliper
- Greatly improved stiffness
- Improved the Tensile in most cases
- Improved the brightness
- Lost opacity.

Based on these results, another trial using a larger pilot paper machine will be conducted.

TASK IV - Western Michigan University: Optimization of surface treatment formulations.

After the initial work, the work had been completed.

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	TASK / MILESTONE DESCRIPTION	Planned Completion Date	Actual Completion Date	Comments
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	12/31/02	Completed
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	6/30/03	Completed
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	8/31/03 9/30/03	Completed Completed
Year 2				
I-2.1	Empirical process models and response surface analysis employing the technique of designed optimization experimentation (DOE)	3/31/04	3/31/04	Completed
I-2.2	Preliminary design for a commercial "Fibrous Filler" plant	3/31/04	3/31/04	Completed
I-2.3	Preliminary design for a prototype "Fibrous Filler" plant	6/30/04	6/30/04	Completed
I-2.4	Additional production trials using 10,000-gallon reactors (Toll Manufactures)	10/30/04	10/30/04	Completed
Year 3	***Goal: Commercial Validation of Fibrous and Engineered Fillers Manufacturing (Tech-4, Tech-6, Tech-8, and SPCC)***			
I-3.1	Lab scale (2.0 gallon reactor) study a) Complete process model and optimization for SNF b) Screening of alternate raw materials screening and optimization	3/31/05		80% Completed Ongoing
I-3.2	Pilot scale (30 gallon reactor) study a) Scale up and verification of lab scale process models b) Scale up with new raw materials c) Repeatability of SMP d) Repeatability of SNF	3/31/05		70% Completed Ongoing

ID Number Scheme: Task - Year . Subtask	**TASK / MILESTONE DESCRIPTION**	**Planned Completion Date**	**Actual Completion Date**	**Comments**
I-3.3	Scale-up/optimization and repeatability study on the pilot scale (30-gallon reactor)	3/31/05		Completed Ongoing
I-3.4	Optimization of Super-PCC (Tech 2) in lab and pilot scale	3/31/05	8/31/05	Completed
I-3.5	Detailed design and engineering of prototype plant to manufacture calcium silicates	3/31/05	6/30/05	Completed
I-3.6	Lab-scale reactor raw material screening (lime and silica)	6/30/05	6/30/05	Completed
I-3.7	Development of a new fibrous filler (Tech 6) for reduced drying energy	6/30/05	3/30/06	95% Completed Ongoing
I-3.8	Scale-up of S-PCC manufacturing to the pilot scale.	6/30/05	6/30/05	Completed
I-3.9	Prototype plant construction started. a) Equipment purchase. b) Business agreements. c) Construction.	6/30/05	3/30/06	Completed
I-3.10	Process models for SMP and SNF and optimize process with alternate raw materials	9/30/05		30% Completed Ongoing
I-3.11	Process models for S-PCC or Tech-2.	9/30/05	9/30/05	Completed
I-3.12	Pilot-scale optimization of alternate lower cost raw materials, process conditions to manufacture, lower cost of silicates (less than or equal to cellulose fiber)	9/30/05		Ongoing
I-3.13	Preliminary PCC-silicate hybrid work	9/30/05		Abondoned*
I-3.14	Final Optimization of raw materials, process conditions to manufacture most cost effective high performance silicate products (Nano-Fibers, Macro-Particles)	10/31/05		
I-3.15	Prototype plant construction complete	10/30/05	4/01/06	Completed
I-3.16	Commercial production trials of nano-carbonates (SPCC or Tech-2)	12/31/05	3/31/06	Completed
I-3.17	Commercial production trials of calcium silicates for papermaking	12/31/05	12/31/06	90% Completed
I-3.18	Ramp time and soak time influences at the pilot-scale.	1/31/06		Completed
I-3.19	Detailed design and engineering of commercial plant to manufacture calcium silicates (Phase II)	12/31/05	12/31/06	Ongoing
I-3.20	Scale of Manufacturing of Silicate Macro Particles	9/30/07		Ongoing
I-3.21	Develop Low Energy using Silicate Micro-Fiber (Tech-7)	9/30/07		Ongoing

ID Number Scheme:	*Task - Year . Subtask* **TASK / MILESTONE DESCRIPTION**	**Planned Completion Date**	**Actual Completion Date**	**Status**
Task II	**(Lawrence Livermore National Laboratory) To study and elucidate the mechanism of Silicate Nano-Fiber and Silicate Macro Particle formation**			
Project task with LLNL cancelled and will be restarted with Pennsylvania State University.				
Year 1				
II-1.1	Characterization of GRI's Silicate Nano-Fibers (SNF)	9/30/03		Completed
II-1.2	Lab preparation of GRI standard silicate products (SNF or T-8) in LLNL reactors	12/31/03		Unable to complete
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		Completed
II-1.4	Special test to characterize silicate products using atomic force microscopy (AFM), Vertical scanning interferometer	12/31/03		Not Completed
Year 2	***Goal: Optimization***			
II-2.1	Preliminary mechanism of "Fibrous Filler" formation	6/30/04	6/30/04	Not Completed
II-2.2	Study the effect of impurities on formation of silicates	6/30/04		Not Completed
II-2.3	Review LLNL's progress by GRI	6/30/04	6/30/04	Completed
II-2.4	Study the alternate lower cost raw materials, silica, lime source for T-8 Silicate Nano-Fibers (SNF)	6/30/04		Not Completed
II-2.5	Review LLNL's progress with DOE	9/31/04	9/31/04	Completed
II-2.6	Process modeling using thermodynamic database and kinetic database available at LLNL	10/31/04		
II-2.7	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-2.8	Improving the process of manufacturing silicate products by employing catalysts, etc.	12/31/04		
Year 3	***Project Task Cancelled***			
II-3.1	Pennsylvania State University: Characterization of mechanism of formation of fibrous filler.	6/30/05		

II.3.2	Final kinetic and thermodynamic models to support design of commercial plant	9/30/05	6/30/06	

ID Number Scheme: *Task - Year . Subtask*	**TASK / MILESTONE DESCRIPTION**	**Planned Completion Date**	**Actual Completion Date**	**Comments**
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	7/31/03	Completed
III-1.2	Evaluate paper manufactured during production trial (both in lab and in field)	9/30/03	9/30/03	Completed
III-1.3	To study the effect of high "Fibrous Filler" (25%-50%) content on paper properties and paper processes (combination of silicate nano-fibers and macro-particles)	12/31/03	12/31/03	Completed
III-1.4	Second and third commercial scale paper machine trial	11/30/03	11/30/03	Completed
III-1.5	Preliminary system wide energy audit comparing existing pulp and paper mills vs. future mills with GRI "Fibrous Filler" on site plants	12/30/03	12/30/03	Completed

Year 2

III-2.1	Preliminary system wide energy audit comparing existing pulp and paper mills vs. future mills with GRI "Fibrous Filler" on site plants	3/31/04	3/31/04	Completed
III-2.2	Paper machine productions trials	10/31/04	10/31/04	Several trials completed
III-2.3	Screen new wet end additives to enhance sheet strength	12/30/05		

Year 3 ***Goal: Validation of Technology of Fibrous/Engineered Fillers***

III-3.1	Study the effects of pressing on drying energy	3/31/05	3/31/05	Completed
III-3.2	Pilot paper machine trial to evaluate Super-PCC, SMP, and SNF in Germany	3/31/05	3/31/05	Completed
III-3.3	Paper quality / performance (printing, dusting)	6/30/05	12/31/06	80% Completed Ongoing
III-3.4	Paper machine trial of S-PCC.	6/30/05	6/30/05	Completed
III-3.5	Energy reduction in papermaking processes due to: a) Higher pressing and lower drying b) Lower refining of SMP and SNF	6/30/05 12/30/05		85% Completed Ongoing
III-3.6	Study the effect of pigment on strength additives, internal sizing, etc. a) Lab-scale evaluation b) Pilot paper machine evaluation	9/30/05	12/31/06	70% Completed Ongoing

III-3.7	Screen new wet end additives to enhance sheet strength and retention	9/30/05	12/31/06	70% Completed Ongoing

ID Number Scheme: Task - Year . Subtask

	TASK / MILESTONE DESCRIPTION	**Planned Completion Date**	**Actual Completion Date**	**Comments**
III-3.8	Confirm value propositions –TiO_2 reduction, basis weight reduction, increase in ash (fiber replacement)	9/30/05	12/31/06	75% Completed Ongoing
III-3.9	New value added paper product development (e.g., inkjet paper, 40% filler composite)	12/30/05		Abandoned*
III-3.10	Study the mechanism of fiber to Silicate Nano-Fiber bonding at higher ash levels (20-50%)	12/30/05		20% Completed, Abandoned*
III-3.11	Commercial paper machine production using commercially produced silicate “Fibrous Filler” (nano-fibers, macro-particles)	12/30/05	12/31/06	75% Completed Ongoing
III-3.12	Field trial of paper produced with commercially produced T-4 and T-8	12/31/05	12/31/06	75% Completed Ongoing
III-3.13	Full life cycle analysis of existing pulp and paper mills vs. future pulp and paper mills with GRI “Fibrous Filler” on site plants	3/31/06		Abandoned*
III-3.14	Electrochemical charge neutralization in paper	6/30/06	12/31/06	Abandoned*
III-3.15	Commercial Paper Machine Trials using Silicate Macro Particles (Grays Harbor Paper Co., Hoquiam, WA)	9/30/07		95% Completed Ongoing
III-3.16	Commercial Paper Machine Trials using a modern paper machine (Georgia Pacific, Camas, WA)	9/30/07		90 % Completed Ongoing
III-3.17	Pilot and Commercial Paper Machine trials using a modern paper machine (Domtar Paper Company)	7/1/10		35 % Completed Ongoing

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

Task completed.

Year 1

IV-1.1	Determine the compatibility of starch, PVOH binders and silicate pigments	6/30/03		Completed
IV-1.2	Maximize coating solids using five different binders	6/30/03		Completed
IV-1.3	Determine minimum pigment-binder ratio for inkjet print quality	9/30/03		Completed
IV-1.4	Study the effect of temperature and solids on silicate coatings	9/30/03		Completed

IV-1.5	Study the dry coating structure, ink density comparison with silica gel	9/30/03		Completed
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 – TASK ON HOLD	12/31/03		Completed

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

IV-2.1	Lab scale Optimization of coating formulation using GRI's fibrous fillers, binders, water fasteners, etc.	6/30/04		No Other Work Done This Quarter

ID Number Scheme: Task - Year . Subtask		**Planned Completion Date**	**Actual Completion Date**	**Comments**
	TASK / MILESTONE DESCRIPTION			

Year 3 **TASK ON HOLD**

IV-3.1	Comparison of optimum formulation with other pigments	6/30/05		No Work
IV-3.2	Pilot coater (cylindrical lab coater) a) Application of optimum coating formulation on a pilot CLC coater	6/30/05		No Work
IV-3.3	Analyze the data and final reports	9/30/05		No Work

*No Funding Available.

**New Task.

Budget Data (as of December 31st, 2006):

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	9/30/04	Note 1	834,325	Note 1	549,600	1,383,925
4Q04	10/1/04	12/31/04	175,000	136,861	75,000	158,922	1,679,708
1Q05	1/1/05	3/31/05	175,000	147,797	75,000	39,200	1,866,705
2Q05	4/1/05	6/30/05	175,000	158,061	75,000	39,200	2,063,966
3Q05	7/1/05	9/30/05	175,000	155,009	75,000	141,100	2,360,075
4Q05	10/1/05	12/31/05	175,000	139,734	75,000	39,200	2,539,009
1Q06	1/1/06	3/31/06	175,000	119,952	75,000	199,200	2,858,161
2Q06	4/1/06	6/30/06	0	98,820	75,000	159,200	3,116,181
3Q06	7/1/06	9/30/06	0	45,325	75,000	159,200	3,320,706
4Q06	10/1/06	12/31/06	0	39,629	75,000	79,200	3,439,535
1Q07	1/1/07	3/31/07	0	33,801	75,000	79,200	3,552,536
2Q07	4/1/07	6/30/07	0	58,126	75,000	40,000	3,650,662
3Q07	7/1/07	9/30/07	0	34,062	75,000	40,000	3,724,724
4Q07	10/1/07	12/31/07	0	41,701	75,000	40,000	3,806,425
1Q08	1/1/08	3/31/08	0	34,378	75,000	40,000	3,880,803
2Q08	3/1/08	6/30/08	0	44,818	75,000	30,000	3,955,621
3Q08	7/1/08	9/30/08	0	73,445	75,000	0	4,029,066
4Q08	10/1/08	12/31/08					
1Q09	1/1/09	3/31/09					
Totals			**2,100,000**	**2,195,844**	**1,200,000**	**1,833,222**	**4,029,066**

			Approved Spending Plan			**Actual Spent to Date**		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	04/03	03/04	700,000	300,000	1,000,000	537,415	399,000	936,415
Year 2	04/04	03/05	700,000	300,000	1,000,000	581,568	348,722	930,290
Year 3	04/05	03/06	700,000	300,000	1,000,000	572,756	418,700	991,456
Year 4	04/06	03/07	0	150,000	150,000	217,575	476,800	694,375
Year 5	04/07	03/08	0	0	0	168,267	160,000	328,267
Year 6	04/08	03/09	0	0	0	118,263	30,000	148,263
		Totals	2,100,000	975,000	3,075,000	2,195,844	1,833,222	4,029,066

Plans for the Next Quarter

Task I

I-3.20 Commercial scale production trials of Silicate Micro-Fiber (SMF).
I-3.21 Commercial scale production trials of Silicate Macro-Particles (SMP).

Task II – LLNL / Pennsylvania State University

Task canceled.

Task III

I-3.12: Optimization of Alternative Silica Sources in pilot (30 –gallon) reactor

Task IV – Western Michigan University

Task completed.

Appendix III-3.17A. Task III-3.17: Pilot Paper Machine Data from the University of Washington

Table III-3.17A 1: Pilot Paper Machine Test Data

Description	Drying Time (min)	Press Solids (%)	Total Ash (%)	CaSi (%)	PCC (%)	Basis Weight (#/3000 ft2)	Calendered		Gurley Porosity (sec/100cc air)	Calendered Haggerty Smoothness (Sheffiled Units)	
							Caliper (mils)	Bulk (cc/g)		Front	Back
Control	19.25	39.886	0.2%	-0.6%	0.7%	35.9	3.90	1.69	3.0	295	275
Market PCC (19 #)	11.02	32.803	17.3%	1.0%	16.3%	44.1	4.37	1.54	3.9	218	182
Market PCC (19 #)	13.03	44.300	21.2%	0.4%	20.8%	42.6	4.39	1.60	2.9	224	180
Market PCC (19 #)	18.07	35.334	33.1%	2.5%	30.6%	42.5	4.02	1.48	3.0	183	164
Aragonite PCC	10.09	37.488	17.7%	0.8%	16.9%	45.0	4.34	1.56	5.1	222	211
Aragonite PCC	13.3	39.130	19.3%	12.3%	7.1%	41.0	4.23	1.59	6.1	202	171
Aragonite PCC	23.43	36.836	33.0%	3.4%	29.7%	43.3	4.15	1.48	3.3	217	188
T5 / T8	19.27	36.956	15.0%	12.7%	2.3%	44.0	6.33	2.31	1.5	331	319
T5 / T8	17.44	34.647	21.7%	7.6%	14.1%	42.7	4.63	1.70	3.4	221	201
T5 / T8	23.57	31.744	27.4%	24.8%	2.6%	41.0	4.43	1.69	5.9	149	139
3 - Way with T8	14.12	38.453	16.8%	4.9%	11.9%	45.7	4.55	1.56	4.4	229	199
3 - Way with T8	17.06	38.422	20.2%	7.4%	12.8%	43.4	4.51	1.63	4.6	239	197
3 - Way with T8	19.52	36.449	31.2%	11.6%	19.6%	42.4	4.31	1.59	3.7	166	143
3-Way with T7	8.52	36.444									
3-Way with T7	25.06	37.911									
3-Way with T7	13.52	36.711									
3 - Way with T8 (18 #)	8.51	35.950	17.9%	5.7%	12.3%	40.9	5.35	2.04	1.5	350	335
3 - Way with T8 (18 #)	7.34	37.196	21.6%	6.7%	14.9%	41.3	4.54	1.71	2.1	235	224
3 - Way with T8 (18 #)			25.3%	7.9%	17.4%	44.4	4.61	1.63	2.7	219	203
3 - Way with T7 (18 #)			18.1%	5.5%	12.6%	40.7	4.48	1.70	2.4	241	225
3 - Way with T7 (18 #)	12.36	33.613	22.0%	5.7%	16.2%	41.1	4.50	1.71	2.6	221	209
3 - Way with T7 (18 #)	7.44	39.828	26.8%	7.2%	19.6%	42.2	4.46	1.64	3.4	208	185

Table III-3.17A 2: Paper Test Data

Description	MD Stiffness (taber)	CD Stiffness (taber)	RMS Stiffness (taber)	Tensile Strength (kN/m)	MD Tensile Index (Nm/g)	TEA	Tensile Strength (kN/m)	CD Tensile Index (Nm/g)	TEA	Tensile Strength (lb/in)	RMS Tensile Index (lb*m2/g/in)	TEA	(
Control	1.04	0.36	0.73	3.50	59.9	3.722	1.19	20.4	2.603	2.62	44.7	3.21	
Market PCC (19 #)	1.39	0.37	0.95	2.07	28.9	1.478	0.77	10.7	1.175	1.56	21.8	1.34	
Market PCC (19 #)	1.19	0.28	0.80	1.91	27.6	1.362	0.53	7.6	0.462	1.40	20.3	1.02	
Market PCC (19 #)	0.84	0.29	0.59	0.89	12.8	0.325	0.37	5.3	0.240	0.68	9.8	0.29	
Aragonite PCC	1.15	0.35	0.80	1.96	26.7	1.123	0.94	12.8	1.415	1.54	21.0	1.28	
Aragonite PCC	1.18	0.37	0.82	1.96	29.4	1.292	0.71	10.7	0.725	1.48	22.1	1.05	
Aragonite PCC	0.86	0.22	0.57	1.12	15.9	0.420	0.40	5.7	0.298	0.84	11.9	0.36	
T5 / T8	4.04	0.74	2.78	2.58	35.9	1.005	0.75	10.5	0.820	1.90	26.5	0.92	
T5 / T8	1.34	0.40	0.93	2.12	30.5	1.478	0.63	9.0	0.623	1.56	22.5	1.13	
T5 / T8	1.37	0.41	0.95	1.56	22.5	0.665	0.49	7.3	0.425	1.16	17.3	0.56	
3 - Way with T8	1.65	0.54	1.17	2.54	34.6	1.820	0.82	11.0	0.898	1.89	25.3	1.44	
3 - Way with T8	1.57	0.44	1.09	1.99	29.8	0.960				1.41	20.0	0.68	
3 - Way with T8	1.16	0.44	0.84	1.28	18.1	0.534	0.47	6.8	0.372	0.96	13.9	0.46	
3-Way with T7													
3-Way with T7													
3-Way with T7													
3 - Way with T8 (18 #)	2.27	0.57	1.57	2.23	33.6	1.060	0.78	11.7	0.620	1.67	25.1	0.87	
3 - Way with T8 (18 #)	1.89	0.40	1.28	2.03	30.2	0.810	0.56	8.3	0.240	1.49	22.2	0.60	
3 - Way with T8 (18 #)	1.79	0.41	1.21	1.96	27.1	0.790	0.45	6.2	0.140	1.42	19.6	0.57	
3 - Way with T7 (18 #)	2.00	0.46	1.36	2.45	36.9	1.217				1.73	26.1	0.86	
3 - Way with T7 (18 #)	1.75	0.37	1.17	2.08	31.0	1.003	0.79	11.8	0.940	1.57	23.5	0.97	
3 - Way with T7 (18 #)	1.46	0.35	0.98	1.94	28.2	0.753	0.70	10.2	0.833	1.46	21.2	0.79	

Table III-3.17A 3: Paper Test Data

Description	Brightness (Technobryte)	Opacity (Technobryte)
Control	78.9	68.0
Market PCC (19 #)	85.6	86.3
Market PCC (19 #)	86.2	84.8
Market PCC (19 #)	88.2	87.3
Aragonite PCC	85.5	84.0
Aragonite PCC	85.1	82.5
Aragonite PCC	88.4	86.9
T5 / T8	83.8	82.6
T5 / T8	85.9	84.2
T5 / T8	85.7	81.2
3 - Way with T8	85.1	85.2
3 - Way with T8	86.0	84.2
3 - Way with T8	87.6	85.6
3-Way with T7		
3-Way with T7		
3-Way with T7		
3 - Way with T8 (18 #)	85.4	82.6
3 - Way with T8 (18 #)	85.9	83.4
3 - Way with T8 (18 #)	86.4	85.7
3 - Way with T7 (18 #)	85.3	82.3
3 - Way with T7 (18 #)	85.9	84.1
3 - Way with T7 (18 #)	86.3	85.3

Table III-3.17A 4: Paper Test Comparison

Description	Drying Time (min)	Press Solids (%)	Total Ash (%)	CaSi (%)	PCC (%)	Basis Weight (#/3000 ft2)	Calendered Caliper (mils)	Calendered Bulk (cc/g)	Gurley Porosity (sec/100cc air)	Calendered Haggerty Smoothness (Sheffiled Units) Front	Calendered Haggerty Smoothness (Sheffiled Units) Back
Difference from 18 % Market											
Market PCC (19 #)	18.24%	35.05%				-3.56%	0.38%	4.36%	-25.11%	2.83%	-1.10%
Market PCC (19 #)	63.97%	7.72%				-3.64%	-8.12%	-3.80%	-21.65%	-15.98%	-10.08%
Aragonite PCC	-8.44%	14.28%				2.04%	-0.75%	1.61%	32.03%	1.68%	15.86%
Aragonite PCC	20.69%	19.29%				-6.99%	-3.21%	3.36%	58.87%	-7.34%	-5.77%
Aragonite PCC	112.61%	12.29%				-1.80%	-5.21%	-3.36%	-15.58%	-0.46%	3.30%
T5 / T8	74.86%	12.66%				-0.28%	44.75%	50.44%	-61.04%	51.76%	75.44%
T5 / T8	58.26%	5.62%				-3.24%	5.86%	10.48%	-11.26%	1.15%	10.45%
T5 / T8	113.88%	-3.23%				-7.03%	1.25%	10.28%	51.95%	-31.50%	-23.37%
3 - Way with T8	28.13%	17.22%				3.68%	3.94%	1.45%	12.99%	5.12%	9.62%
3 - Way with T8	54.81%	17.13%				-1.72%	3.18%	5.96%	19.48%	9.56%	8.43%
3 - Way with T8	77.13%	11.12%				-3.88%	-1.35%	3.30%	-5.19%	-23.70%	-21.63%
3-Way with T7	-22.69%	11.10%									
3-Way with T7	127.40%	15.57%									
3-Way with T7	22.69%	11.91%									
3 - Way with T8 (18 #)	-22.78%	9.59%				-7.31%	22.32%	32.80%	-61.90%	60.47%	84.33%
3 - Way with T8 (18 #)	-33.39%	13.39%				-6.31%	3.85%	11.43%	-46.75%	7.57%	23.10%
3 - Way with T8 (18 #)						0.72%	5.39%	5.89%	-28.83%	0.61%	11.37%
3 - Way with T7 (18 #)						-7.67%	2.53%	10.96%	-38.53%	10.63%	23.74%
3 - Way with T7 (18 #)	12.16%	2.47%				-6.79%	2.90%	11.23%	-33.77%	1.15%	14.94%
3 - Way with T7 (18 #)	-32.49%	21.41%				-4.48%	2.01%	6.84%	-12.12%	-4.43%	1.47%

Table III-3.17A 5: Paper Test Comparision

Description	MD Stiffness (taber)	CD Stiffness (taber)	RMS Stiffness (taber)	Tensile Strength (kN/m)	MD Tensile Index (Nm/g)	TEA	Tensile Strength (kN/m)	CD Tensile Index (Nm/g)	TEA	Tensile Strength (lb/in)	RMS Tensile Index (lb*m2/g/in)	TEA (
)ifference from 18 % Market												
Market PCC (19 #)	-14.41%	-22.37%	-15.99%	-7.67%	-4.27%	-7.89%	-31.78%	-29.27%	-60.71%	-10.26%	-6.94%	-23.86%
Market PCC (19 #)	-39.38%	-21.46%	-37.77%	-57.16%	-55.54%	-78.02%	-52.21%	-50.41%	-79.57%	-56.53%	-54.89%	-78.61%
Aragonite PCC	-17.17%	-5.02%	-16.04%	-5.56%	-7.45%	-24.01%	21.91%	19.47%	20.43%	-1.81%	-3.77%	-4.33%
Aragonite PCC	-15.25%	0.91%	-13.49%	-5.29%	1.83%	-12.63%	-7.68%	-0.74%	-38.30%	-5.58%	1.52%	-21.56%
Aragonite PCC	-38.30%	-39.27%	-39.53%	-45.89%	-44.89%	-71.59%	-48.24%	-47.29%	-74.68%	-46.17%	-45.18%	-72.74%
T5 / T8	190.76%	103.65%	192.91%	24.31%	24.31%	-32.02%	-2.38%	-2.11%	-30.21%	21.38%	21.72%	-31.31%
T5 / T8	-3.24%	9.59%	-1.62%	2.00%	5.76%	0.00%	-18.62%	-15.89%	-46.95%	-0.28%	3.06%	-15.04%
T5 / T8	-1.32%	13.24%	0.60%	-24.84%	-22.00%	-55.02%	-36.44%	-31.63%	-63.83%	-26.15%	-20.57%	-58.21%
3 - Way with T8	18.97%	48.40%	23.60%	22.36%	19.92%	23.11%	6.28%	2.51%	-23.55%	20.52%	16.25%	7.48%
3 - Way with T8	13.21%	20.55%	14.68%	-3.93%	3.29%	-35.06%	-100.00%	-100.00%	-100.00%	-9.96%	-8.39%	-49.16%
3 - Way with T8	-16.57%	20.55%	-11.77%	-38.32%	-37.19%	-63.88%	-39.46%	-37.02%	-68.37%	-38.46%	-35.98%	-65.55%
3-Way with T7												
3-Way with T7												
3-Way with T7												
3 - Way with T8 (18 #)	63.27%	56.62%	65.38%	7.73%	16.23%	-28.30%	0.91%	8.87%	-47.23%	6.92%	15.36%	-34.97%
3 - Way with T8 (18 #)	36.25%	10.05%	34.66%	-1.98%	4.62%	-45.21%	-27.24%	-22.34%	-79.57%	-4.70%	1.73%	-55.26%
3 - Way with T8 (18 #)	29.05%	11.87%	28.16%	-5.64%	-6.32%	-46.56%	-41.66%	-42.07%	-88.09%	-9.26%	-9.90%	-57.51%
3 - Way with T7 (18 #)	43.70%	26.03%	43.49%	17.97%	27.78%	-17.70%	-100.00%	-100.00%	-100.00%	10.57%	19.76%	-35.57%
3 - Way with T7 (18 #)	25.81%	2.28%	23.99%	0.10%	7.40%	-32.13%	2.27%	9.73%	-20.00%	0.37%	7.68%	-27.19%
3 - Way with T7 (18 #)	4.80%	-4.11%	3.82%	-6.65%	-2.28%	-49.04%	-9.36%	-5.12%	-29.15%	-6.98%	-2.62%	-40.55%

Table III-3.17A 6: Paper Test Comparison

Description	Brightness (Technobryte)	Opacity (Technobryte)
ifference from 18 % Market		
Market PCC (19 #)	0.62	-1.45
Market PCC (19 #)	2.62	1.05
Aragonite PCC	-0.08	-2.33
Aragonite PCC	-0.48	-3.78
Aragonite PCC	2.78	0.58
T5 / T8	-1.82	-3.65
T5 / T8	0.33	-2.13
T5 / T8	0.10	-5.13
3 - Way with T8	-0.45	-1.10
3 - Way with T8	0.37	-2.07
3 - Way with T8	2.00	-0.70
3-Way with T7		
3-Way with T7		
3-Way with T7		
3 - Way with T8 (18 #)	-0.23	-3.67
3 - Way with T8 (18 #)	0.30	-2.88
3 - Way with T8 (18 #)	0.85	-0.60
3 - Way with T7 (18 #)	-0.33	-3.97
3 - Way with T7 (18 #)	0.35	-2.20
3 - Way with T7 (18 #)	0.67	-0.95

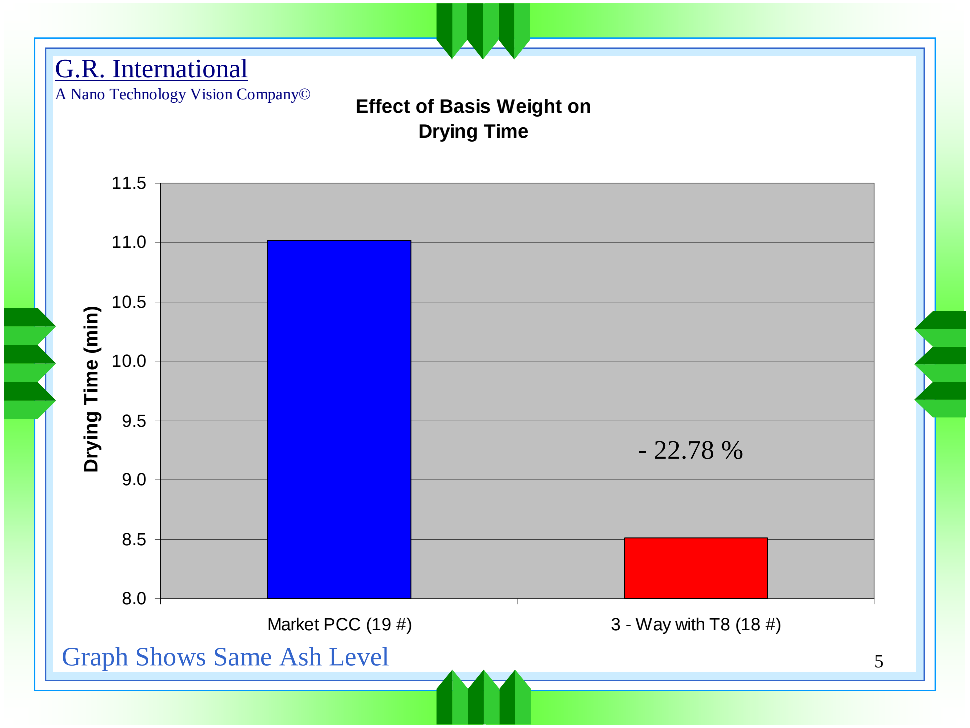
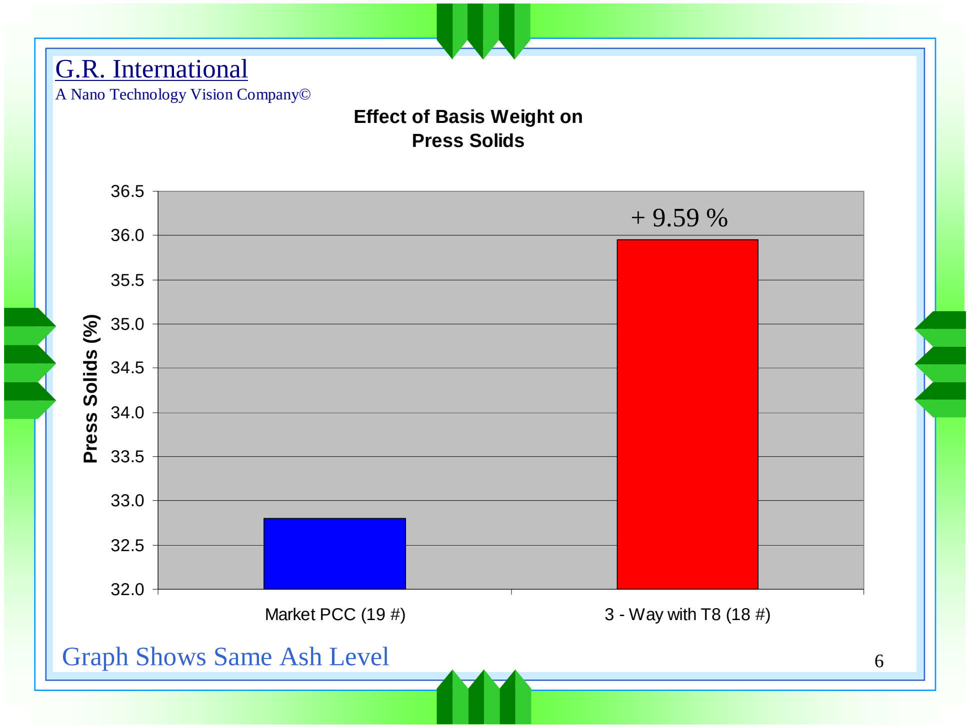


Figure III-3.17A 1: Drying Time changes based on Basis Weight



G.R. International
A Nano Technology Vision Company©

Effect of Basis Weight on Press Solids

Graph Shows Same Ash Level

6

Figure III-3.17A 2: Press Solids changes based on Basis Weight

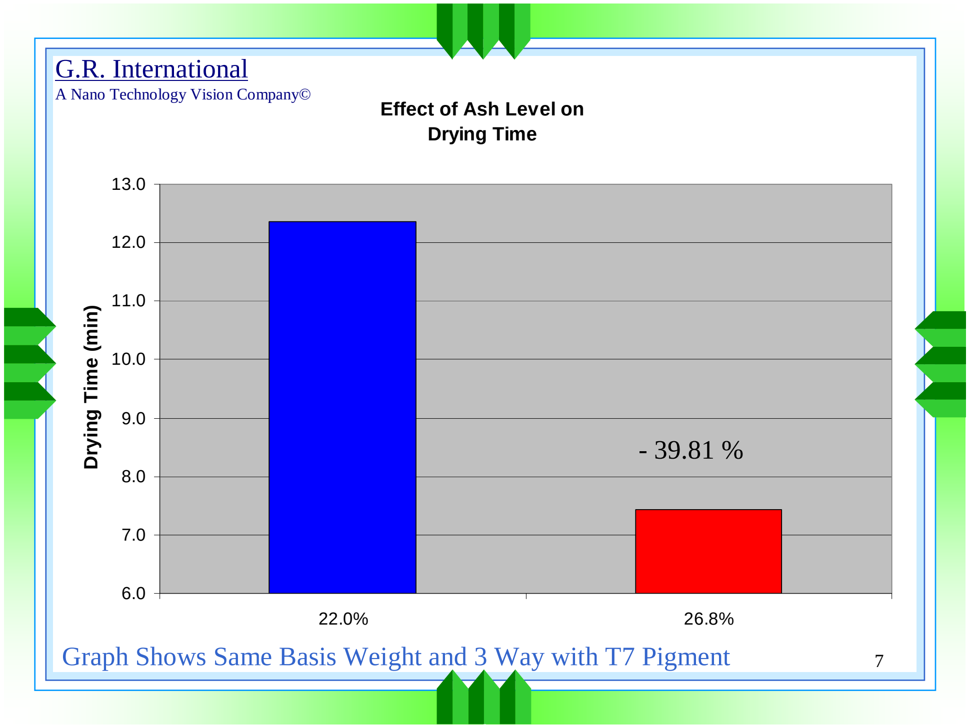
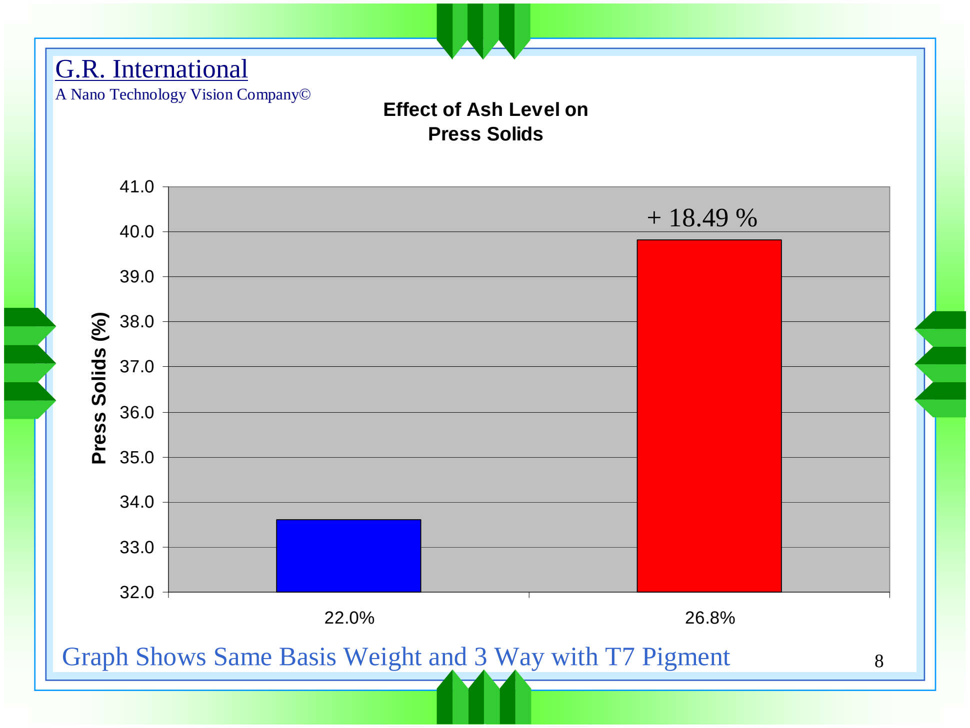


Figure III-3.17A 3: Drying Time changes based on Ash Level



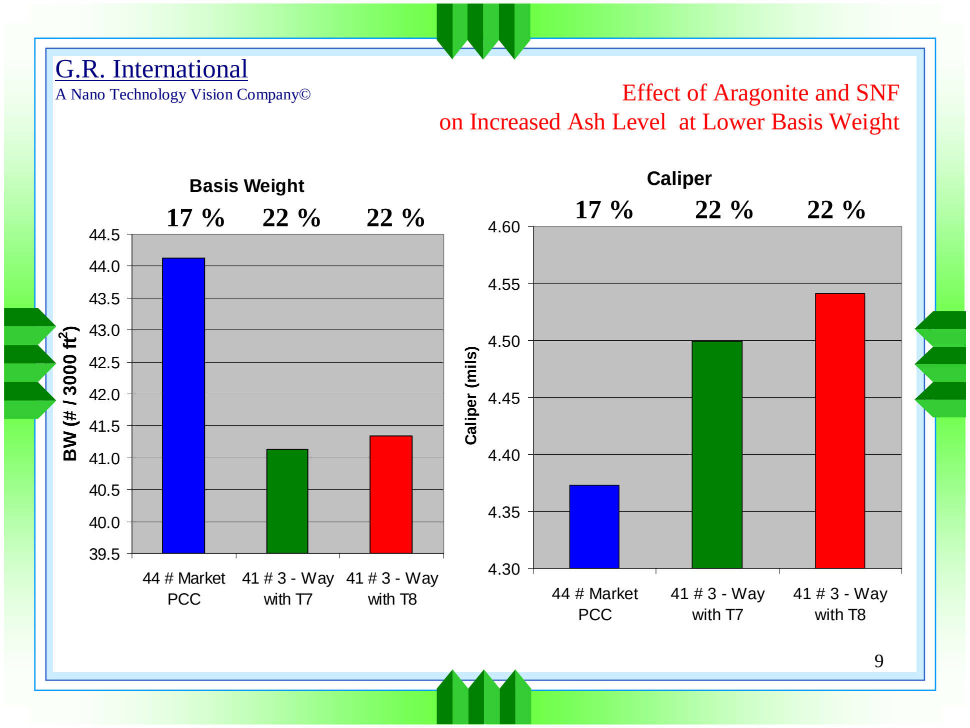
G.R. International

A Nano Technology Vision Company©

Graph Shows Same Basis Weight and 3 Way with T7 Pigment

8

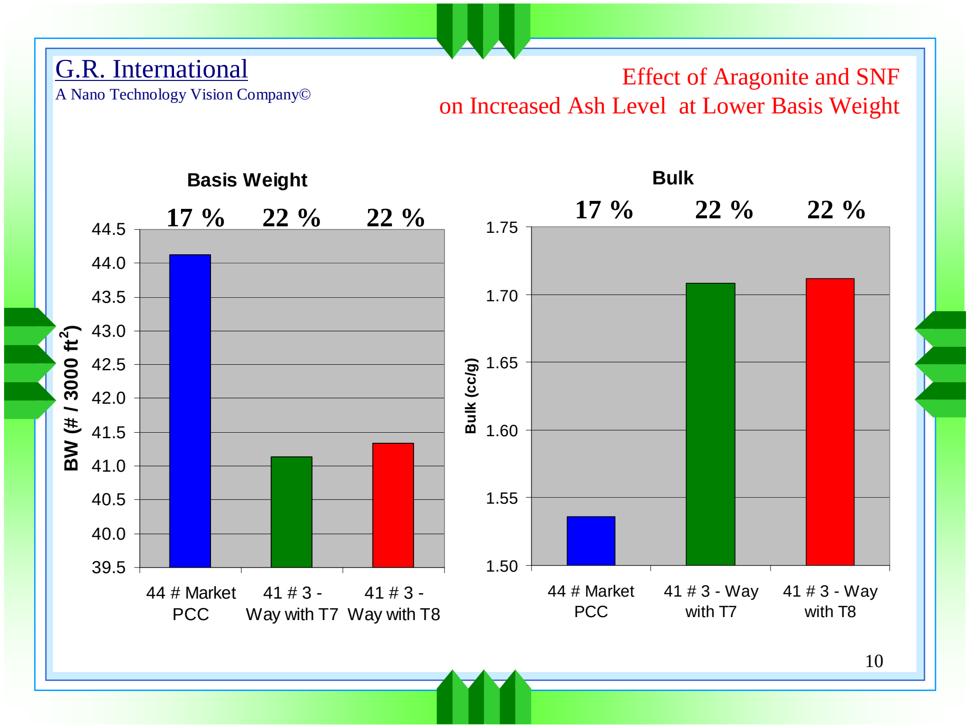
Figure III-3.17A 4: Press Solids changes based on Ash Level



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

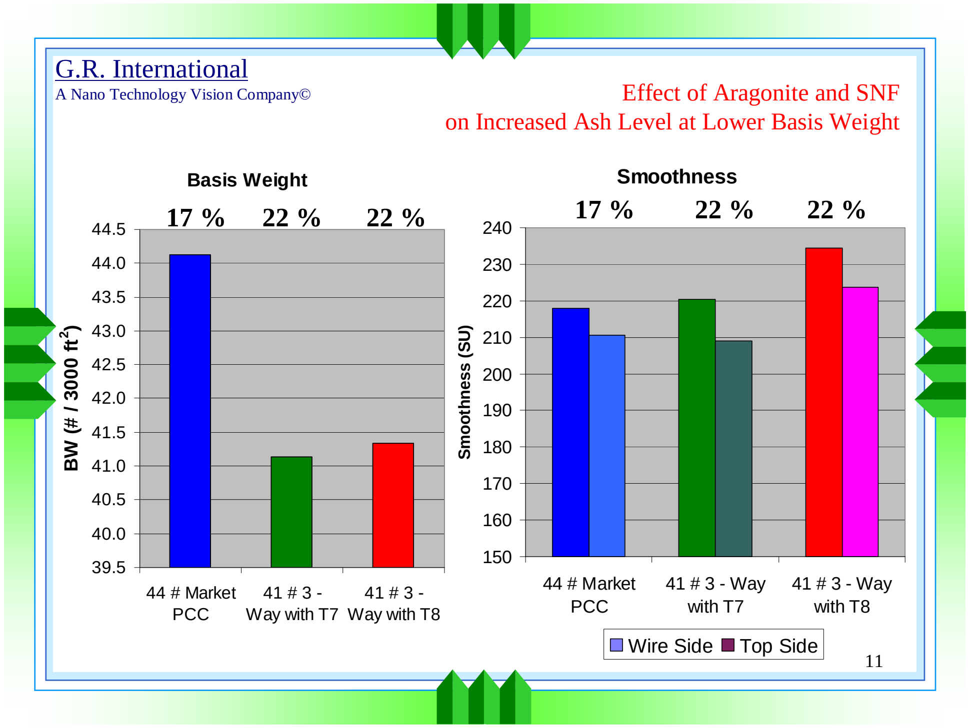
Figure III-3.17A 5: Caliper



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

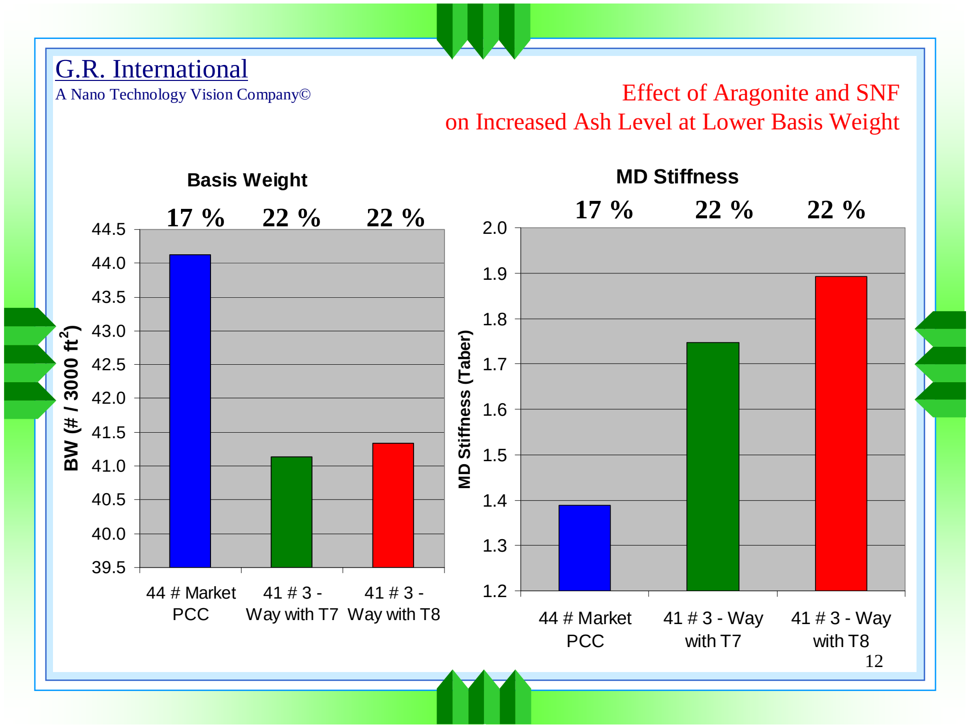
Figure III-3.17A 6: Bulk



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

Figure III-3.17A 7: Smoothness

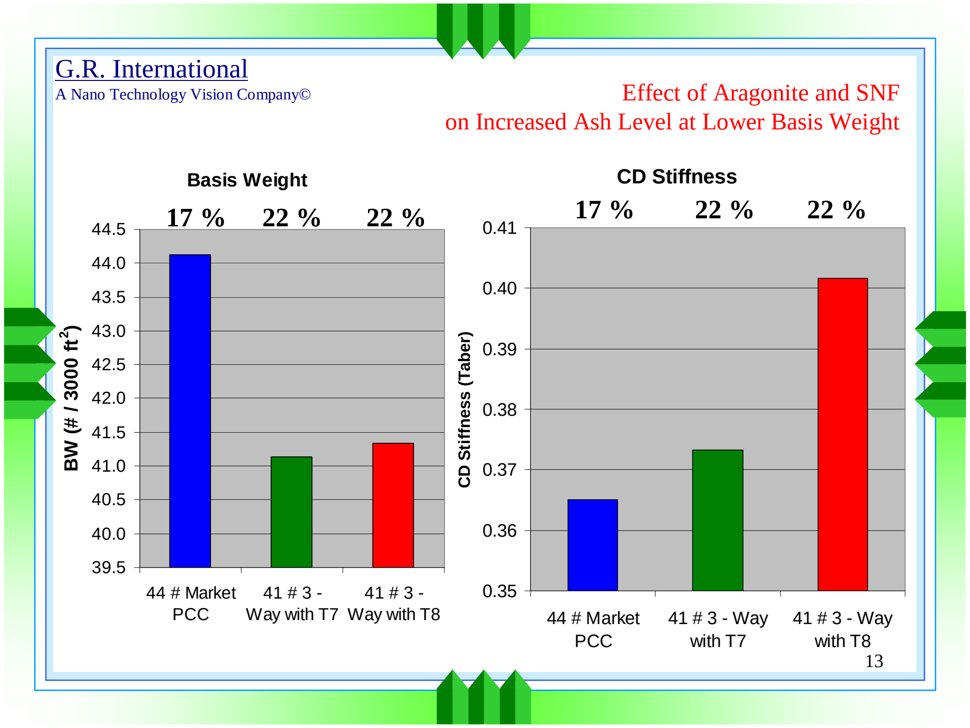


G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

12

Figure III-3.17A 8: MD Stiffness

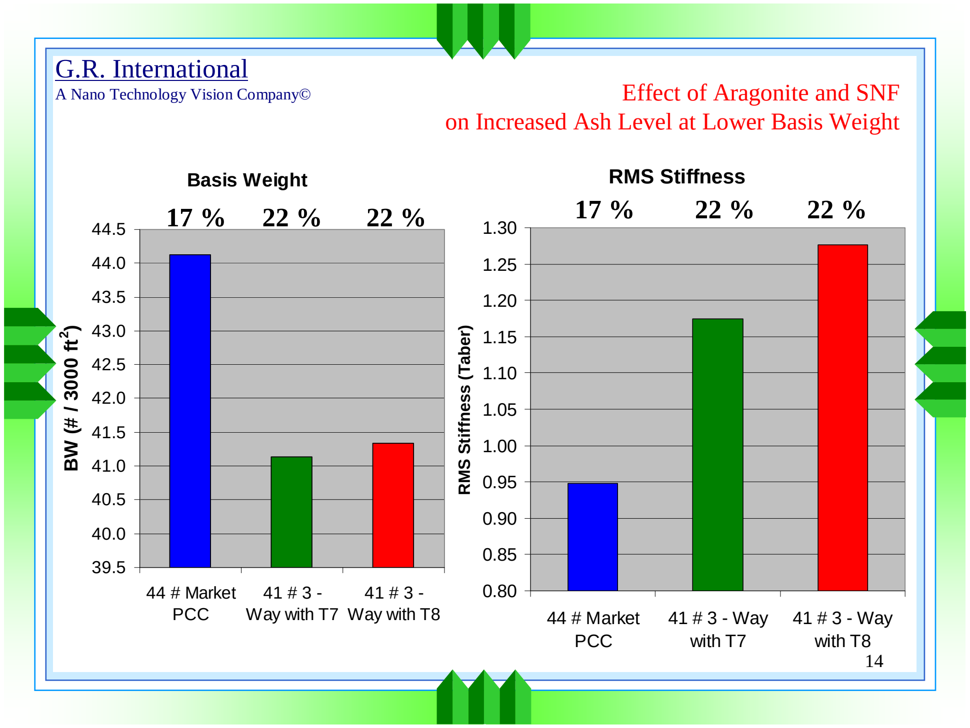


G.R. International

A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

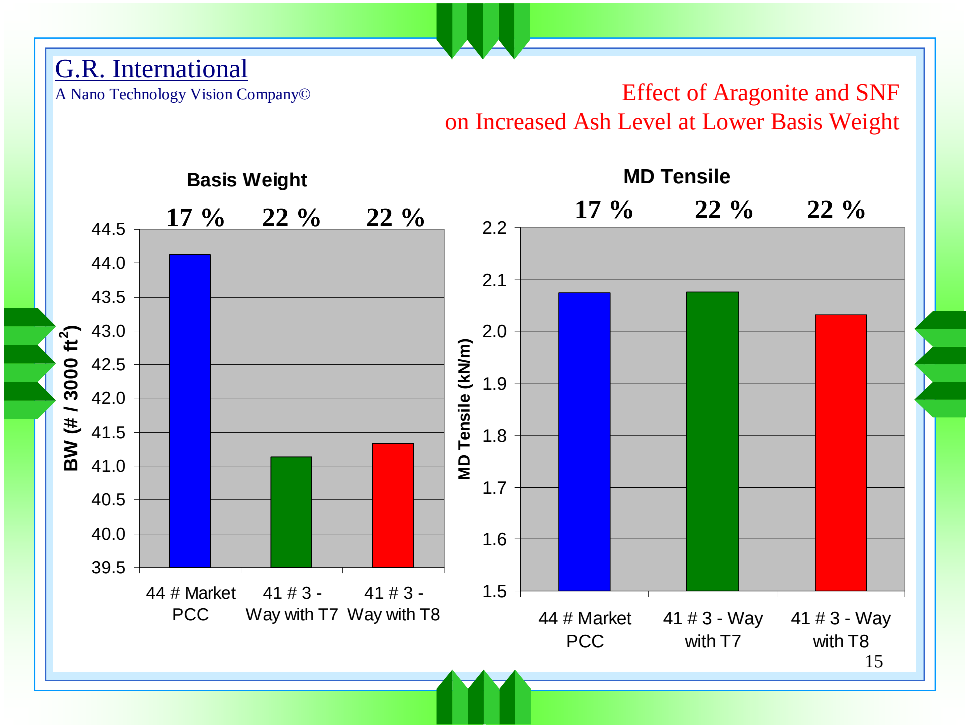
Figure III-3.17A 9: CD Stiffness



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

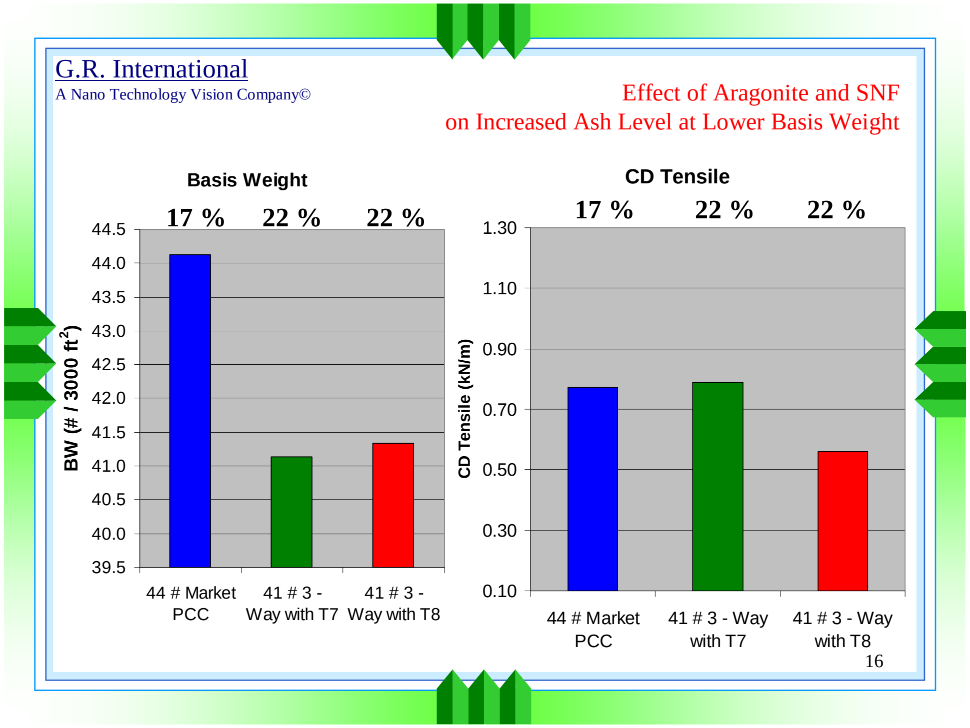
Figure III-3.17A 10: RMS Stiffness



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

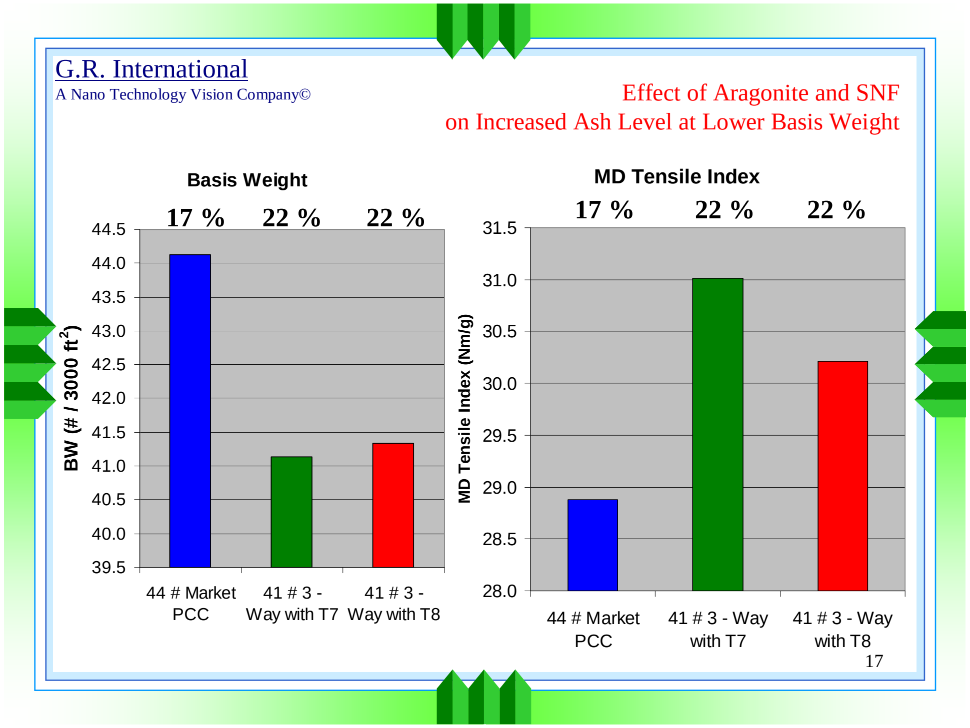
Figure III-3.17A 11: MD Tensile



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

Figure III-3.17A 12: CD Tensile

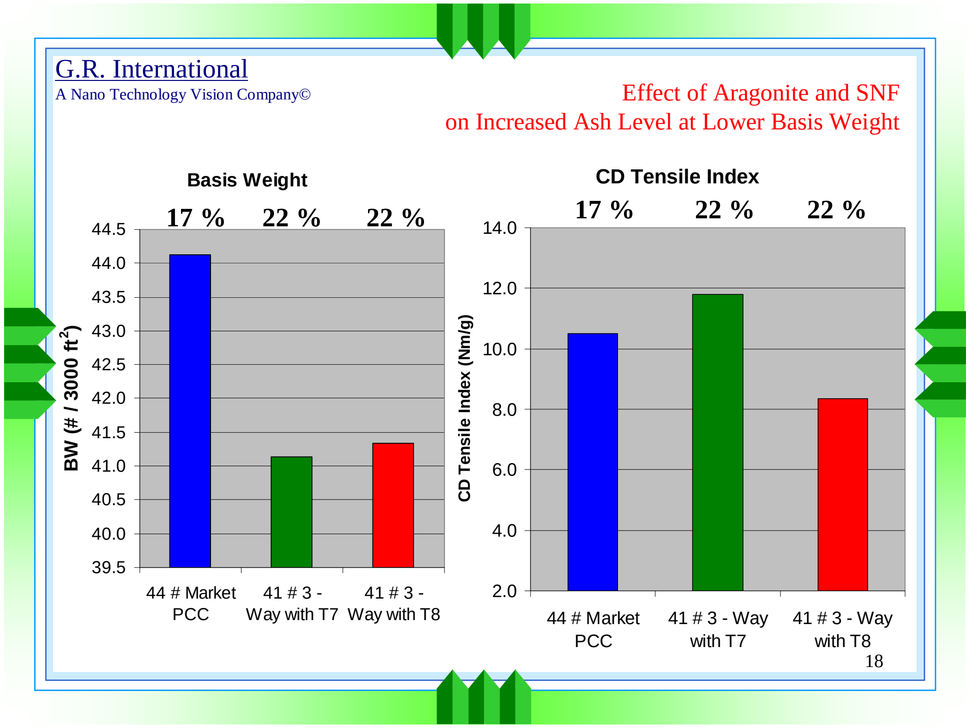


G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

17

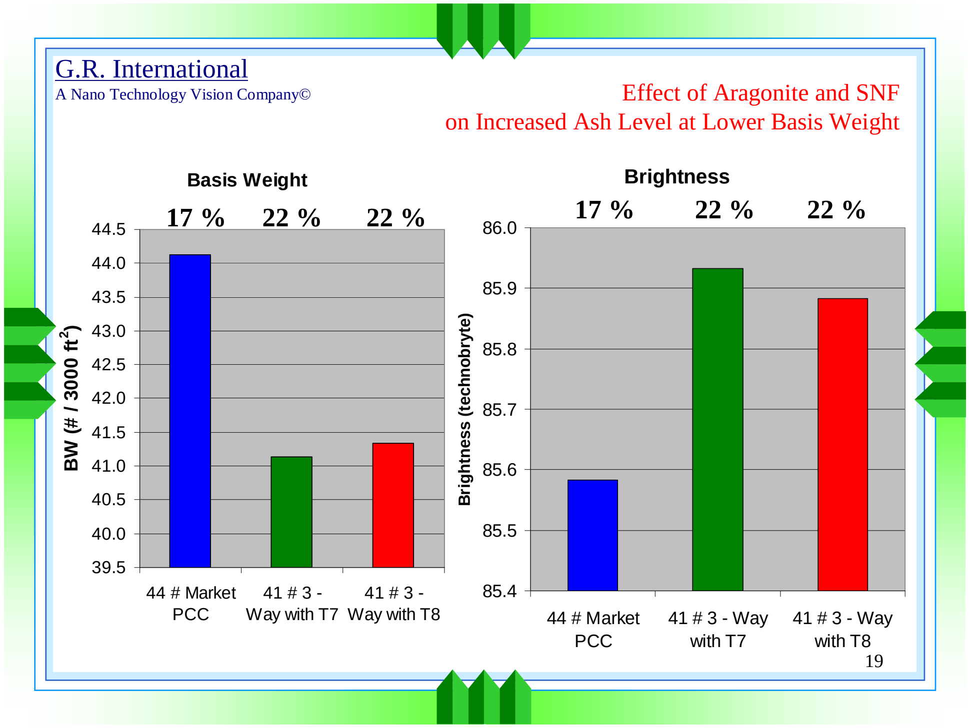
Figure III-3.17A 13: MD Tensile Index



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

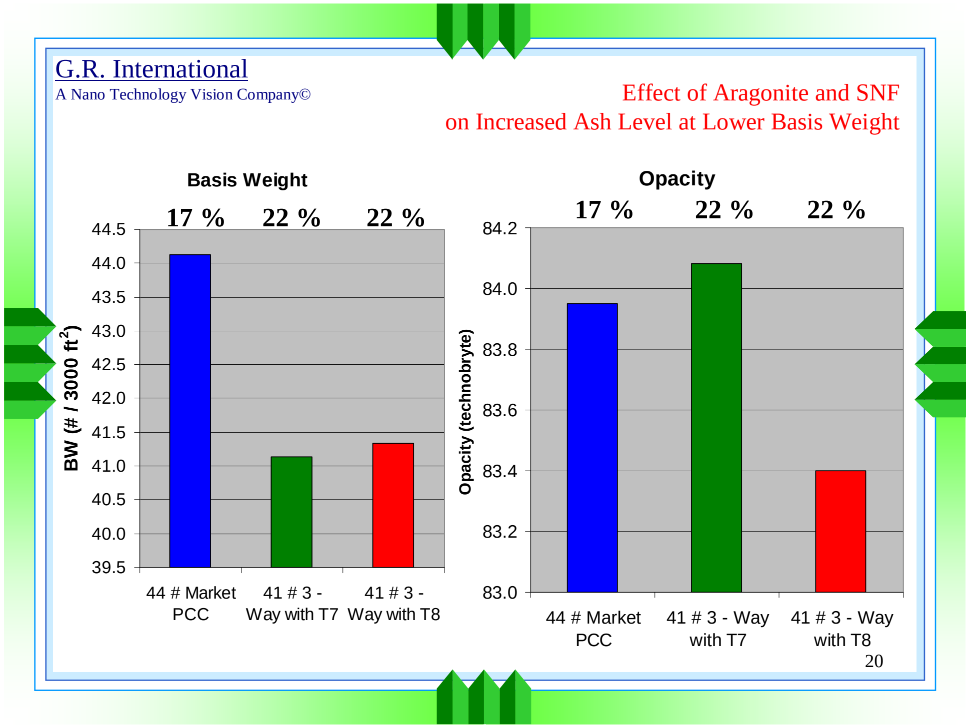
Figure III-3.17A 14: CD Tensile Index



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

Figure III-3.17A 15: Brightness



G.R. International
A Nano Technology Vision Company©

Effect of Aragonite and SNF
on Increased Ash Level at Lower Basis Weight

Figure III-3.17A 16: Opacity

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

Michigan Technological University, NREL

ID14440

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: July 1, 2008 to September 30, 2008

Date of Report: October 31, 2008

Recipient:
Michigan Technological University
1400 Townsend Drive, Houghton, MI 49931-1295
Congressional District: MI Ist

Award Number: DE-FC36-03ID14440

Subcontractors:
North Carolina State University, Room 1 Leazer Hall, Campus Box 7514, Raleigh, NC 27695-7514
Matt Ronning, Associate Vice Chancellor
Ph: (919)-513-2148
11th Congressional District, NC.

Other Partners:

(1) ArborGen ($240,000 cash contribution), P.O. Box 840001, 180 Westvaco Road, Summerville, SC 29484
Maud A. W. Hinchee, Chief Technology Officer
Ph: (843) 851-4676, 1st Congressional District, SC.

(2) MeadWestvaco, P.O. Box 1950, 180 Westvaco Road, Summerville, SC 29484
David S. Canavera, Director of Tree Improvement
Ph: (843) 851-4774, 1st Congressional District, SC.

(3) Weyerhaeuser Company, WTC, 2D39, P.O. Box 9777, Tacoma, WA 98063-9777
Robert C. Eckert, Director of Strategic Technology
Ph: (253) 924-6503, 9th Congressional District, WA.

(4) International Paper Company, P.O. Box 7910, Loveland, OH 45140-7910
Richard B. Phillips, Senior Vice President-Technology
Ph: (513) 248-6001, 71st Congressional District, OH.

Contact(s):

Chandrashekhar P. Joshi, Plant Biotechnology Research Center, School of Forest Resources and Environmental Science, Michigan Technological University, Houghton, MI 49931, 906-487-3480; cpjoshi@mtu.edu
(subcontract) Vincent L. Chiang, Forest Biotechnology Group, College of Natural Resources, North Carolina State University, 919-513-0098; vincent_chiang@ncsu.edu

Quarterly Progress Report Date:
DE-FC36-03ID14440 October 31, 2008

Project Team:

DOE-HQ contact: Joe Springer, PE, PMP
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
joseph.springer@go.doe.gov

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

A no-cost extension of the project to October 31, 2008 has been approved. During this no-cost extension period we are focusing on (1) the development of a microscale technique for isolating lignin from spruce seedlings for NMR study and (2) the establishment of a correlation between spectroscopy (NMR) based and chemical (nitrobenzene oxidation) based quantitation of the lignin S/G ratio.

Progress Report

During this period of the project, we focused on micro-scale lignin isolation for NMR analysis. We completed the analysis and characterization of lignins isolated from black spruce (*Picea mariana*) and black cottonwood (*Populus trichocarpa*).

Black spruce and black cottonwood woodmeal (<60 mesh) was extracted with ethanol/toluene, 1:2 (v/v). The extracted woodmeal was then subjected to dry milling (48 h) in a zirconium planetary ball mill under nitrogen atmosphere followed by dioxane extraction. The preparations obtained underwent purification common for milled wood lignin (MWL). The yield of the purified MWL ranged from 30 to 50% per Klason lignin in wood.

^{13}C and HSQC NMR spectra were recorded using Bruker AVANCE 300-MHz spectrometers, respectively, using 8% sample solutions in DMSO-*d*6. Conditions for the HSQC analysis were as follows: temperature, 300 K; 908 pulse width of 10 ms; 1.5-s pulse delay (d1). and 1*J*C-H, 147 Hz.

Structures:	Cotton wood	Spruce
β-O-4/α-OH	41	36
β-O-4/α-CO	<1	2
DBDO	nd	7
Phenylcoumaran	3	9
Pinoresinol	3	2
β-1/α-OH	nd	1
Spirodienone	2	2
Secoisolariciresinol	nd	1
Coniferyl alcohol	8	2
Dihydroconiferyl alcohol	<1	2
Ar-CO-CH$_2$-CH$_2$OH	nd	2
Ar-COH	3	5
Ar-CH=CH-COH	3	4
p-benzoate	4	-
S/G	1.3	na

The types and quantities of key interunits in lignins of these two species are consistent with our current knowledge. No syringyl units could be detected in spruce, while nearly 60% of the structure units in black cottonwood are of the syringyl type. Dibenzodioxocin (DBDO) moieties are present only in spruce lignin. Phenylcoumaran units are one of the key structure feature of spruce lignin, but are less significant in black cottonwood. However, coniferyl alcohol units are present, as end groups, at a significantly higher level in black cottonwood than in spruce. This database of key lignin structure units and interunit linkages provides baseline information for future characterization of lignins in transgenic spruce.

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	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	Complete
NCSU Task 4	Molecular genetic and biochemical characterization of transgenic black spruce plants	6/1/06	Complete
NCSU Task 5	Lignin content and S/G protocol establishment	6/1/05	Complete
NCSU Task 6	NIR-based characterization of cellulose and xylan contents	6/1/07	Complete
NREL Task	^{13}C NMR quantification of the S/G ratios and other lignin structural details	11/1/08	Complete
	Final Report	12/1/08	See note in the “Status” section of this report

Patents: None

Publications/Presentations: None

Budget Data (as of date): The actual spending should reflect the money actually spent on the project in the corresponding periods.

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	9/30/04		**600,406.09**		**128,491.96**	**728,898.05**
4Q04	10/1/04	12/31/04		**12,000.08**		**119,186.03**	**131,186.11**
1Q05	1/1/05	3/31/05		**0**		**0**	**0**
2Q05	4/1/05	6/30/05		**119,446.26**		**0**	**119,446.26**
3Q05	7/1/05	9/30/05		**9,950.03**		**0**	**9,950.03**
4Q05	10/1/05	12/31/05		**59,038.19**		**42,200.82**	**101,239.01**
1Q06	1/1/06	3/31/06		**71,182.66**		**0.00**	**71,182.66**
2Q06	4/1/06	6/30/06		**49,476.56**		**0.00**	**49,476.56**
3Q06	7/1/06	9/30/06		**49,030.76**		**79,993.34**	**129,024.10**
4Q06	10/1/06	12/31/06		**17,005.37**		**22,116.05**	**39,121.42**
1Q07	1/1/07	3/31/07		**98,683.69**		**-9,284.04**	**89,399.65**
2Q07	4/1/07	6/30/07		**45,408.27**		**0**	**45,408.27**
3Q07	7/1/07	9/30/07		**63,548.08**		**62,173.52**	**125,721.60**
4Q07	10/1/07	12/31/07		**108,261.89**		0	**108,261.89**
1Q08	1/1/08	3/31/08		**21,396.96**		**5,309.32**	**26,706.28**
2Q08	4/1/08	6/30/08		**10,454.71**	0	**0.00**	**10,454.71**
3Q08	7/1/08	9/30/08		**11,031.30**	0	0.0	**11,031.30**
4Q08	10/1/08	12/1/08	**25,521.10** (final bills & closeout)**		0		
Totals				**1,346,320.90**		**450,187.00**	**1,796,507.90**

**** MTU received a total of $1,370,842 from DOE. A sum of $50,000 was sent directly to NREL from DOE.**

* Update quarterly

General Note: DOE Laboratory partner spending should not be included in the above table. If a DOE Laboratory is a partner, report their spending and spend plan information in the table below (use separate tables if multiple DOE Laboratories are involved):
Note 1: Leave blank. Only the actual DOE/Cost Share amounts spent through 6/30/04 are needed.
Note 2: Amount for this quarter and subsequent quarters should be updated as necessary on a quarterly basis. Estimates need to be provided for the entire project. If spending for a given quarter is different than estimated, then the remaining quarter's estimates should be updated to account for the difference. Total DOE and Cost Share amounts should be the same as the Award amount.
Note 3: This should match the amount on the SF269A section 10.c. Column III (10.j. Column III on the SF269).
Note 4: This should match the amount on the SF269A section 10.c. Column II (10.j. Column II on the SF269).

Note 5: This should match the amount on the SF269A section 10.b. Column III (10.i. Column III on the SF269).
Note 6: This should match the amount on the SF269A section 10.b. Column II (10.i. Column II on the SF269).
Note 7: This should match the amount on the SF269A section 10.a. Column III (10.d. Column III on the SF269).
Note 8: This should match the amount on the SF269A section 10.a. Column II (10.d. Column II on the SF269).

Development of Renewable Microbial Polyesters for Cost Effective and Energy-Efficient Wood-Plastic Composites

Idaho National Laboratory

Agr:11428

QUARTERLY PROGRESS REPORT

Project Title: Development of Renewable Microbial Polyesters for Cost Effective and Energy-Efficient Wood-Plastic Composites

Covering Period: July 1, 2008 through September 30, 2008

Date of Report: October 31, 2008

Recipient:
Idaho National Laboratory
P.O. Box 1625
Idaho Falls, ID 83415

Project Number: CPS Number: 11428

Project Period: October 1, 2004 – September 30, 2009

Subcontractor:
Washington State University
P.O. Box 643140
Pullman, WA 99164-3140

Other Partners:
ECO:LOGIC, Inc.
Glatfelter Corporation
Strandex Corporation
University of California-Davis

Contact:
Principal Investigator (PI):
David N. Thompson
Phone: (208) 526-3977
E-mail: David.Thompson@inl.gov

Project Team:
WSU PI:
Michael P. Wolcott
Phone: (509) 335-6392
E-mail: wolcott@wsu.edu

ECO:LOGIC PI:
Robert W. Emerick
Phone: (916) 773-8100
E-mail: emerick@ecologic-eng.com

Glatfelter PI:
Katherine A. Wiedeman
Phone: (740) 772-3387
E-mail: KWiedeman@glatfelter.com

Strandex PI:
Alfred B. England
Phone: (513) 624-6281
E-mail: al@strandex.com

UC-Davis PI:
Frank J. Loge
Phone: (530) 754-2297
E-mail: fjloge@ucdavis.edu

DOE-HQ contact:
Dickson Ozokwelu
Phone: (202) 586-8501
E-mail: dickson.ozokwelu@ee.doe.gov

Project Objectives:

Objective 1: Determine preferred PHA monomer compositions, PHA/cell debris ratios, and PHA/wood ratios for the production of superior wood-PHA composites

Objective 2: Define feedstock compositional ranges for WTE and PPE for production of PHAs meeting PHA monomer composition ranges specified in Objective 1

Objective 3: Determine the efficacy of supplementing WTE and PPE to improve PHA production from these effluents

Objective 4: Test the material properties of wood-PHA composites produced from waste-derived PHA made and used without extraction or purification

Objective 5: Produce and test wood-PHA composites made from PPE-derived PHA at the pilot-scale.

Background:

This is a collaborative project among the Idaho National Laboratory, Washington State University, the University of California-Davis, Glatfelter Corporation, Strandex Corporation, and ECO:LOGIC Engineering, Inc. The purpose of the project is to develop and produce wood-plastic composites using bacterial polyhydroxyalkanoates (PHA) in place of petroleum-derived plastic. This will be made economical and environmentally friendly by reducing or eliminating costly steps in PHA production. Specifically, this will be accomplished by utilizing PHA produced inherently in wastewater treatment processes, and by utilizing the PHA directly in the composite without removal of the cell debris. The forest products industry will benefit most from this research, both from the perspectives of environment, recycling, and new composite products. The municipal waste treatment industry, as the basis for production of PHAs from effluents, provides the starting point for application to forest products industry effluents and also benefits.

This project is comprised of five tasks. The first four tasks address PHA production, extrusion, and composite properties. Laboratory testing to determine preferred feedstock compositions, together with ease of processing and material properties of composites produced therefrom, will be completed by WSU for pure commercial PHAs (Task 1) and for unpurified effluent-derived PHAs (Task 4). This information will be used to define appropriate effluent feedstocks (Task 2) and optimize supplements (Task 3) to support the preferred composite formulations. Task 5 will include a ca. 1000 lb/h pilot-scale extrusion of wood-PPE-derived PHA composites using the appropriate supplements in the production of the PPE utilized. The project is being completed in three phases. Phase 1 includes determination of PHA compositions and amounts for superior wood-thermoplastic composites. Phase 2 includes determination of feedstock supplements for production of effluent-derived PHAs of the desired monomer compositions. Phase 3 includes pilot-scale testing to identify and mitigate processing issues at the commercial scale.

Status:

Tasks scheduled to be active during this quarter included

- Task 3, "Supplementation of Waste Effluents for Production of PHA,"
- Task 4, "Waste Effluents PHA Composite Processing & Material Properties," and
- Task 5, "Pilot-scale Extrusion Testing of Waste Effluents PHA Composites."

Task 1 and Task 4 work scopes are performed at Washington State University (WSU). Task 2 and Task 3 work scopes are performed at INL, UC-Davis, and Glatfelter. Task 5 work scopes are performed at Glatfelter, Strandex, WSU, UC-Davis, and INL.

Task 1 Status: Task 1 was completed during the fourth quarter of FY2007.

Task 2 Status: Task 2 was completed during the second quarter of FY2007.

Task 3 Status: Two manuscripts describing the final portion of Greg Mockos' work at the INL were prepared and are awaiting completion of intellectual property assessment before submittal to journals. The first manuscript details the results of the C:N ratio optimization using methanol-grown and foul condensate-grown consortia enriched from secondary waste activated sludge. The second describes the optimization of PHA yield in foul condensate-grown enrichment cultures by the adjustment of F:M, HRT and SRT at a fixed C:N.

Task 4 Status: In this quarter two more formulations of PHB/wood flour/biomass composites were prepared and tested using the same method described in the previous report. The two new formulations had 80 and 100% of wood flour replaced by biomass, respectively (Table 1). To study polymer penetration, the composites were cryo-sectioned with a diamond knife to generate a flat and damage-free surface.

Table 1. *Formulations of PHB/WF control and PHB/WF/Biomass composites.*

Formulation / Components	PHB/WF	PHB/WF/ 20% biomass	PHB/WF/ 40% biomass	PHB/WF/ 60% biomass	PHB/WF/ 80% biomass	PHB/WF/ 100% biomass
Biomass*	0	11.4	22.8	34.2	45.6	57
Wood Flour (pine)*	57	45.6	34.2	22.8	11.4	0
PHB	35	35	35	35	35	35
Talc-Nicron 403	8	8	8	8	8	8
pMDI	4	4	4	4	4	4
Lubricant (WP2200)	3	3	3	3	3	3
Nucleating agent (Boron Nitride)	0.2	0.2	0.2	0.2	0.2	0.2

*: 60 mesh particle size.
WF: Wood Flour.
All units are in parts.

The replacement of wood flour with biomass had little influence on the densities of the composites (Figure 1). The six composites exhibited an average density of 1.38 with a standard deviation of 0.013. This indicates that the biomass and the wood flour possess similar densities.

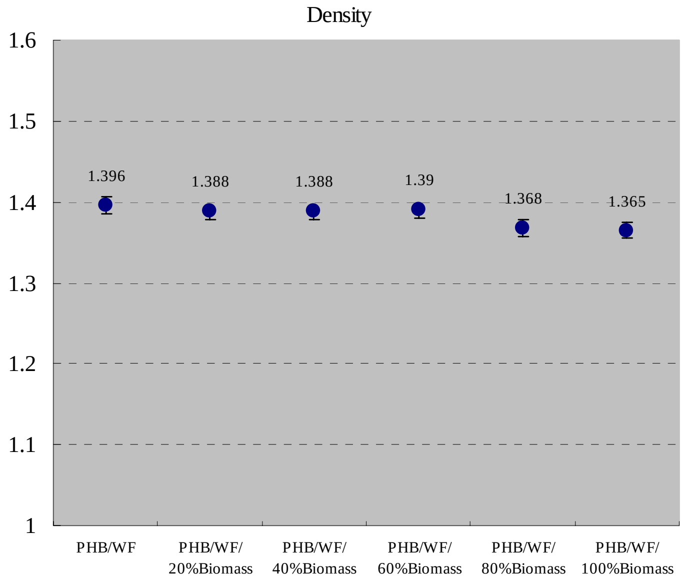


Figure 1. *The densities of the six formulations of PHB/WF/biomass composites.*

All tested mechanical properties, i.e., tensile, flexural and impact properties, decreased with increasing content of the biomass (Figures 2-4). This was believed to be due to lower strength and modulus of the biomass, unfavorable shape of biomass particles and weaker interfacial bonding (as evidenced by SEM micrographs below) between the biomass and the PHB matrix.

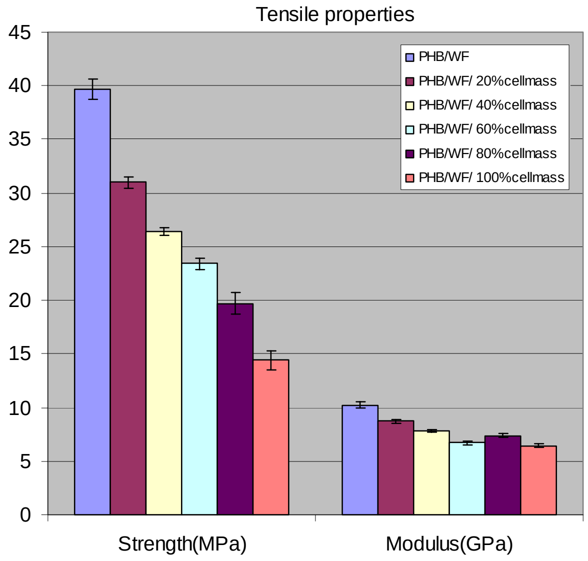


Figure 2. *Tensile properties of the six formulations of PHB/WF/biomass composites.*

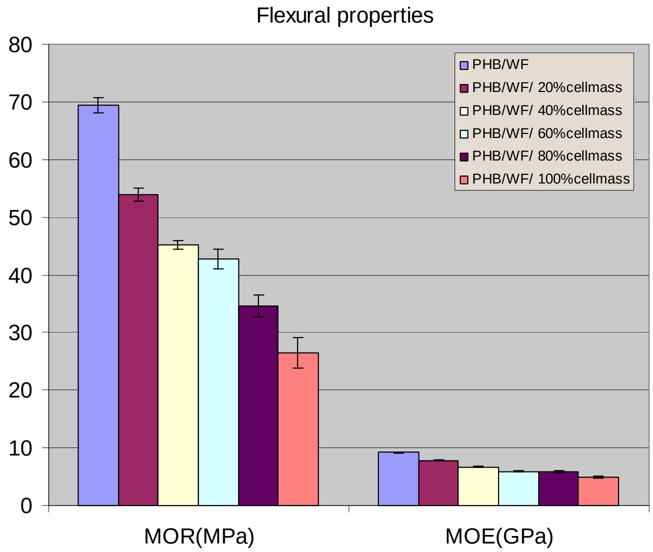


Figure 3. *Flexural properties of the six formulations of PHB/WF/biomass composites.*

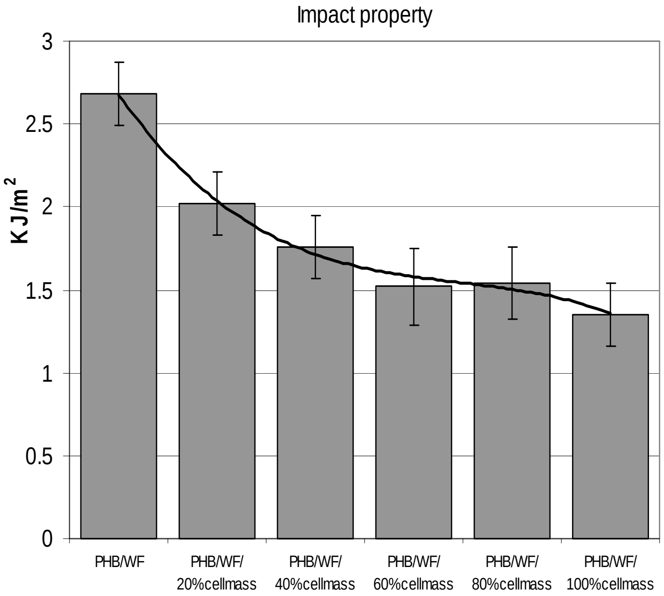


Figure 4. *Impact strength of the six formulations of PHB/WF/biomass composites.*

SEM micrographs taken on tensile fracture surfaces showed homogeneous distribution of cubic-shaped biomass and fiber-shaped wood flour particles (Figure 5). Cubic-shaped fillers are not preferred in composites because they result in stress concentration and cannot effectively share the load from composite matrix. This led to reduced mechanical properties of the composites as evidenced in the PHB/WF/biomass system. Another reason for the deteriorating properties was

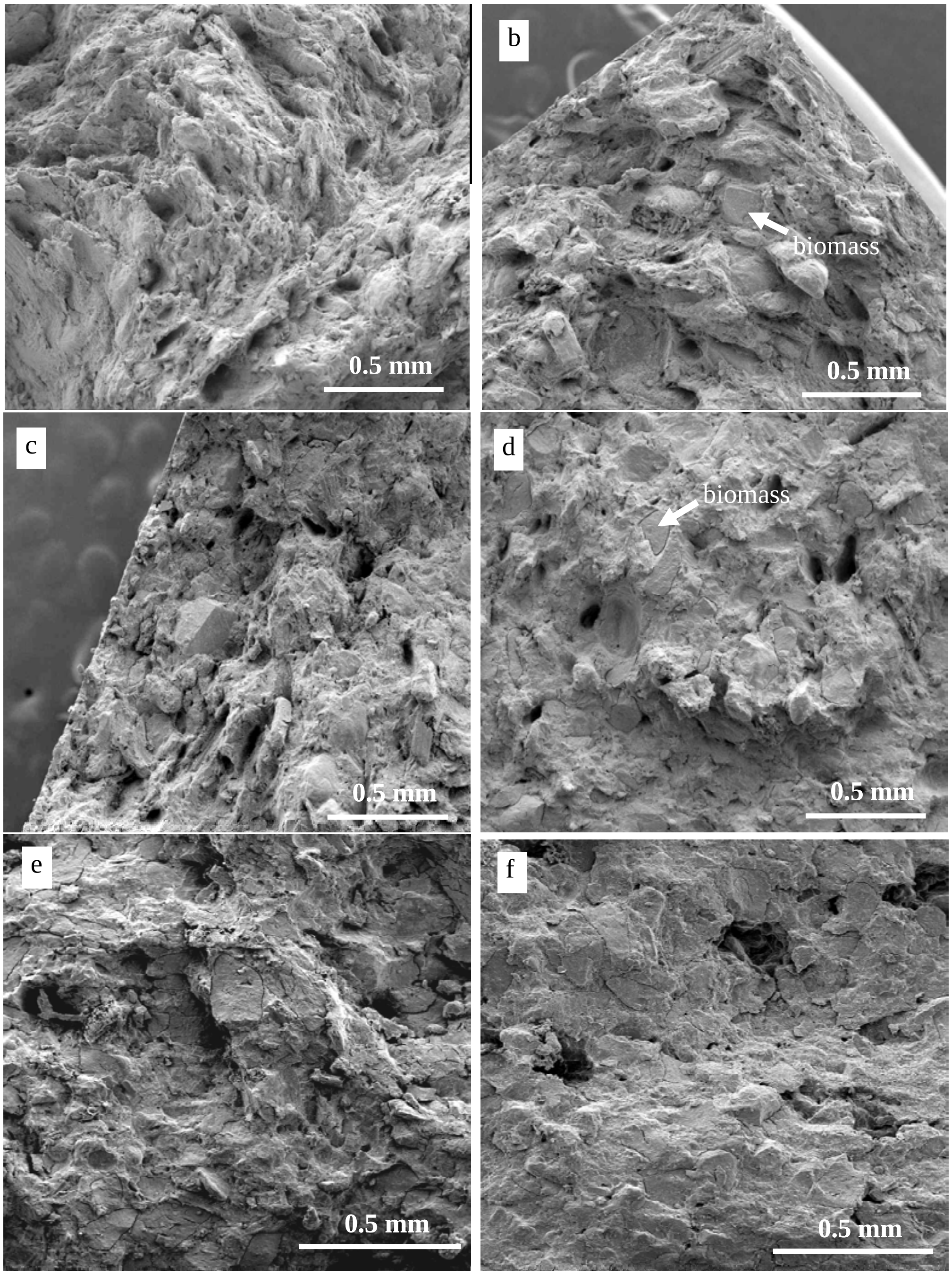


Figure 5. *Fracture surfaces of composites: (a) PHB/WF; (b) PHB/WF/20%biomass; (c) PHB/WF/40%biomass; (d) PHB/WF/60%biomass; (e) PHB/WF/80%biomass; and (f) PHB/WF/100%biomass. Magnification: X150.*

poor interfacial bonding between the biomass and the PHB matrix. This was clearly illustrated in Figure 6a-b, where gap/debonding appeared between the biomass particles and the matrix.

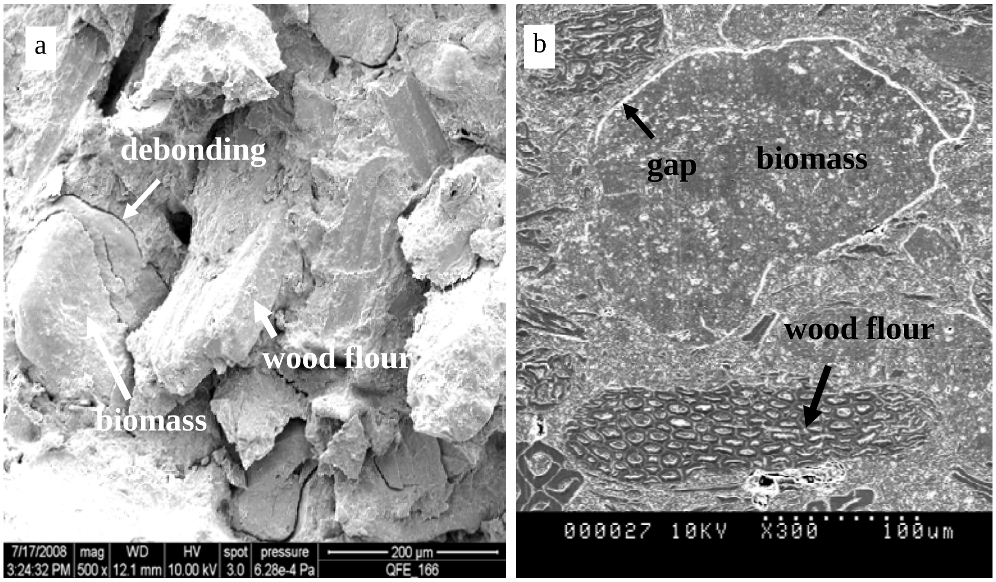


Figure 6. *Fracture surface (a) and sectioned surface (b) of PHB/WF/biomass composites.*

The sectioned sample surfaces were also examined to study polymer penetration. Due to the high pressure in injection processing, many wood cells were crushed or severely deformed (Figure 7). The high pressure also forced polymer melt into some cells. From Figure 8 it is clear that polymer melt was forced into the cells through longitudinal or transverse lumens. The

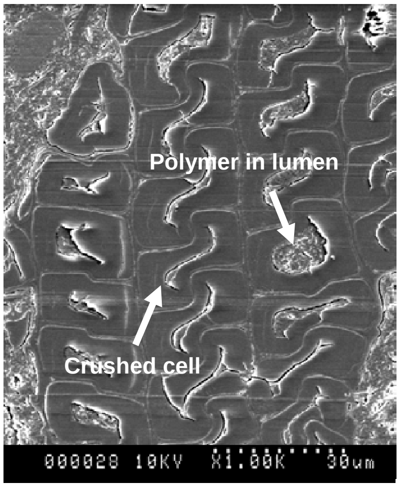


Figure 7. *Crushed or deformed wood cells.*

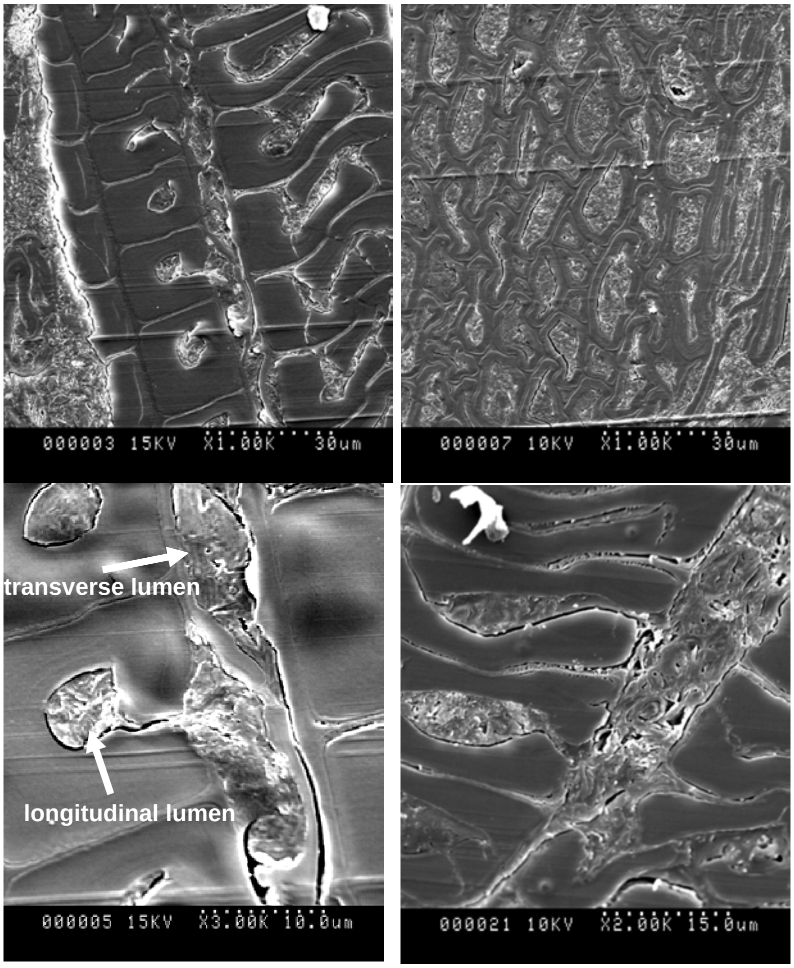


Figure 8. *Wood lumens and cells filled with polymer.*

penetration of polymer into the wood cells generated a mechanical interlock between the polymer and the wood fiber, which substantially improved stress transfer between the two phases. In contrast, biomass particles seemed to be solid and cannot be deformed or penetrated (Figure 6b). As a result, they formed poor interfacial bonding with the polymer and resulted in deteriorated properties.

Task 5 Status: The brewery wastewater pilot unit at UC Davis was shut down and all of the biomass samples collected were analyzed for PHA content. This biomass will be used to support Task 4 composite formulation testing at WSU.

The Glatfelter PHA-production pilot unit was restarted in mid-July. Project personnel from both UCD and INL were onsite for one week during the restart. Several design changes were made to the unit before the restart in order to address operational difficulties experienced in earlier trials, as follows. The reactor was improved by adding insulation and the ability to control reactor temperature during cold weather operation. A foam breaker was added to eliminate the need to add antifoam, and this further allowed the working volume to be increased from 500L to 700L. A more robust timer control system was added to replace the computer control, which was previously found to be poor due to challenging conditions in the operating pulp mill. In addition, the housing for the controls was improved to make them more splash resistant and thereby eliminate interruptions to operation during scheduled cleaning operations at the mill. Finally, cooling fans were added to reduce heat stress on the equipment during warm weather operation.

The reactor was restarted as follows. Frozen cultures produced in Task 3 enrichments on foul condensate and primary clarifier effluent were used as the inoculum source. Cultures were chosen based on COD and methanol removal and maximum MLVSS concentrations observed during the laboratory enrichments. Utilizing these cultures provided an inoculum that was pre-enriched for microbes having the correct physiology and growth characteristics, and improved the chances for dominance of the desired community in the pilot reactor. Sixteen liters of this inoculum were thawed and added to the reactor, along with 150L of unsterile tap water. Methanol Medium B (nutrient media) was added to further improve the chances of successfully establishing the desired microbial community in the more challenging conditions onsite at the mill. Reagent-grade methanol was added as the primary carbon source. The reactor was brought to a final working volume of 700L by performing a series of successive daily doublings of reactor volume using unsterile tap water containing nutrient media and methanol. On the last day of this process, ¼ of the reactor volume was wasted and the reactor was refilled with unsterile tap water containing nutrient media and methanol to ensure that the cells continued to grow. The reactor was then operated at an HRT of 4 days and SRT of 4 days, replacing the tap water with primary clarifier effluent amended with nutrient media, and with increasing amounts of neutralized foul condensate replacing methanol as the carbon source. As performed previously in the laboratory, only the aqueous fraction of the foul condensate was added to the reactor. COD, pH, and MLVSS were monitored to indicate the progress of the enrichment. By 36 days of operation (9 HRTs), 95% of the COD supplied was from neutralized foul condensate and 5% from exogenously-added methanol. At this point, addition of the nutrient medium was discontinued. The reactor is currently operating at HRT = SRT = 4 days and is functioning correctly and producing biomass. The next step for the pilot reactor will be to adjust the C:N ratio and initiate PHA production in the reactor.

Plans for Next Quarter:

For Task 3, the two manuscripts describing the final portion of Greg Mockos' work at the INL will be submitted to journals once the intellectual property assessments are completed. Pending available funds, work will begin on the characterization of the microbial population dynamics that occurred during the enrichment process using foul condensate.

For Task 4, water absorption testing will be performed on all six formulations. Water diffusion behavior and swelling coefficient will be studied and calculated to understand the effect of biomass. Water soaking time will be set for 120 days at room temperature.

For Task 5, the centrifuge and drying oven will be shipped to the Glatfelter mill in Chillicothe and integrated into the pilot plant to begin biomass collection. To induce PHA production, the C:N ratio of the feed will be increased to 30 with the addition of methanol to the feed tank (supplementing the neutralized foul condensate/primary clarifier effluent mixture that is currently serving as the carbon source for reactor operation). Because of challenges introduced by uncertain funding over the course of the project, the PHA-production pilot unit is undersized relative to the scale needed to fully support the pilot extrusion tests. Hence, the PHA-production pilot units will be operated for up to 6 months in production mode, and sufficient data will be collected to assess PHA production, reactor yield, and reactor productivity. Two larger-volume biomass sources, PHA-laden brewery waste biosolids produced at UCD, and PHA-free municipal wastewater treatment biosolids from ECO:LOGIC’s Lincoln, CA plant will be utilized in future quarters to support Tasks 4 and 5. To this end, during the next quarter dried PHA-free biomass collected from the ECO:LOGIC wastewater treatment plant, and dried PHA-laden biomass produced in the UCD brewery pilot unit will be shipped to WSU. Both the PHA-laden brewery waste biosolids and the PHA-free municipal biosolids (with added commercial PHA) will be used in future quarters to perform intermediate-scale extrusion tests in Task 4. Municipal biosolids will be mixed with commercial PHA to support the future large scale extrusion tests in Task 5.

Patents:

No patents resulting from the project were awarded or applied for during this quarter.

Publications/Presentations:

No publications were submitted or published during this quarter. No presentations were given during this quarter.

Milestone Status Table (as of September 2008 accounting month end):

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1.0	**Task 1 – Purified PHA ± Cell Debris Composite Processing & Material Properties**			
1.1	Physical & rheological properties of PHAs and WFRTCs defined	3/31/06	6/30/07	Moisture testing completed 9/30/07
1.2	Composite processing/mechanical properties of pure PHA WFRTCs completed	7/31/06	6/30/06	
1.3	Wood/purified PHA composites with integrated cell debris produced having MOR ≥ 1500 psi and MOE ≥ 0.20 Mpsi	8/4/06	12/31/05	Met and exceeded
2.0	**Task 2 – Effect of Feedstock on PHA Type/Amount**			
2.1	WTE survey of several waste treatment facilities completed	7/1/06	6/30/06	Further tests useful but not critical
2.2	Enriched paper mill inoculum source and/or ATCC Sphaerotilus culture ready for testing	11/30/06	11/1/06	Five enriched mill sources
2.4	PHA produced from a PPE source by indigenous or inoculated laboratory cultures at ≥ 1 wt% of the dry cell mass	4/1/07	6/5/06	Met and exceeded
2.3	Unsupplemented PHA from PPE completed	8/1/07	3/31/07	
3.0	**Task 3 – Supplementation of Waste Effluents for Production of PHA**			
3.1	PPE supplements & production criteria for pilot test defined	12/15/07	11/12/07	
3.2	In situ PPE process requirements for pilot test defined	12/15/07	11/12/07	
4.0	**Task 4 – Waste Effluents PHA Composite Processing & Material Properties**			
4.1	Material & properties defined for waste-PHA composites	2/6/09		Date shifted re: no-cost extension
4.2	Wood/purified PHA composites with integrated cell debris produced having MOR ≥ 2000 psi and MOE ≥ 0.25 Mpsi	8/15/07	3/31/08	Met and exceeded
4.3	Basic processing conditions defined for pilot test	3/6/09		Date shifted re: no-cost extension
4.4	Formulations identified for pilot extrusions	4/3/09		Date shifted re: no-cost extension
5.0	**Task 5 – Pilot-scale Extrusion Testing of Waste Effluents PHA Composites**			
5.1	Pilot test plan completed	12/15/07	11/16/07	
5.2	Supplemented or unsupplemented PPE biosolids produced for pilot extrusions	3/15/09	9/30/08	PHA-free biosolids produced, to be supplemented with commercial PHA for pilot extrusions
5.3	Pilot extrusions completed	7/15/09		Date shifted re: no-cost extension
5.4	Project completion and transition planned to technology demonstration phase	7/31/09		Date shifted re: no-cost extension
5.5	Final Report delivered to DOE	9/30/09		Date shifted re: no-cost extension

Budget Data (as of September 2008 accounting month end):

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Yr 1	10/1/04	9/30/05	$262,000	$305,411	$567,411	$260,204	$334,364	$594,568
Yr 2	10/1/05	9/30/06	$225,000[a]	$459,726	$684,726	$224,382	$293,090	$517,472
Yr 3	10/1/06	9/30/07	$350,000[b]	$482,006	$1,032,520	$275,856[d]	$148,672	$424,528
Yr 4	10/1/07	9/30/08	$400,000[c]	$137,400	$539,886	$475,458[e]	$ 0	$475,458
Yr 5	10/1/08	9/30/09	$203,000[f]	$ 0	$203,000			
Totals			$1,440,000	$1,384,543	$2,824,543	$1,235,900	$776,126	$2,012,026

a An amount of $1,797 was carried over from FY2005 to FY2006 and is not included in this figure.

b An amount of $2,417 was carried over from FY2006 to FY2007 and is not included in this figure.

c An amount of $1,628 was carried over from FY2007 to FY2008 and is not included in this figure.

d $75K committed under subcontract with WSU but not accrued in FY2007 were carried over to FY2008 and immediately recommitted. These funds were spent under subcontract in FY2007 by WSU but were not yet billed at the end of FY2007.

e This value includes the recommitted FY2007 subcontract funds referenced in item d and the amount carried over from FY2007.

f An amount of $1,170 was carried over from FY2008 to FY2009 and is not included in this figure.

Index of Award CID Numbers

Index of Award CID Numbers