MECHANICAL PULPING

ANNUAL RESEARCH REVIEW

April 3, 1991
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INTRODUCTION

The current research program of the Pulping and Bleaching Group encompasses work on chemical pulp bleaching, chemical pulping, mechanical pulping, mechanical pulp bleaching and topics related to these areas (Table 1). Although the work is funded primarily by Institute member dues, substantial funding has also been obtained from the American Paper Institute (API) and private sources. The privately funded work is usually done on a confidential basis, but the cooperators often grant permission for complete or partial disclosure of the results.

PROJECTS

In the chemical pulp bleaching area, the projects are mainly directed towards reducing the formation of chlorinated organic compounds. Project 3474 adopts a dual approach by examining organochlorine formation during bleaching with chlorine containing agents, while at the same time investigating the mechanism by which certain pretreatments enhance the performance of oxygen bleaching. An important objective of this project is to look beyond NO2 by determining the effects of specific residual lignin structural modifications on oxygen bleachability. Private contract work for a particular mill (Project 3675) complemented this project by providing additional information regarding effects of bleaching process changes on effluent characteristics. Another privately funded project (Project 3649), completed earlier but only recently released for publication, examined effects of oxygen bleaching of incompletely washed, unscreened sulfite pulp. Ph. D. Thesis work by Mr. Todd Schwantes, just now beginning, will thoroughly investigate the effect of process changes such as oxygen bleaching and 100% substitution of chlorine dioxide for chlorine. Major objectives are to determine the fundamental nature of the AOX produced under these conditions and the kinetics of its formation. A Ph.D. thesis by Barbara Burns, nearly completed, will describe kinetics and other phenomena associated with three-phase chlorination at medium consistency.

Projects related to chemical pulping include two M.S research projects. One, by Ms. Victorine McDonald, will investigate the kinetics of solvent assisted pulping in the alkaline sulfite-anthraquinone-methanol system. The other, by Mr. James Kramer, will examine the kraft pulping behavior of Florida plantation grown eucalyptus, as well as evaluating fundamental and papermaking properties of the resulting pulps. Project 3716, funded by the Containerboard and Kraft Papers Group (CKPG) of the API was recently initiated to develop a method for rapidly measuring the yield of semichemical pulps. Project 3699, funded by the Measurement
Technology Committee of the API, has as its objective the comparative evaluation of several in-line sensors for measuring the conductivity of pulping liquors and other process streams.

Mechanical pulping is the subject of Project 3566, the objective of which is to find ways of mechanically separating wood fibers while retaining their strength and integrity. Most of the recent activity on this project has been directed toward implementation of a chemithermomechanical pulping pilot plant, in collaboration with Georgia Tech and the Herty Foundation. A privately funded project, Project 3697, dealt with the interstage chemical treatment of a chemimechanical pulp, and its effect on pulp properties.

Pulp properties are the central issue in Project 3712. It is privately funded and aims to determine the effects of a fibrous additive on the physical properties of sheets made from both chemical and mechanical pulps. This project, together with the M.S. research of Mr. J. Kramer, represents an important aspect of our research: the interrelationships between pulping and bleaching conditions, fiber properties and sheet properties. These interrelationships are especially important in mechanical pulping, where they dictate pulping conditions.

Our final research area, the improvement of mechanical pulp brightness, brightness stability, and other optical properties, is represented by a dues funded project on mechanical pulp bleaching (Project 3694), a privately funded project (Project 3701), and activity aimed at interfacing with the Wood Chemistry Group, where fundamental dues-funded work aims to determine the mechanism of mechanical pulp yellowing (Project 3524). Project 3694 was recently initiated to explore potential new methods for bleaching mechanical pulps to high and stable brightness. Thus far, it has focussed on the use of mixtures of oxygen and hydrogen peroxide. Project 3701 has examined modifications of known peroxide-based methods for bleaching chemithermomechanical pulp.

A NOTE TO THE PROJECT ADVISORY COMMITTEES

The projects discussed above have been described as dues funded, API funded, privately funded or academic. Although the major remit of the PACs is to monitor and advise on the directions taken in the dues-funded research, we also welcome their review of, and advice on, the other types of projects. In addition, presenting as complete a picture as possible of our full range of activity offers the PACs the opportunity to suggest potential beneficial interactions with dues-funded projects and to appreciate how our resources have been allocated. For these reasons, and wherever possible within constraints imposed by the funding agencies, industry groups or companies, we will present accounts of our research in non-dues-funded areas. Within the same constraints, we will seek the advice of the PACs in these areas. Every effort will be made to forestall confusion by identifying those projects that are funded from sources other than member dues.
ORGANIZATION OF THE REPORT

The present report will summarize the total range of projects, emphasizing the rationale governing the directions taken in each one and interrelationships between them. It will be followed by a series of more focused reports, each giving more detail on a relevant project area.

CHEMICAL PULP BLEACHING

PROJECT 3474 CHLORINE-BASED (DUES-FUNDED) AND RELATED ACTIVITIES

Project 3474, Environmentally Compatible Production of Bleached Pulp, is a dues-funded project that encompasses objectives relating to both chlorine-based and nonchlorine bleaching. The first objective is to decrease discharges of chlorinated organic compounds. The second is to eliminate the use of chlorine. In the near future, we propose to change the second objective to elimination of all chlorine-containing bleaching agents. Our research in the chlorine-based area over the past two years has emphasized dioxins and, more recently, chlorinated organic compounds in general, measured as adsorbable organically bound halogen (AOX).

Dioxins

Project 3664, as yet unmentioned, is closely related to Project 3474. It was entitled "Precursors and Variables in Dioxins Formation". This project, funded by the API through the National Council of the Paper Industry for Air and Stream Improvement (NCASI), was established in late 1989 to address questions concerning the mechanism of dioxins formation during kraft pulp bleaching. Bleaching experiments funded by NCASI were conducted at IPST and analysis of the resulting pulps and effluents was provided by NCASI at their Corvallis, Oregon, analytical facility. This work has resulted in one publication, and a second one is pending.

Since this project was established, the funding arrangement has changed to one in which IPST both funds and performs the bleaching experiments and NCASI analyzes the resulting samples without cost to IPST. Effectively, therefore, Project 3664 ceased to exist as a billing vehicle, and the corresponding research was assimilated by Project 3474.

Within the past year, a statistically designed study of effects of changes in chlorination stage variables was completed and a study of mixing effects was performed.
Oxygen predelignification significantly decreased dioxins generation in the chlorination stage, the decrease being greater when chlorine dioxide was added before chlorine and when the temperature was low. Adding chlorine first significantly reduced dioxins formation, particularly when the incoming pulp was not well washed and when the temperature was low. Increasing the temperature had a beneficial effect, while the effects of black liquor carryover and chlorination filtrate recycle were smaller.

Improved mixing at a kappa factor of 0.25 gave significantly lower E-stage kappa number, but did not result in any decrease in dioxins. In fact, a significant increase was observed. This suggests that the rate of formation of dioxins levels off sharply as the chlorine concentration is increased beyond the range of exponential dioxin increase. Increasing the chlorination consistency from 4 to 6% caused a small but statistically significant increase in TCDD formation, as expected on the basis of the resulting increase in average chlorine concentration. These effects have to be viewed in relation to the corresponding effects on AOX, which were similar at 0.25 kappa factor. As noted below, however, both the magnitude and direction of the consistency effect on AOX depend on kappa factor. It seems likely that the same will be true of the effect on dioxins. Samples generated in experiments designed to test this hypothesis are in NCASI's hands, awaiting analysis.

Analysis of all tetra- through octachlorinated dioxin and furan congeners provided some insight into relevant mechanisms. The TCDF fingerprint, for example, suggests a low probability of chlorination of the ring position adjacent to the ether linkage. This may be an indication of steric hindrance resulting from interaction of the furan oxygen with a pulp component. Another example is the occurrence of a relatively large amount of the 123467/123478 isomer pair, in which both members have a "lopsided" distribution pattern. This is unexpected in view of the ring-deactivating effect of chlorine substituents, and suggests the participation of a non-DBF precursor or steric interaction of partially chlorinated DBF with a fiber component.

AOX

Conditions were established for "poor" and "good" mixing in our laboratory high shear mixer/reactor at two different consistencies, 4 and 7.7%. This was done by simulating a standard laboratory chlorination experiment, but replacing unbleached pulp with fully bleached pulp and replacing chlorine water with dye solution. The dye was injected and the pulp mixed for various times at various speeds, after which a syringe was used to withdraw numerous small samples from various places within the mixture of bleached pulp and dye. The light absorbance at a wavelength corresponding to the dye's absorption maximum was then measured. The coefficient of variation of all such measurements from a given set of experiments was taken as an inverse measure of degree of mixing. In this way conditions were defined that gave good mixing (CV 2-3%) and poor mixing (CV 15-37%).

The second set of experiments consisted of trials at the two different mixing conditions and two different consistencies, 4 and 6%. These experiments all employed a relatively high chlorine charge, corresponding to a kappa factor of 0.25.
Consistency had no effect on the amount of AOX produced, but the degree of mixing had a significant effect which was the same at both consistencies. Poor mixing gave 20% lower total AOX and 5% less delignification. At this high kappa factor, making the mixing poorer concentrates the added chlorine in "pockets". Within these pockets conversion of precursors to AOX is complete and excess chlorine remains. Outside of them, aox precursors remain unconverted. The net result is inefficient conversion to AOX when the mixing is poor. Delignification is also inefficient, but in regions of low chlorine concentration delignification is less hindered by lack of chlorine than is AOX formation. This behavior is to be expected in situations where AOX increases linearly with increasing chlorine concentration, since delignification is known to be more efficient (albeit less complete) at low chlorine concentration than when the chlorine concentration is high. Linear dependences of AOX on kappa factor have been reported in the literature.2,3

The third set of experiments was designed to investigate the effect of mixing on the relationship between AOX formation and kappa factor. Chlorinations were conducted at both mixing conditions and kappa factors ranging from 0.1 to 0.22. The results showed that the negative effect of mixing on AOX, observed previously at high kappa factor, underwent a reversal as the kappa factor was decreased below about 0.15. At the lower values, poor mixing gave higher AOX. Concentrating the chlorine in pockets, where the chlorine concentration nevertheless remained low enough (because of the low kappa factor) so that it was all consumed, resulted in efficient local AOX generation which was not compensated for by the limitation placed on AOX precursor conversion by low chlorine concentration elsewhere. This requires an AOX-chlorine concentration relationship that is nonlinear in the concave upwards sense (less AOX formed per unit increase in chlorine concentration at low chlorine concentrations), in apparent contradiction to linear relationships that have been reported in the literature2,3. A possible explanation may be that the literature correlations were developed, at least in part, by progressively replacing chlorine with chlorine dioxide rather than simply reducing the amount of chlorine added. Berry4, on the other hand, has presented AOX-kappa factor data that approximate a concave upwards nonlinear relationship.

Concurrently with the work described above, experiments were conducted to determine the effect of acidifying or combining effluent samples on the result of the AOX determination. These experiments showed that combining C- and E-stage effluents gave a result that could be predicted by assuming additivity. In other words, no reaction occurs that either generates or destroys AOX when the effluents from the two stages are mixed. This was true even if the combined effluents were subjected to prolonged heating; small losses under these conditions can be attributed to volatilization.

Academic Research On AOX

Mr. Todd Schwantes has begun work on a thesis concerned with the kinetics of formation, and characterization, of AOX generated during the bleaching of kraft pulp in "chlorine-free" sequences. The particular sequences to be investigated are based on the use of oxygen predelignification, 100% substitution of chlorine dioxide for chlorine, and various types of oxidatively reinforced extraction stages.
One objective is to better define, in chemical and physical terms, just what AOX consists of in sequences likely to be used by the industry. Characterization of the AOX formed will include determination of chloroform and other volatile chlorinated compounds, partitioning into ether extractable and non extractable fractions, determination of the molecular weight distributions of both fractions, further partitioning of the ether extractable material into chlorophenols, acids, and neutrals, and determinations of the chlorine:carbon ratio in each fraction. A second objective is to determine how the concentration, molecular weight distribution, and chlorine:carbon ratio of each of these classes of chlorinated compounds develops over time in the chlorine dioxide stage, for all of the sequences to be examined.

This thesis may be expected to produce a variety of useful results, including documentation of the inappropriateness of AOX as an effluent parameter for regulation, possible identification of alternative parameters, and identification of opportunities for eliminating significant environmental impact by appropriate choice of reaction time and sequence.

**Academic Research on Chlorination Kinetics**

Ms. Barbara Burns has completed experimental work on a thesis aimed at obtaining an improved understanding of the critical phenomena governing pulp chlorination when gaseous chlorine is injected into a fluidized medium consistency kraft pulp suspension in a high shear mixer. The experiments were conducted in a specially constructed continuous flow-through high-shear mixer.

Although analysis of the data and preparation of the thesis are as yet incomplete, some general observations can be made. The rate of transfer of chlorine to a suspension of fully bleached pulp increased with increasing rotor speed and chlorine injection rate at a given pulp flow rate, but was only slightly affected by temperature. Increasing the driving force for gas-liquid mass transfer by adding sodium hydroxide to the bleached pulp suspension increased the mass transfer rate, and transfer to a suspension of unbleached pulp in pure water was about as fast as transfer to the bleached pulp in sodium hydroxide. The results can be interpreted to mean that the rate of chlorination of unbleached kraft pulp is gas-liquid mass transfer limited, the transfer rate being effectively determined by bubble size. Reaction of chlorine with the pulp is so fast that its effect is simply to keep the liquid phase concentration from building up to the point where it offers significant resistance to gas-liquid mass transfer.

This thesis provides insight into important processes governing the interaction of reactive gases with unbleached kraft pulp. The knowledge gained will provide a good starting point for similar studies of medium consistency ozone and oxygen treatments.

**PROJECT 3474 NONCHLORINE (DUES-FUNDED) AND RELATED ACTIVITIES**

The second major part of Project 3474 seeks bleaching alternatives that employ no chlorine or chlorine-containing compounds. Our research in this area has been directed toward gaining an understanding of how certain pretreatments, notably nitrogen dioxide, chlorine or bromine, improve the selectivity for lignin of a subsequent oxygen bleaching stage. This work was
interrupted by the departure in March, 1990 of Dr. H. Ohi who was responsible for these studies. Since then, Mr. Kyle Reed has joined our group and assumed this responsibility.

Our current objective is to establish relationships between features of the chemical structure of the residual lignin in unbleached kraft pulp and its subsequent behavior during oxygen bleaching. This is a logical extension of our earlier objective, which was to determine structural changes brought about by treatment with nitrogen dioxide, which is known to have a beneficial effect on oxygen bleachability. A number of such changes were identified, including introduction of carboxyl groups, introduction of alpha-carbonyl groups, depolymerization, and a likely decrease in phenolic hydroxyl group content. Our aim is now to quantify these changes, to introduce them to varying degrees by means other than nitrogen dioxide treatment, and to observe the ensuing effects on the behavior of the pulp in an oxygen stage.

In principle, if the chemical structure of the residual lignin were completely known the oxygen bleaching behavior should be completely predictable; it would then become possible to define a set of desirable structural features and systematically seek a treatment that would approximate them. In practice, it should be possible to correlate oxygen bleachability with a subset of structural features of the incoming residual lignin, for example, carboxyl groups, phenolic hydroxyl groups, alpha carbonyl groups and average molecular weight.

During the current reporting period, a significant part of our effort has been devoted to familiarizing Mr. Reed with the required techniques, as well as re-establishing, improving and validating experimental techniques for nitrogen dioxide pretreatment and oxygen bleaching. In addition, new information has been obtained on the effect of nitrogen dioxide on acid group content of unbleached pulp and on soluble reaction products.

The nitrogen dioxide pretreatment procedure was reestablished and validated by several demonstrations of good precision, including excellent relationships of pretreatment level with filtrate properties and oxygen bleaching behavior. Also the identity of a new pretreatment reaction product, 4,6-dinitroguaiacol, was established.

An immediate objective is to determine the significance of carboxylic acid groups. A conductometric titration method for the determination of total acid groups has been implemented, and preliminary indications of a correlation of acid group content with oxygen stage selectivity have been obtained.

A Related, Privately Funded Project

Project 3694 was conducted on behalf of a member company to investigate potential benefits of oxygen bleaching of an incompletely washed, unscreened sulfite pulp.
CHEMICAL PULPING AND PULP PROPERTIES

Several ongoing activities can be classified as relating to the manufacture or properties of chemical pulps. These include two M.S. student projects, two API funded projects and one project funded by a single company.

ACADEMIC RESEARCH ON PULPING

Ms. V. McDonald has begun an M.S. research project with the objective of quantifying the effect of methanol addition on the kinetics of the early stage of soda, soda-AQ and sulfite-AQ pulping processes. This will capitalize on an opportunity provided by the recently completed Ph.D. thesis of Ms. Karyn Biasca, who constructed an appropriate flow through digester system, equipped with a fluorescence-based dissolved lignin sensor, and used it to derive rate laws for the early phases of the systems mentioned.

Mr. J. Kramer has also begun an M.S. project, this one dealing with the pulping and papermaking properties of Florida plantation grown eucalyptus species. Well characterized trees have been furnished for this study, which will examine kraft pulping behavior and bleachability, as well as fibre and sheet characteristics.

API PROJECTS RELATED TO PULPING

Semichemical Pulp Yield Determination (API-CKPG Funded)

The main objective of this new project, Project 3716, is to develop a method for determination of semichemical pulp yield. It is desirable, but not necessary, that this method should lend itself to real time, on line process control application. Such a method will allow yield-related pulp properties such as compressive strength, to be predicted.

Work to date has centered on near infrared reflectance spectroscopy (NIR) and UV-visible fluorescence spectroscopy. Laboratory pulps have been prepared at different yield levels and subjected to both types of measurements. Both have given promising results. NIR wavelengths have been identified where spectral properties can be used to differentiate between yield levels. Similarly, it has been shown that when dry pulp samples are irradiated with light of a suitable wavelength, the intensity of their fluorescence at 490 nm is apparently related to yield.
Conductivity of Pulping Liquors (API-MTC Funded)

This project, Project 3699, has as its major objective the evaluation of three commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams. A test stand was constructed, incorporating a laboratory digester to serve as a liquor reservoir and heater, a circulating pump, a pipe loop to accommodate the sensors, and a data acquisition system. Temperature-sensor output relationships have been developed for all 3 sensors simultaneously, using sodium hydroxide solutions. Subsequently, it was established that liquor velocity had no effect, and white liquor testing over a range of temperatures and concentrations of sodium hydroxide, sodium sulfide, sodium carbonate, sodium sulfate and calcium carbonate. The testing is now in progress. Multiple regression analysis will be used to determine the influence of each variable on the conductivity. Present indications are that the conductivity can be strongly correlated with active alkali.

Evaluation of a Pulp Additive (Privately Funded)

Project 3712 is concerned with the effect of a fibrous additive on the physical properties of sheets made from both chemical and mechanical pulp.

MECHANICAL PULPING AND PULP PROPERTIES

PROJECT 3566 (DUES-FUNDED) AND RELATED ACTIVITIES

Project 3566 is entitled "Strong, Intact High-Yield Fibers" and was established to investigate ways of separating fibers without damaging them. Recent activity has included cooperative work with the Center for High Yield Pulping Science (CHYPS) and research on effects of wood compression on fiber properties.

CHYPS Support and Effects of CHIP Compression on Fiber Properties

Recent activity has consisted of start-up support for the Center for High Yield Pulping Science. CHYPS combines the capabilities of IPST, Georgia Tech, and the Herty Foundation to support research in high yield pulping. The Center has access to a two stage thermomechanical pulping pilot plant donated to Georgia Tech by the Mead Corporation. A Proposal has been submitted to the DOE for the initial projects to be undertaken by the Center.

In November CHYPS conducted a project to evaluate operating capabilities of the pilot plant and develop data in support of the proposed projects. The project was implemented as a $2^{-1}$ fractional factorial design with main factors of southern pine tree age (10 and 24 years), density (0.37 g/cc to 0.53 g/cc), and chip size (1/8 - 3/4 and 1/4 - 5/4).
Analysis of the Tensile Index, specific energy relationship for the five wood samples confirms a decrease in strength when pulping lower density southern pines.

The appended report on Project 3566 by A.W. Rudie describes the work.

Effects of Chip Compression on Fiber Properties

A new phase of the project started this year, expanding on the earlier project work to develop high strength high yield fibers. The initial emphasis is an investigation of fiber damage in plug screw feeders. Current work is evaluating sodium chlorite holopulping to develop pulps for paper testing and quantify fiber damage.

Evaluation of Interstage Chemical Treatment of Chemimechanical Pulp

This privately funded project compared the effects of interstage chemical treatment on pulp properties with the effects of a corresponding post treatment.

MECHANICAL PULP BLEACHING AND BRIGHTNESS REVERSION

PROJECT 3694 (DUES-FUNDED) AND RELATED ACTIVITIES

Project 3694, entitled "High Brightness, High Yield Pulps" was established at the beginning of the fiscal year 1990-91 to investigate new bleaching methods. Thus far, activity has focused on the use of combinations of oxygen and hydrogen peroxide.

The work is described in detail in the appended report by A.W. Rudie. The main conclusions are as follows.

Oxygen at 80 psig and 80°C will raise the brightness of mechanical pulps by one to two points if used at a pH around 8. The brightness gain does not appear to be additive with second stage bleaching processes using other bleaching agents such as hydrogen peroxide and sodium hydrosulfite. Higher brightness gains are possible when hydrogen peroxide is added to the oxygen process but net bleached brightness is well below what is achievable with peroxide alone. Additional sodium hydroxide can be added in a second stage to make use of the considerable peroxide residual remaining after the oxygen/peroxide treatment. This process raises the overall brightness gain to within several points of what can be achieved with peroxide alone.

When oxygen is used at 120 psig of oxygen and 120°C a substantial loss in brightness is obtained which cannot be recovered in a second stage peroxide or hydrosulfite bleach stage.
Under conditions more typical of a conventional peroxide bleach stage, oxygen is beneficial to bleaching, raising the final brightness by \( \approx 1 \) point GE from what is obtained in a nitrogen atmosphere or a conventional bag bleach. Oxygen when used in a peroxide bleach stage has a larger impact at lower than optimum alkali charges where it can increase brightness by up to 4 points relative to a control bleached in a bag or a nitrogen atmosphere. At present it is not known how sensitive the brightness gain is to oxygen pressure and this will be determined in follow-up experiments.

**A MODIFIED Peroxide BLEACHING PROCESS (PRIVATELY FUNDED)**

Project 3701 evaluated a modified peroxide bleaching process for CTMP.

**PROJECT 3524 (DUES-FUNDED; WOOD CHEMISTRY GROUP)**

This recently-established project is under the leadership of Dr. A.J. Ragauskas of the IPST Wood Chemistry Group.

Quinones appear to be produced during photoyellowing. Their photochemical behavior on a solid matrix may account for color development and is, therefore, being studied in this project. Mono and dimethoxybenzoquinone were synthesized by a unique route in good yield. Both quinones have been absorbed onto a solid support and photolyzed. Dimethoxybenzoquinone was relatively stable to the photolysis conditions. Photolysis of monomethoxybenzoquinone yielded several products, with the predominant compound being the hydroquinone. Apparently, a photo-reduction occurred which suggests that the cellulose is in turn oxidized during the photochemical reaction.

A more complete report is appended.
PROJECT 3566

STRONG, INTACT HIGH YIELD FIBERS

RESEARCH REVIEW

April 3, 1991

Alan R. Rudie
### PROJECT SUMMARY FORM

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**IPST GOAL:**
A significant increase in the yield of useful fibers

**OBJECTIVE:**
Develop wood fiber separation and treatment methods that will allow good control of the strength, physical form and bonding characteristics of the resulting fibers.

**PRIOR RESULTS:**

Chemimechanical pulps have been prepared with sheet strength approaching that of kraft by vigorous sulfonation before refining and post treatments with chlorine dioxide and sodium hydroxide. Fibers sampled from high yield pulps have been shown to be stronger than corresponding wood sections, indicating that at least some of the fibers in the pulp have retained much or all of their native strength. On the other hand, strong correlations between fiber length, fiber strength and compacted fiber cross-sectional area indicate that the less robust (earlywood) fibers are routinely damaged and broken in refining.

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

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

Efforts to cause strong intact chemimechanical fibers to form a sheet with kraftlike strength were pursued. Chemimechanical treatment followed by refining gave sheets of tensile strength in excess of 8 km breaking length; hot pressing and artificial bonding were less successful (6 to 5 km respectively). Addition of kraft fines gave promising initial results with unrefined samples.

In related student research, the distribution of bound sulfite in the cell walls of chemically treated wood has been investigated in view of its implications for chemimechanical pulp properties. A gradient within the \( S_2 \) layer was observed under all treatment conditions. The distribution can be manipulated to a limited extent by varying liquor pH and \( Na_2SO_3 \) concentration\(^2\). In addition, a study of prehydrolysis as a pretreatment in chemimechanical pulping has revealed beneficial effects that may lead to a new pulping process.

**GEORGIA TECH CENTER FOR HIGH YIELD PULP SCIENCE:**

Most recent activity has consisted of start up support for the Center for High Yield Pulp Science (CHYPS). The center combines the research capabilities of IPST, Georgia Tech, and the Herty Foundation, and is led by Georgia Tech.

The Center has use of a two stage continuous pilot refining system consisting of a Sunds Defibrator CD-300 pressurized first stage refiner and a Defibrator ROP-20 atmospheric second stage refiner. It is also equipped with a KMW chip classifier, atmospheric presteaming, atmospheric pre-impregnation, a pressurized second stage of impregnation, pressurized steaming, and interstage washing. The system was donated to Georgia Tech by the Mead Corporation and has been installed at the Georgia Power Technology Applications Center near IPST.

Proposals have been developed for three initial projects to be undertaken by the Center. They deal with chip size effects, manufacture of CTMP from dense hardwoods, and the pulping of juvenile wood of southern pines. A grant proposal has been submitted to the U. S. Department of Energy for additional project funding. The Center is still awaiting a decision by DOE on this proposal. Without this additional funding, the activities of the center will be seriously constrained.

An initial mini-project was carried out last year to evaluate the centers operating capabilities and develop data in support of the proposed projects. The project was implemented as a \( 2^{3-1} \) fractional factorial design with main factors of southern pine tree age (10 and 24 years), density (0.37 g/cc to 0.53 g/cc), and chip size (1/8 - 3/4 and 1/4 - 5/4). Each experiment was performed twice to obtain additional information on reproducibility.
Analysis of the freeness, specific energy relationship (Fig. 1) for the five wood samples indicates that there may be a decrease in energy requirements when increasing chip size, increasing wood density, and using juvenile wood. The experimental error within a run and between the duplicate runs is sufficient to discourage drawing firm conclusions from the data. The majority of the error is thought to be in the motor load instrumentation. This is in the process of being upgraded.

Results for tensile index are clearer. Analysis of the tensile index vs. specific energy relationship in Figure 2 shows a good correlation to wood chip average specific gravity. The sample of low density mature wood with a small chip size was obtained at extraordinarily low plate gaps on the second stage refiner (0.06 mm) and is probably not representative of strength development under normal refining conditions.
Figure 2. Tensile Index vs. Specific Energy Consumption for the five wood supplies. Chip specific gravity is OD mass over green volume in g/cc.

SUMMARY OF RESULTS SINCE LAST REPORT:

Since the CTMP Center is still waiting for project funding from the Department of Energy, we have not started the projects on The Production of TMP and CTMP From Juvenile Southern Pines, The Manufacture of CTMP From Dense Southern Hardwoods, and The Influence of Chip Size in the Manufacture of TMP and CTMP When Using Compression Type Plug Screw Feeders. DOE has indicated that the proposal may still be funded later on this year.

An alternative project was started in February that is more in accord with the stated goals of the project. Although the overall objective is to evaluate the Alkaline Peroxide Mechanical Pulping process for producing high strength pulps, the initial step is to evaluate the effect of compression feeders and impregnators on fiber integrity and develop alternatives to single fiber tensile testing for measuring fiber strength.
For the lab study, a compression cell has been constructed to compress wood chips using a Carver hydraulic press. A procedure is being evaluated where-by the chips are delignified with sodium chlorite and alkaline extractions to complete the pulping without inducing additional fiber damage. The resulting pulp should develop sufficient bond strength to give reliable zero span tensile tests and useful fiber strength information from the tear and tensile tests. In practice, this procedure has much in common with the chlorine dioxide, alkaline extraction treatments evaluated for improving inter-fiber bonding strength in high yield pulps in project 3476.

Since the wood chips are still normal size after compression impregnation in the press, the typical chlorite procedures using pin chips and extracted wood samples are not entirely successful. The initial 25 gram sample required two chlorite treatments and alkaline extraction with 0.1 N NaOH before it was sufficiently delignified to break up into pin chips. Both of the initial treatments had high chlorite/chlorine dioxide residuals indicating that the delignification process is not proceeding to completion. The presence of hard chip centers after the first two treatments suggests that the limitation may be a diffusion or chip penetration problem. At present, we anticipate one or two additional treatments of chlorite and extraction will be required to obtain pulps suitable for testing.

PLANNED ACTIVITIES THROUGH FISCAL YEAR 1991:

The pilot plant run generated a large amount of data which still needs analysis both for improving our operating and control capabilities, and information on the refining differences between the five wood sources. The projects proposed in the Center Prospectus cannot proceed until the DOE funding is received or alternative funding is secured.

Research will continue on the laboratory Alkaline peroxide pulping as time permits. The near term focus is to improve the chlorite delignification procedure. Options to be evaluated include adding sodium chlorite to the solution absorbed by the wood chips when the press pressure is released and steam impregnation of the sodium chlorite to reduce wood chip penetration problems with the existing soak impregnation process. There may also be an advantage to initiate the chlorite delignification procedure with an alkaline extraction to remove extractives and other alkali soluble material prior to the initial chlorite treatment. Final pulps will be tested for zero span tensile, tensile index, tear index, kajaani fiber length and freeness. The physical test results can be adjusted by the yield from the chlorite delignification to obtain the initial fiber strength.

Once the chlorite procedure has been improved and validated, it will be used to evaluate fiber damage from chip compression using compression ratios ranging from three to one to six to one, and temperature ranging from room temperature to 80° C. The initial work will use the laboratory Carver press to compress the chips, follow-up work will evaluate fiber damage from the CHYPS pilot plant plug screw feeders where there is considerably more shear and chip size reduction. The CHYPS pilot plant has plug screw feeders with compression ratios of 3 to 1, 4 to 1 and 5 to one, allowing for a thorough study of the variables in this process step.
Once an evaluation of fiber damage in compression impregnators is completed, the project will focus on alkaline peroxide pretreatment of softwood and hardwood chips and fiber strength after subsequent refining.

**POTENTIAL FUTURE ACTIVITIES:**

Future activities will be coordinated with the project proposals of the Center. IPST member funded research will build on both DOE and Center member-funded projects. Emphasis will be on translation of fiber strength to improved paper properties. The consortium program for 1991 will concentrate on the refining process. Likely projects to be considered will be alternative chemical treatment methods to reduce energy demand and/or improve pulp properties, development of refiner plates for production of high yield pulps from dense hardwoods, and evaluation and development of new process instrumentation.
1. INTRODUCTION

Previous work on this project has demonstrated that chemimechanical pulps can be obtained with sheet strengths approaching that of kraft by vigorous sulfonation before refining and post treatments with chlorine dioxide and sodium hydroxide. Fibers sampled from high yield pulps have been shown to be stronger than corresponding wood sections, indicating that at least some of the fibers in the pulp have retained much or all of their native strength. On the other hand, strong correlations between fiber length, fiber strength and compacted fiber cross-sectional area indicate that the less robust (earlywood) fibers are routinely damaged and broken in refining\(^1\).

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

A series of trials were conducted in a member company’s thermomechanical pulping pilot plant to established the effects of fiberization temperature on fiber strength retention. The results show that fiberization at 160\(^\circ\) C gives stronger fibers than 120\(^\circ\) C, and that fiber fragments tend to be weaker than intact fibers\(^1\). These findings suggest that fiber strength is reduced during fiber separation and the extent of fiber damage increases with increasing resistance to separation. This confirms that conventional thermomechanical pulping sacrifices fiber strength for surface development by separating fibers at less than optimal temperatures for fiber strength retention.

Efforts to cause strong intact chemimechanical fibers to form a sheet with kraft-like strength were pursued. Chemimechanical treatment followed by refining gave sheets of tensile strength in excess of 8 km breaking length; hot pressing and artificial bonding were less successful (6 to 5 km respectively). Addition of kraft fines gave promising results with unrefined samples.

A related student project determined the distribution of bound sulfite in the cell walls of chemically treated wood. A gradient in the concentration of bound sulfur was observed within the S\(_2\) layer under all treatment conditions\(^2\). The distribution can be manipulated to a limited extent by varying liquor pH and Na\(_2\)SO\(_3\) concentration. In addition, a study of prehydrolysis as a pretreatment in chemimechanical pulping revealed beneficial effects that may lead to a new pulping process.
1.2 Georgia Tech Center for High Yield Pulp Science

Recent project activity has consisted of start up support for the Center for High Yield Pulp Science (CHYPS). The Center combines the expertise and research capabilities of IPST, Georgia Tech, and the Herty Foundation, and is led by Georgia Tech.

The Center has a two stage continuous pilot plant consisting of a Sunds Defibrator CD-300 pressurized first stage refiner and a Defibrator ROP-20 atmospheric second stage refiner. It is also equipped with a KMW chip classifier, atmospheric presteaming, atmospheric pre-impregnation, a pressurized second stage of impregnation, pressurized steaming, and interstage washing. The system was donated to The Georgia Institute of Technology by the Mead Corporation and has been installed at the Georgia Power Technology Applications Center near IPST and the Georgia Tech campus.

A proposal for the following three initial projects has been submitted to the U. S. Department of Energy:

1. The Effects of Chip Size in the Manufacture of TMP and CTMP
2. The Manufacture of CTMP From Dense Southern Hardwoods
3. The Preparation of TMP and CTMP From the Juvenile Wood of Southern Pines.

The Center is still awaiting a decision by DOE on this proposal. This funding is needed to avoid placing serious constraints on the operation of the Center.

A preliminary investigation of the proposed projects has been carried out to evaluate the Center’s operating capabilities and develop data in support of the proposed projects. Since the pulping conditions and constraints for preparing high yield pulps from dense hardwoods precludes combining this study with the softwood projects, the influence of southern pine tree density was substituted for the dense hardwood part of the project. The investigation was implemented as a 2^3-1 fractional factorial design with main factors of southern pine tree age (10 and 24 years), wood density (0.37 g/cc to 0.53 g/cc), and chip size (1/8 - 3/4 and 1/4 - 5/4). Each experiment was performed twice to obtain information on reproducibility.

1.3 Alkaline Peroxide Mechanical Pulping

An investigation of the alkaline peroxide mechanical pulping process (APMP) was started in February. The project is expected to provide initial operating parameters for the CHYPS high density southern hardwoods project and is also intended to evaluate the effects of chip compression and plug screw feeders on high yield pulp quality and retention of fiber strength. The initial effort is an investigation of alternatives to single fiber tensile testing for measuring fiber strength.
The principle test for determining fiber strength is the zero span tensile test. Unfortunately, with poorly bonded pulps like a high freeness high yield pulp, there is enough slippage under the clamps of the tensile tester to affect the outcome of the test. In addition, the test cannot be conducted on crushed wood samples without first rendering them to fibers suitable for papermaking. The chlorite and peracetic acid holopulping methods are capable of performing this pulping process without inducing additional fiber damage. The resulting pulp should develop sufficient bond strength to give reliable zero span tensile tests and useful fiber strength information from the tear and tensile tests as well. In practice, this procedure has much in common with the chlorine dioxide, alkaline peroxide/extraction treatments evaluated for improving inter-fiber bonding strength in high yield pulps.

2. RESULTS AND DISCUSSION

2.1 CHYPS Preliminary Project

The results of the pilot plant preliminary project are reported in Tables 1 and 2 at the end of this report. More was learned about the operation of the pilot equipment than about the influence of the wood supply variables on TMP production and quality. The agreement between replicates is poor, primarily because of the improvement in operating capability during the first round of experiments. Sample date for the replicate runs on juvenile low density wood in a small chip size is displayed in figure 1. This data graphically shows the improvement in ability to load the refiners between the first experiment and the seventh experiment of the project.

Analysis of the freeness, specific energy relationship (Fig. 2) for the five wood samples indicates that there may be a decrease in energy requirements when increasing chip size, increasing wood density, and using juvenile wood. However, the experimental error within a run and between the duplicate runs is sufficient to discourage drawing firm conclusions from this data. The results do show a significant degree of uniformity that offers considerable evidence of the future capabilities of the equipment. The majority of the error is thought to be in the motor load instrumentation and high motor loads on the second stage refiner caused by plugging of the refiner casing. Both problems are in the process of being resolved.

Results for tensile index are clearer but still should not be considered statistically significant. Analysis of the tensile index vs. specific energy relationship in Figure 3 shows a surprisingly good correlation to wood chip average specific gravity. An apparent exception was the pulp obtained from the sample of low density mature wood with a small chip size. It was obtained using extraordinarily low plate gaps on the second stage refiner (0.06 mm) and is probably not representative of strength development under normal refining conditions.

The overall increase in pulp quality associated with an increase in wood density within the southern pines finds support in the literature for radiata pine. This observation of course runs contrary to the well known general improvement in pulp quality when using lower density
softwoods from different species (see, for example, Figure 5). This apparent contradiction is good reason to pursue the project on juvenile pines. The project is expected to advance our understanding of the role of fiber morphology on high yield pulp quality and provide a means to identify southern pine varieties with improved high yield pulping capabilities.

2.2 Alkaline Peroxide Mechanical Pulping

An impregnation cell has been constructed to compress wood chips using a Carver hydraulic press (Figure 4). With this device, wood chips can be subjected to compression ratios typical of commercial plug screw devices, but without the shear and chip shredding of the commercial equipment. The combined effects of compression and shear will be investigated later using the CHYPS pilot scale screw feeders and samples from commercial impregnators.
Figure 2. Freeness vs. Energy relationship for the five wood samples.

To impregnate chips in the laboratory impregnator, the screen cylinder (item 5 in figure 4) is placed inside the immersion vessel (item 8). The handles on the cylinder are aligned with slots in the sides of the immersion vessel to allow the cylinder to sit on the bottom of the vessel over the bottom plate (item 9). The screen cylinder is loaded with 250 - 300 g OD wood chips. Chips can be heated by pushing a flexible, low pressure steam line through the wood chips to the bottom of the cylinder and steaming for the desired length of time. The impregnator is shaken to compact the chips, the ram (item 1) placed on the chip mass and a measurement taken from a scale on the side of the ram to determine the initial chip volume.

The impregnator is then placed in the press and compressed to the desired final volume again using the scale on the side of the ram. A 3-inch spacer is available to complete the compaction when the desired volume reduction exceeds the cylinder travel of the press. After completing the compaction, the immersion vessel is drained of any expressed filtrate and then filled with the solution to be added to the chips. The press pressure is released and the screen cylinder
Figure 3. Tensile Index vs. Specific Energy Consumption for the five wood supplies. Chip specific gravity is OD mass over green volume in g/cc.

raised and turned so that the handles sit on the top rim of the immersion vessel. Generally, the majority of the chip plug will remain compacted in the screen cylinder. The plug can then be forced out of the screen cylinder into the bottom of the immersion vessel by applying pressure to the ram.

The initial effort on using sodium chlorite to delignify wood chips has highlighted some difficulties with the procedure. Since the wood chips are still normal size after compression impregnation in the lab press, the typical chlorite procedures using pin chips and extracted wood samples are not entirely successful. The initial 25 gram wood sample required two chlorite treatments and alkaline extraction with 0.1 N NaOH before it was sufficiently delignified to break up into pin chips. Both of the initial treatments had high chlorite/chlorine dioxide
Figure 4. Drawing of the laboratory impregnation cell. The cell capacity is 250 OD grams of wood chips with a maximum compression ratio of ≈ 5 to 1.
residuals indicating that the chlorine dioxide is unable to react with much of the wood lignin. The presence of hard chip centers after the first two treatments suggests that the problem is insufficient chemical penetration of the wood chips. Two additional treatments with sodium chlorite and alkaline extraction are required to obtain a pulp suitable for testing.

An additional problem is the slow pulp filtration experienced after the alkaline extraction stages. This appears to be caused by hemicellulose forming a film over the filter paper and impeding drainage.

3. PLANNED ACTIVITIES THROUGH FISCAL YEAR 1991

Project 3566 is being terminated at the end of fiscal year 1990 and will be replaced by a new project. The following activities will take place under the new project.

3.1 CHYPS

The pilot plant run last November generated a large amount of data which still needs analysis both for improving our operating and control capabilities, and whatever information can be obtained on the refining differences between the five wood supplies. Because of the improvements in operating performance that occurred during the project, and hoped-for improvements in refiner performance from planned maintenance, it is not clear how much useful information can be obtained from this data and it is not intended to spend much additional time on analysis. This effort will be completed by mid-summer so that any information will be available in case project funding is obtained this fall. The projects proposed in the Center Prospectus cannot proceed until the DOE funding is received or alternative funding is secured.

3.2 Alkaline Peroxide Mechanical Pulping

Research will continue on the laboratory APMP project. The near term focus is to improve the chlorite delignification procedure. Options to be evaluated include adding sodium chlorite to the solution absorbed by the wood chips when the press pressure is released and steam impregnation of the sodium chlorite. Both procedures should reduce the wood chip penetration problem but the steam impregnation process is preferable since it is suitable for use on control experiments as well. There may also be an advantage to initiate the chlorite delignification procedure with an alkaline extraction to remove extractives and other alkali soluble material prior to the initial chlorite treatment.

In the next attempts at delignifying wood with this process, the washing step will be performed by centrifuging the pulp and pouring off the filtrate to avoid plugged filter papers and eliminate the resulting yield losses.
The pulp obtained from the delignification procedure will be tested for zero span tensile, tensile index, tear index, kajaani fiber length and freeness. The physical test results will be adjusted by the yield from the chlorite delignification to obtain the initial fiber strength.

Once the chlorite procedure has been improved and validated, it will be used to evaluate fiber damage from chip compression using compression ratios ranging from three to one up to five to one, and temperature ranging from room temperature to 80\(^\circ\) C. The initial work will use the laboratory Carver press to crush the chips, follow-up work will evaluate fiber damage from the CHYPS pilot plant plug screw feeders where there is considerably more shear and chip size reduction. The CHYPS pilot plant has plug screw feeders with compression ratios of 3 to 1, 4 to 1 and 5 to one, allowing for a thorough study of the variables in this process step.

On completion of the evaluation of fiber damage in compression impregnators, the project will focus on alkaline peroxide pretreatment of softwood and hardwood chips and fiber strength after subsequent refining.

4. STUDENT RESEARCH

In reviewing the literature, and attempting to understand the influence of fiber morphology on mechanical pulping, it was observed that a graph of tree density against mechanical pulp breaking length did not give a straight line. If one looks at a mechanical pulp under a microscope, it becomes obvious that the much of surface area developed is from the fiber cell wall and the best way to predict the mechanical pulping potential of a particular tree or species would be to determine the amount of fiber surface that exists per unit of fiber volume or fiber mass. This can be estimated from fiber dimensions using the ratio of average fiber circumference to average fiber cross sectional area. When this ratio is plotted against breaking length at 2000 kWh/BDT it gives a straight line (figure 5.).

This relationship can be derived from the Shallhorn, Karnis equation for tensile strength in a bond strength limited paper given the following assumptions:

* The yield of surface area per unit of applied energy is different for cleavage between fibers and cleavage across the fiber through the secondary fiber wall.

* The yield of surface area per unit of energy for a given fracture location is independent of softwood species and therefore the overall yield of surface area is dependent only on fiber morphology and pulping conditions.

* Bond strength and relative bonded area are either constant or linearly dependent on surface area developed from a specific fracture type.
Figure 5. Average fiber circumference divided by fiber cross sectional area gives a straight line relationship to TMP breaking length at 2000 kWh/BDT.

The first assumption needs little explanation. The differences in energy requirements and average fiber length between stone groundwood and TMP is evidence that there are at least two different fracture mechanisms and locations in wood and that the relative frequency of fracture from the two mechanisms can be controlled by changes in the operating conditions.

Strictly speaking, the second assumption requires that the chemical nature and distribution of lignin, cellulose and hemicellulose within the cell wall and their relative concentrations be constant in the softwoods. Obviously, the assumption is false since the lignin content of the species in figure 5 ranges from 27% for Black Spruce and Douglas Fir up to 29% for the Western Hemlock. It is however, certainly true that the basic nature and location of the cell wall constituents is relatively uniform throughout the softwoods and it is probably a safe assumption that the relatively small variations in the chemical nature of the softwoods cannot account for the 100% difference in breaking lengths observed in figure 5.
As for the third assumption, it is probably true that bond strength per unit bonded area is relatively constant throughout the softwoods and is largely dependant on the location in the cell wall from which the surface area is derived, i.e. the point of fiber cleavage or fracture. It is probably not true that relative bonded area is a constant fraction of total surface area because, for instance, it is well known that thick cell walled fibers do not bond as well as thinner cell walled fibers that can readily collapse in the paper. It is probably also unrealistic to hope that the relationship between relative bonded area and total surface area is linear to fiber circumference divided by cross sectional area. Again, appears to be safe to assume that the contribution of these factors to a well refined, low freeness TMP is small in comparison to other factors such as the ease of developing surface area as determined by the differences in average fiber morphology.

Regardless of theory, the graph of breaking length vs. the ratio of fiber circumference divided by cross sectional area is a straight line (Figure 5). Unfortunately, the data used to generate figure 5 is not all derived from the same source. In fact, the mechanical pulp data and fiber dimensional data are from different sources in most cases. The relationship needs to be demonstrated under controlled conditions where the fiber dimensions can be obtained on the same wood supply as the pulp and paper data and where equipment and procedure are constant.

A Masters Degree candidate, Mr. Joe Morra, has decided to investigate this relationship as an independent study project. The project requires collecting fiber dimensions and thermomechanical pulping performance data for four or five softwood species and using the CHYPS pilot plant to produce the thermomechanical pulp. Because of the number of samples required to obtain statistically reliable data in the pilot plant, we are proposing to support the Academic project with lab assistance from the new project budget.

POTENTIAL FUTURE ACTIVITIES

Future activities will be coordinated with the project proposals of the Center. IPST member funded research will build on both DOE and Center member-funded projects. Emphasis will be on translation of fiber strength to improved paper properties. The consortium program for 1991 will concentrate on the refining process. Likely projects to be considered will be alternative chemical treatment methods to reduce energy demand and/or improve pulp properties, development of refiner plates for production of high yield pulps from dense hardwoods, and evaluation and development of new process instrumentation.
REFERENCES


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<td>0.30</td>
</tr>
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<td>9.4</td>
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<td>59.1</td>
<td>88.5</td>
<td>39.7</td>
<td>1.4</td>
<td>9.9</td>
<td>1.7</td>
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</table>
PROJECT 3694

HIGH BRIGHTNESS, HIGH YIELD PULPS

RESEARCH REVIEW

April 3, 1991

Alan R. Rudie
PROJECT SUMMARY FORM

Project Title: HIGH BRIGHTNESS, HIGH YIELD PULPS
Division: Chemical and Biological Sciences
Project No.: 3694
Project Code: HIBRT
Project Leader: Alan W. Rudie
FY 91-92 Budget: $100,000

IPST GOAL:
A significant increase in brightness and a decrease in bleaching cost for high yield pulps

OBJECTIVE:
Develop a cost effective method to produce high yield pulps of high and stable brightness.

PRIOR RESULTS:
New Project

SUMMARY OF RECENT RESULTS:
Several series of scoping experiments using oxygen and peroxide at various pH values have been performed. Results to date have been tantalizing but we have been unable to identify oxygen/peroxide treatment conditions that give an overall brightness gain relative to conventional peroxide bleaching.

In the first series of experiments, a News grade TMP was treated with 80 psig oxygen at 80°C for 90 minutes, both with and without added hydrogen peroxide. Reactions were carried out at high alkali charge (2% NaOH on OD pulp) and at a starting pH of 8, 5, and 3. Samples that did not receive peroxide in the oxygen treatment stage were bleached with hydrogen peroxide under standard conditions after the oxygen treatment. All samples were post bleached with sodium hydrosulfite as well. All samples were compared to a standard hydrogen peroxide bleach control.
Samples treated with oxygen, or oxygen and peroxide at pH ranges between 8 and 5 all showed increases in brightness relative to the unbleached starting pulp. The sample using both oxygen and peroxide at pH 8 gave the best brightness gain, 8 pts. relative to the unbleached control. Samples post treatment bleached with 1% hydrogen peroxide all gave a 10 to 12 point brightness gain with net gains relative to the unbleached pulp of about 12 points.

A second series of experiments were conducted, using 120 psig oxygen at 120° C. The pH levels selected were all conditions from the first series of experiments that did not lose brightness relative to the unbleached pulp, i.e. pH 8, 5 and 3. All samples treated under these conditions lost brightness. Additional pulp samples were treated with oxygen or oxygen and peroxide at pH 8, 80 psig and 80° C. Again, these samples were compared to a conventionally bleached hydrogen peroxide control experiment. The sample without peroxide gave no change in brightness (compared to a 1 point gain in the first experiment) and the sample with peroxide gained just 4 pts. (compared to 8 in the first experiments). Interestingly, the peroxide residual indicated that little or no peroxide was consumed in the oxygen/peroxide treatment.

To confirm this result, a third series of experiments was performed investigating oxygen/peroxide treatments around pH 8, 80°C and 80 psig of oxygen for 90 minutes. After the oxygen/peroxide treatment, the sample was divided and 1/2 was fortified with sodium hydroxide, and held at 60° C for an additional 90 minutes. The other half of the sample was worked up as before. Brightness gains after oxygen/peroxide were on the order of 1 to 3 points relative to the unbleached control but in all cases, the peroxide residual was equal to or higher than the starting peroxide charge. Unfortunately, the samples fortified with caustic and held at temperature for an additional 90 minutes gave final brightness within 1 point of the peroxide bleached control pulp.

**PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:**

A final series of scoping experiments is underway to determine if the oxygen/peroxide treatment will be effective at high (4%) peroxide charges and whether increases in peroxide residual and/or brightness can be obtained with slight changes in process conditions. These experiments will also include an accelerated light reversion test to evaluate brightness stability of the pulps.

Present plans are to follow the scoping experiments with a complete factorial design experiment to determine optimum pH, temperature and O₂ pressures. This work will probably be carried out at the 4% peroxide level since an additional 2 points brightness is of much greater value in the higher brightness ranges. Additional work on a hardwood high yield pulp is also planned.

If the brightness stability of the oxygen/peroxide treated pulps is improved, we will follow up with additional experiments to determine the quinone and hydroquinone/catechol concentration of the pulps.
POTENTIAL FUTURE ACTIVITY:

This project will emphasize development of effective processes for achieving high and stable brightness in high yield pulps. Possible future activities include: an evaluation of metal and metal complex catalyzed oxygen and/or peroxide bleaching of high yield pulps, an evaluation of peroxide bleaching at ultra-high pulp consistencies, and an evaluation of the effects of autoxidizable peroxide forming organic additives on brightening by oxygen, with or without added peroxide.
HIGH BRIGHTNESS, HIGH YIELD PULPS

1. INTRODUCTION:

For many years, the rallying cry of high yield pulping research has been 90-90-9; 90 points brightness, 90% yield and 9 km breaking length. Although still far from 90 GE brightness and 9 km breaking length, with development of market aspen CTMP at 80 - 83 ISO brightness and 6 km breaking length¹ the high yield pulping community is approaching the most significant properties of the bleached Kraft hardwood pulps used in many integrated southern mills². We are now seeing a shift in the R & D emphasis to other characteristics of high yield pulps that still fall far short of chemical pulp performance. At present, the brightness reversion of high yield pulps is considered to be the primary characteristic preventing bleached aspen CTMP from making significant inroads into the printing and writing papers market³.

Although brightness reversion is a significant barrier to market penetration in some paper grades, in the U.S. the problem is a bit more basic: high brightness CTMP simply costs too much. With a specific energy requirement of 1000 kWh/BDT and bleach requirement of 3-4% hydrogen peroxide, the manufacturing costs of a softwood CTMP approaches or exceeds the manufacturing cost of hardwood kraft pulp in much the country.

The obvious means to reduce the manufacturing costs of high yield pulps in the U.S. are to reduce the electrical energy requirements of the process or reduce the cost of bleaching to high brightness. This proposal is concerned with investigating alternative bleaching processes with potential to reduce bleaching costs and/or increase bleached brightness in high yield pulps.

In reviewing low cost oxidizing and reducing agents capable of bleaching pulp, one obvious alternative is oxygen. The similarities in reactivity of hydrogen peroxide and oxygen in kraft pulp bleaching⁴ suggest that oxygen alone or in combination with hydrogen peroxide, might also work in bleaching mechanical pulps.

2. RESULTS AND DISCUSSION:

2.1 Preliminary Experiments

The initial phase of the project has been to carry out a series of preliminary experiments to evaluate the effects of oxygen on mechanical pulps under a wide variety of process conditions. (Table 1). These experiments using oxygen at 80 psig and carried out at 80° C indicate that oxygen is capable of increasing mechanical pulp brightness by about 1 point when used at a pH near neutral (experiments 3 and 5). Experiments conducted in the same pH range in the presence of hydrogen peroxide (exp. 4 and 6) show even better brightness gains, but well below the overall brightness achieved using oxygen alone in the first stage and a follow-up second stage peroxide bleach.
Nearly all samples show a normal response to bleaching with sodium hydrosulfite in a second stage, about a ten point brightness gain. The exception is experiment 4 using oxygen and peroxide in the first stage to obtain six points in brightness which gained only four points brightness in the second stage hydrosulfite bleach. The low brightness gain in the peroxide bleached control raises some concerns on the interpretation of results. It was decided to repeat several experiments and to investigate stronger conditions at acid pH where the first group of experiments are indecisive.

Table 1. Scoping Experiments on Using Oxygen in Bleaching TMP

<table>
<thead>
<tr>
<th>Exp #</th>
<th>NaOH/pH</th>
<th>H₂O₂</th>
<th>pH off</th>
<th>GE</th>
<th>First Stage Results</th>
<th>Second Stage</th>
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<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>H₂O₂</td>
<td>GE</td>
</tr>
<tr>
<td>1.1</td>
<td>2%</td>
<td>0</td>
<td>9.9</td>
<td>39.0</td>
<td>51.5</td>
<td>47.7</td>
</tr>
<tr>
<td>1.2</td>
<td>2%</td>
<td>1</td>
<td>9.8</td>
<td>46.2</td>
<td>56.8</td>
<td>3.2</td>
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<tr>
<td>1.3</td>
<td>8</td>
<td>0</td>
<td>5.3</td>
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<td>1.4</td>
<td>8</td>
<td>1</td>
<td>7.4</td>
<td>59.3</td>
<td>62.4</td>
<td>2.1</td>
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<tr>
<td>1.5</td>
<td>5</td>
<td>0</td>
<td>4.9</td>
<td>52.1</td>
<td>62.9</td>
<td>62.6</td>
</tr>
<tr>
<td>1.6</td>
<td>5</td>
<td>1</td>
<td>5.2</td>
<td>54.3</td>
<td>64.7</td>
<td>2.0</td>
</tr>
<tr>
<td>1.7</td>
<td>3</td>
<td>0</td>
<td>4.1</td>
<td>51.3</td>
<td>63.4</td>
<td>62.3</td>
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<tr>
<td>1.8</td>
<td>3</td>
<td>1</td>
<td>4.2</td>
<td>52.9</td>
<td>63.5</td>
<td>1.8</td>
</tr>
<tr>
<td>C</td>
<td>%</td>
<td>1</td>
<td>9.2</td>
<td>55.1</td>
<td>63.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>

All experiments were carried out on a commercial news grade southern pine TMP of 51.6 GE starting brightness. Experiments are at 80°C, 80 psig of oxygen for 90 minutes. In all cases, the peroxide charge was 1% on OD pulp and experiments 1, 3, 5, and 6, which did not receive peroxide in the first stage were bleached with 1% hydrogen peroxide as a second stage. Second stage hydrosulfite bleaching was with 1% hydrosulfite on OD pulp. See the experimental section for details.

The second series of experiments is reported in Table 2. The first six experiments (2.1 to 2.6) were conducted at 120°C and 120 psig of oxygen to determine if the more aggressive conditions would increase the activity of the oxygen. The second group of experiments (2.7 to 2.9) includes repeats of experiments 1.3 and 1.4 to confirm the earlier results.

All experiments carried out at the higher temperature and pressure gave a substantial loss in pulp brightness. In the experiments that did not receive hydrogen peroxide in the first stage, a second
Stage peroxide bleach regained much of the brightness lost in the first stage but in all cases the final brightness was below the starting pulp brightness of 55.9.

Table 2. Preliminary Experiments on Oxygen Treatment of TMP

<table>
<thead>
<tr>
<th>Exp #</th>
<th>H₂O₂</th>
<th>pH on H₂O₂ (NaOH)</th>
<th>O₂ psig</th>
<th>Temp °C</th>
<th>pH off</th>
<th>% H₂O₂</th>
<th>GE 2nd Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0</td>
<td>8</td>
<td>120</td>
<td>120</td>
<td>3.4</td>
<td>0.002</td>
<td>38.6</td>
</tr>
<tr>
<td>2.2</td>
<td>1.0</td>
<td>8</td>
<td>120</td>
<td>120</td>
<td>3.3</td>
<td>0.002</td>
<td>38.8</td>
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<td>2.3</td>
<td>0</td>
<td>5</td>
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<td>0.002</td>
<td>41.0</td>
</tr>
<tr>
<td>2.4</td>
<td>1.0</td>
<td>5</td>
<td>120</td>
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<td>2.6</td>
<td>0.002</td>
<td>37.0</td>
</tr>
<tr>
<td>2.5</td>
<td>0</td>
<td>3</td>
<td>120</td>
<td>120</td>
<td>3.2</td>
<td>0.002</td>
<td>42.0</td>
</tr>
<tr>
<td>2.6</td>
<td>1.0</td>
<td>3</td>
<td>120</td>
<td>120</td>
<td>2.8</td>
<td>0.30</td>
<td>33.2</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>(1.0)</td>
<td>0</td>
<td>60</td>
<td>8.0</td>
<td>0.25</td>
<td>65.1</td>
</tr>
</tbody>
</table>

2.7 1.0 (1.5) 80 80 7.0 0.08 65.0
2.8 0 8 80 80 5.8 0.002 56.6 66.9
2.9 1.0 8 80 80 5.1 0.55 60.9
C    1.0 (1.0) 0 60 8.4 0.33 67.9

All experiments conducted on a laboratory southern pine RMP of starting brightness 55.9. Pulp was pre-treated with DTPA before starting, and experiments 2.2, 2.7, 2.9 and the two controls received 3% sodium silicate and 0.25% magnesium sulfite.

Experiment 2.7 with 1% peroxide and 1.5% sodium hydroxide resulted in a brightness gain of 9 points, still lower than the peroxide bleached control experiments. Although in all cases, the final brightness is below the brightness of the peroxide bleached control, experiment 2.9 has an intriguingly high peroxide residual.

The activity of oxygen at a pH around 8 does not come as a surprise. The primary chromophores in mechanical pulps, α-carbonyls and ring conjugated olefins on free phenolic lignin units, are the most acidic of the phenolic groups and should undergo alkaline activation at near neutral pH where the majority of the lignin phenolic structures are still in their acid form. For example, the α-carbonyl acetoguiacone, reacts with oxygen at a pH of 7.5⁵ and milled wood samples are still very reactive to oxygen delignification in bicarbonate buffers⁶.
2.2 Two Stage Bleaching to Utilize the Peroxide Residual

The third series of experiments was designed to determine if the residual peroxide observed in experiment 2.9 could be used to further bleach the pulp by adding sodium hydroxide and holding the temperature at 60°C in a second stage. Since it was thought that hydroquinones might be autoxidizing to give hydrogen peroxide, a small amount of anthraquinone was added to experiment 3.3 to see if it would undergo reduction by the pulp and generate additional peroxide. Results are reported in table 3.

Table 3. Evaluation of Post-treatment with Sodium Hydroxide.

<table>
<thead>
<tr>
<th>Exp #</th>
<th>pH on (NaOH)</th>
<th>Temp °C</th>
<th>pH off</th>
<th>H₂O₂ Resid, %</th>
<th>GE %</th>
<th>2nd % NaOH</th>
<th>Stage GE</th>
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<tbody>
<tr>
<td>3.1</td>
<td>8</td>
<td>80</td>
<td>5.4</td>
<td>0.42</td>
<td>57.6</td>
<td>1</td>
<td>60</td>
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<td>3.2</td>
<td>8</td>
<td>80</td>
<td>5.4</td>
<td>1.56</td>
<td>57.8</td>
<td>1.25</td>
<td>60.3</td>
</tr>
<tr>
<td>3.3</td>
<td>8.1% AQ</td>
<td>80</td>
<td>5.9</td>
<td>0.6</td>
<td>58.4</td>
<td>1</td>
<td>62.2</td>
</tr>
<tr>
<td>3.4</td>
<td>9</td>
<td>80</td>
<td>5.6</td>
<td>0.7</td>
<td>56.5</td>
<td>1</td>
<td>61.1</td>
</tr>
<tr>
<td>3.5</td>
<td>8</td>
<td>60</td>
<td>6.9</td>
<td>0.7</td>
<td>56.6</td>
<td>1</td>
<td>60.1</td>
</tr>
<tr>
<td>C</td>
<td>(1.3)</td>
<td>60</td>
<td>8.1</td>
<td>0.21</td>
<td>61.4</td>
<td></td>
<td></td>
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</table>

All experiments are carried out on a CHYPS pilot plant southern pine TMP of 55.3 GE starting brightness. Samples were pre-treated with DTPA prior to starting the experiments. In all cases a peroxide bleach liquor containing 1% hydrogen peroxide, 3% sodium silicate and 0.25% magnesium sulfate is added to the pulp with the oxygen when the reactor reached the target reaction temperature.

The results of the third series of experiments confirms the high peroxide residuals from the oxygen/peroxide treatment and demonstrates that the residual peroxide can be activated with sodium hydroxide to give additional brightness increases in a second stage treatment. The Anthraquinone appears to have participated in the bleaching process but the benefit is insignificant considering the expense of AQ. In all cases, the final brightness was in the same range as the peroxide bleached control experiment.
Table 4. Factorial Design Study on Peroxide, pH and Temperature

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>H₂O₂ %</th>
<th>pH</th>
<th>O₂ psig</th>
<th>Temp. °C</th>
<th>pH off</th>
<th>%H₂O₂ res.</th>
<th>GE</th>
<th>GE₂</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>8</td>
<td>80</td>
<td>80</td>
<td>5.4</td>
<td>0.52</td>
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<tr>
<td>2</td>
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<td>9.5</td>
<td>80</td>
<td>60</td>
<td>6.1</td>
<td>0.56</td>
<td>57.8</td>
<td>62.8</td>
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<td>8.75</td>
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<td>60</td>
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<tr>
<td>C</td>
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<td>(1.0)</td>
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<td>66.5</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
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<td>10.1</td>
<td>0.6</td>
<td>74.0</td>
<td>-</td>
</tr>
</tbody>
</table>

All experiments conducted on a pilot plant southern pine TMP with a starting brightness of 56.5 GE. Samples were pre-treated with DTPA and all samples received 3% sodium silicate and 0.1% Magnesium sulfite with the peroxide. The second stage was held at 60 °C for 90 minutes using a sodium hydroxide charge varied according to the initial peroxide charge, 1% NaOH at 1% peroxide, 1.9% NaOH at 2% peroxide, and 3.3% NaOH at 4% peroxide. Brightness after the second stage is reported as GE₂.

Since overall brightness gains in the third series of experiments were close to the brightness achievable with peroxide, it was concluded that an overall increase in bleached brightness might be achieved by optimizing the sodium hydroxide charged to the second stage. However, any brightness advantage of the oxygen/peroxide process was expected to be small. The project focus was shifted to high peroxide charges where the additional brightness is of more interest. The initial series of experiments at high peroxide charge were carried out as part of a 2²⁻¹ fractional factorial design study to evaluate the effects of the peroxide charge (1% and 4%), the starting pH for the O₂ stage (8.0 and 9.5), and the temperature of the O₂ stage (60° and 80° C). Results are presented in Table 4.
Analysis of the data indicates that the temperature does not have a significant effect on intermediate or final brightness. The lower starting pH (8.0) and higher starting peroxide charge both have significant effects. Final brightness is consistently lower than a peroxide bleached control, 2 to 3 points low at 1% peroxide, rising to 4 points when using 4% peroxide. This is a larger brightness penalty than observed in the previous experiments.

In several experiments, the residual peroxide was tested using a two stage titration procedure to determine if peracids were generated in the oxygen/peroxide stage. Peracid residuals were insignificant.

2.3 Second Stage Optimization

![Graph showing brightness response for bleaching with oxygen and peroxide followed by an alkaline stage. All pulps were pretreated with DTPA and bleached with 4% peroxide.](image).

Figure 1. Brightness response for bleaching with oxygen and peroxide followed by an alkaline stage. All pulps were pretreated with DTPA and bleached with 4% peroxide.
In a final series of experiments, the oxygen/peroxide process was investigated using 4% hydrogen peroxide and large enough samples to evaluate the second stage at a variety of sodium hydroxide charges. Results are summarized in Table 5 and Figure 1.

Table 5. Second Stage Optimization and Nitrogen Control Experiments

<table>
<thead>
<tr>
<th>Exp #</th>
<th>pH</th>
<th>Temp °C</th>
<th>O₂ psig</th>
<th>%H₂O₂ resid.</th>
<th>pH off</th>
<th>GE</th>
<th>2% NaOH</th>
<th>3% NaO H</th>
<th>4% NaOH</th>
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<td>80</td>
<td>80</td>
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<td>70.9</td>
</tr>
<tr>
<td>1C</td>
<td>8.0</td>
<td>80</td>
<td>0</td>
<td>2.7</td>
<td>5.4</td>
<td>61.4</td>
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<td>-</td>
<td>70.0</td>
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<td>60</td>
<td>30</td>
<td>3.2</td>
<td>5.6</td>
<td>60.6</td>
<td>68.2</td>
<td>67.7</td>
<td>70.2</td>
</tr>
<tr>
<td>C/90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>55.7</td>
<td>68.4</td>
<td>69.4</td>
<td>71.3</td>
</tr>
<tr>
<td>C/180</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>55.7</td>
<td>70.5</td>
<td>71.8</td>
<td>73.5</td>
</tr>
</tbody>
</table>

All experiments were conducted on a pilot plant southern pine TMP of starting brightness 55.7. Pulp was pre-treated with DTPA before starting. All experiments received 3% sodium silicate and 0.05% magnesium sulfate and 4% hydrogen peroxide. The control experiments 1C, 2C, and 3C were treated identically to experiments 1, 2, and 3 except they were pressurized with 15 psig of nitrogen instead of the oxygen. The final two control experiments are conventional peroxide bleaching experiments held at 60 °C for 90 minutes and 180 minutes.

The samples bleached with oxygen and peroxide gave a final brightness slightly below the 90 minute peroxide control (straight dotted line, Figure 1) and 3 points lower than the 180 minute peroxide control (heavy straight line Figure 1).

Several additional control experiments were performed to determine the fate of pulp and peroxide under identical process conditions but substituting Nitrogen for the Oxygen gas. All results are within experimental error of the results from the oxygen/peroxide process demonstrating rather convincingly that the oxygen has little or no influence on the process at these conditions.

2.4 Influence of Oxygen in Peroxide Bleaching

Since all the oxygen/peroxide experiments had been conducted in the laboratory peg mixer and all of the peroxide controls had been carried out in plastic bags, it was decided to conduct several peroxide experiments to determine if there was a difference in the bleach response between bags and the peg mixer. These experiments were conducted under both oxygen and nitrogen atmospheres to confirm literature reports that oxygen as a decomposition product of peroxide, participated in peroxide bleaching of high yield pulps. The experiments were conducted on pilot plant TMP pulp which was pre-treated with DTPA. Bleaching was carried
out using 4% hydrogen peroxide, 3% sodium silicate and 0.05% Magnesium sulfate. The atmosphere in the peg mixer was 60 psig, either O₂ or N₂. The results are summarized in Table 6 with complete results listed in Table 7 at the end of the report.

Table 6. Influence of Atmosphere on Peroxide Bleaching

<table>
<thead>
<tr>
<th>% NaOH</th>
<th>Nitrogen</th>
<th>Bag Bleach</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%</td>
<td>70.5</td>
<td>-</td>
<td>74.3</td>
</tr>
<tr>
<td>3.3/3.5</td>
<td>73.8</td>
<td>74.4</td>
<td>74.5</td>
</tr>
<tr>
<td>4.0</td>
<td>72.4</td>
<td>72.6</td>
<td>73.2</td>
</tr>
<tr>
<td>4.5</td>
<td>69.4</td>
<td>-</td>
<td>69.8</td>
</tr>
</tbody>
</table>

All bleaches carried out using a pilot plant southern pine TMP of starting brightness 55.7 GE. Pulp was pre-treated with DTPA and bleached with 4% hydrogen peroxide, 3% sodium silicate and 0.05% magnesium sulfate on OD pulp. Several entries are the average of two or more experiments and the bag bleach brightnesses are estimated using brightness at 90 minutes and 180 minutes to two hour retention times.

In general, the samples bleached under nitrogen were very close to the brightness obtained by a conventional peroxide bleach experiment conducted in a plastic bag. With one exception, all experiments conducted in an oxygen atmosphere gave higher brightness than the comparable experiment conducted under nitrogen (Figure 2). This difference was most pronounced at low initial caustic charge where the sample bleached in an oxygen atmosphere was nearly 4 points higher than the sample bleached under nitrogen.

3. CONCLUSIONS:

Oxygen at 80 psig and 80° C will raise the brightness of mechanical pulps by one to two points if used at a pH around 8. The brightness gain does not appear to be additive with second stage bleaching processes using other bleaching agents such as hydrogen peroxide and sodium hydrosulfite. Higher brightness gains are possible when hydrogen peroxide is added to the oxygen process but net bleached brightness is well below what is achievable with peroxide alone. Additional sodium hydroxide can be added in a second stage to make use of the considerable peroxide residual remaining after the oxygen/peroxide treatment. This process raises the overall brightness gain to within several points of what can be achieved with peroxide alone.

When oxygen is used at 120 psig of oxygen and 120° C a substantial loss in brightness is obtained which cannot be recovered in a second stage peroxide or hydrosulfite bleach stage.
Under conditions more typical of a conventional peroxide bleach stage, oxygen is beneficial to bleaching, raising the final brightness by ≈ 1 point GE from what is obtained in a nitrogen atmosphere or a conventional bag bleach. Oxygen when used in a peroxide bleach stage has a larger impact at lower than optimum alkali charges where it can increase brightness by up to 4 points relative to a control bleached in a bag or a nitrogen atmosphere. At present it is not known how sensitive the brightness gain is to oxygen pressure and this will be determined in follow-up experiments.

4. PLANNED ACTIVITY THROUGH FISCAL YEAR 1992:

Plans are to follow up on the influence of oxygen during conventional peroxide bleaching. Of most interest is to determine the sensitivity of the process to oxygen pressure and to confirm the results at low initial alkali charge.

Based on the results of the oxygen/peroxide work, oxygen might be effective at the end of a peroxide bleaching process where the pH and residual peroxide are already in a range that is suitable for oxygen treatment. Completion of this work will finalize the evaluation of the use of oxygen in bleaching high yield pulps.

Peracetic acid has been shown to bleach groundwood pulp at neutral pH, or delignify and increase the bond strength of groundwoods when used at acidic pH\(^8\). Oxygen and peroxide are known to react with various organic and inorganic\(^9\) compounds to generate peroxide and peracid compounds that might be suitable for bleaching high yield pulps. These materials are often distinguished from hydrogen peroxide by their ability to carry out the epoxidation of olefins and the Baeyer-Villiger oxidation of ketones to lactones and esters. The recent research on delignifying wood and pulp with performic acid generated in-situ from hydrogen peroxide and formic acid\(^10\) is an attempt to use the unique reactivity of the peracids while avoiding the cost of commercial peracetic acid.

An initial evaluation will be conducted to determine the potential for high yield pulp bleaching by organic peroxides and peracids. Commercial peracetic acid will be used in these experiments to evaluate bleach potential for the peracid type compounds. The goal is to determine the brightness response vs peracetic acid charge for TMP pulps, and the maximum brightness obtainable without significant delignification. This investigation will also determine the process capability following and preceding conventional peroxide and hydrosulfite bleaching.

The project will then proceed to investigate bleaching with peroxyacids using transition metal catalysts such as tungsten and osmium oxides to activate the hydrogen peroxide.

5. POTENTIAL FUTURE ACTIVITY:

This project will continue to emphasize development of effective processes for achieving high and stable brightness in high yield pulps. Possible future activities include: an evaluation of peroxide bleaching at ultra-high pulp consistencies, and an evaluation of the effects of
autoxidizable peroxide forming organic additives on brightening by oxygen, with or without added peroxide.

6. EXPERIMENTAL

All pulp samples were pre-treated by mixing with 0.25% DTPA as the penta-acid salt at 3% consistency for 1 hour and dewatered to 20+ % consistency.

All reactions except the controls are carried out in a laboratory peg mixer (single shaft) designed for high consistency oxygen bleaching. The mixer was loaded with 150 to 250 grams of 20+ % consistency pulp, sealed, and heated to temperature. Except as indicated in the text, all peroxide liquors contained 3% on OD pulp of 42 Bé sodium silicate, 0.05% on OD pulp of Magnesium Sulfate and sufficient distilled water to reduce the pulp consistency to 20% on OD pulp. The pH was adjusted to the target after all other chemicals were added, using either sodium carbonate or sulfuric acid as needed. For the preliminary experiments, when a sodium hydroxide charge is indicated, sodium hydroxide was added to the dilution water before addition of sodium silicate.

The peroxide solution was charged to a liquor injection cell and added when the reactor reached the target temperature. Either oxygen or nitrogen gas was used to pressurize the injector. The reactor was brought up to pressure simultaneous to solution injection. Standard reaction time was 90 minutes.

For the two stage experiments, pulp was removed from the reactor on completion of the first stage, mixed with sodium hydroxide in a Hobart® mixer, transferred to a plastic bag and placed in a constant temperature water bath for an additional 90 minutes

Control bleaches were conducted at 20% consistency in plastic bags using peroxide bleach liquors made up as specified above except that sodium hydroxide was used as the source of caustic and added to the distilled water before the sodium silicate.

Sodium hydrosulfite bleaching was performed under nitrogen using a 4 l resin kettle equipped with a mechanical stirrer and glass rod sparging tube. Pulp was diluted to 3.5% consistency and DTPA as the penta-acid added at the rate of 0.5% on OD pulp. The pH was adjusted to pH 6 with either sodium carbonate or sodium bicarbonate and the resin kettle was placed in a 60° C water bath and purged with N2 while it came up to temperature. Sodium hydrosulfite was dissolved in sufficient nitrogen flushed distilled water to reduce the pulp consistency to 3% and the solution adjusted to pH 6 with sodium bicarbonate. The sodium hydrosulfite solution was then added to the stirred resin kettle and the contents held at temperature for 1 hour.

Peroxide residuals and sodium hydroxide residuals were determined by titration using standard procedures\textsuperscript{11}. The titration used to distinguish peracids and peroxides is a two step titration that relies on the difference in reactivity of peracids and peroxide at neutral pH\textsuperscript{12}
REFERENCES


PROJECT 3716

ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMI-CHEMICAL PULPING

RESEARCH REVIEW

April 3, 1991

Clark P. Woitkovich
PROJECT SUMMARY FORM
FY 90-91

Project Title: ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMI-CHEMICAL PULPING
Division: Chemical and Biological Sciences
Project Number: 3534-43 (1st half of FY)
                 3716 (2nd half of FY)
Project Staff: Thomas J. McDonough and Clark P. Woitkovich
FY 90-91 Budget: $5,000 (1st half of FY)
                  $37,500 (2nd half of FY)

IPST GOAL:
To improve the control of semichemical pulping processes.

OBJECTIVE:
To identify or develop an analytical test method for the estimation of yield in high-yield semi-
chemical pulping and to develop empirical correlations between the analytical test data, estimated
yield, and specific end-use properties.

FY 90-91 GOALS:
1. Prepare laboratory pulps, cooked under NSSC conditions to several different yield levels.
2. Explore the applicability of the following spectroscopic methods to the analysis of the laboratory pulps and spent liquors:
   Near-infrared spectroscopy
   Ultraviolet-visible luminescence spectroscopy
   Ultraviolet absorption spectroscopy
Identify spectral features that exhibit sensitivity to yield level.

Determine the effects of sample form, particle size, moisture content, and sample presentation on the appearance of yield-sensitive spectral features.

Develop correlations between laboratory yield and spectral data.

3. Explore the applicability of the following methods to the analysis of spent liquors:

   - Refractive index
   - Total organic carbon (TOC)
   - Total dissolved solids

Determine the effects of sample and instrument variability on measured values.

Develop correlations between laboratory yield and measured values.

RECENT RESULTS AND CURRENT ACTIVITY:

Preliminary results indicate significant differences in near-infrared absorption spectra acquired from two laboratory pulps cooked to different yield levels. Promising differences are also observed in the fluorescence excitation spectra recorded from the same pulps. This represents the first direct evidence that these two techniques are potentially useful for yield estimation in high-yield pulps.

Work is in progress to assess the statistical significance of the observed differences and to generate a database that will allow a comparison of the three spectroscopic methods.
ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMI-CHEMICAL PULPING

OBJECTIVES:

The main objective of this project is to identify or develop an analytical test method for the estimation of yield in high-yield semi-chemical pulping. A secondary objective is to develop empirical correlations between the analytical test data, estimated yield, and specific end-use properties so that it may become possible to predict product properties from a single pulp measurement.

Work directed towards these objectives has, to date, been focused on generating basic information regarding the applicability of near-infrared spectroscopy (NIRS) and ultraviolet-visible luminescence spectroscopy to the analysis of this type of pulp. The results described here lay the groundwork for a more in-depth investigation of the potential usefulness of these methods as estimators of yield in semi-chemical pulping.

INTRODUCTION:

Pulp yield is probably the parameter that most aptly summarizes the extent to which a pulping process has progressed. Yield is defined as:

\[
\text{% Yield} = \frac{\text{weight of pulp} \times \text{pulp consistency}}{\text{weight of wood} \times \text{wood consistency}} \times 100
\]

An accurate gravimetric determination of this quantity requires precise measurements of weight and consistency, a difficult task on an industrial-scale process line. In practice, yield is usually inferred indirectly from measurements of lignin content. Although lignin content can be quantified directly ("Klason" or acid-insoluble lignin; Tappi Method T222 om-88), the method is relatively laborious and time-consuming. A more typical approach to the estimation of yield is to estimate lignin content by determining pulp kappa number (Tappi Method T236 cm-85). Yield can then be estimated by referring to a predetermined laboratory correlation that relates yield to kappa number.
This approach can be relatively quick but suffers from two important limitations. First, any correlation between lignin content and yield is tenuous at best. This is because a measurement of lignin content ignores the other two principal constituents of pulp: cellulose and hemicellulose. If, for example, the selectivity of a pulping reaction were to be negatively altered, it is conceivable that a yield decrease could be accompanied by an actual increase in lignin content. For this reason, it becomes desirable to develop a method that is sensitive to not one, but all of the major chemical constituents found in wood pulp.

Another drawback with the use of kappa number as a yield estimator is that the usefulness of the kappa number technique is generally limited to pulps below 70% yield. This means that in the middle to high-yield range of semi-chemical pulping, there exists no reasonably quick way of obtaining a quantitative estimate of yield.

The benefit of being able to determine the yield of a pulping process, or any other chemical process, arises out of its potential usefulness as an important process control parameter. By making it possible to control the extent of the pulping reaction, the ability to measure yield may also enable the direct control of product properties. This achievement can only be realized, however, if correlations can be demonstrated between yield and end-use properties in middle to high-yield pulps. Such correlations are well known for pulps in the low (50-60%) yield range (1).

Even more exciting is the prospect of being able to monitor yield in real-time, thereby enabling the development of on-line control strategies. This would be a significant advance for the semi-chemical pulping industry.

Several analytical methods have been determined to be good candidates for this type of application and they are being applied to the pulp and/or liquor generated in laboratory pulping experiments. In addition to the two spectroscopic techniques reported on here, several other promising techniques will be evaluated in future work. These include two other optical methods: ultraviolet absorption spectroscopy and refractive index. The three spectroscopic techniques are applicable to both pulps and liquors. The measurement of refractive index is applicable only to liquors. This is also the case for two other non-optical methods to be investigated: total organic carbon (TOC) and total dissolved solids.

BACKGROUND

Near-infrared Spectroscopy

In near-infrared spectroscopy, a sample is sequentially irradiated with bands of light energy having an extremely narrow wavelength range (approximately 10 nanometers). During exposure to each individual band, the absorption of radiation is measured indirectly by detecting the amount of incident energy that has interacted with and reflected from the sample. Exposing a sample to a continuum of such bands results in absorption measurements that cover a wide spectral region (1100 to 2500 nm). A plot of absorption as a function of wavelength for a particular sample is called its absorption spectrum.
Near-infrared absorption spectra consist primarily of overlapping bands that result in broad spectral features from which it is difficult to derive structural information. The spectra, however, have been found to be very useful for quantitative analysis and the technique is widely employed as an analytical tool in a variety of industries. The appeal of NIRS lies in its fast analysis time with minimal sample preparation, its relatively compact and rugged design, and its recently emerged compatibility with fiber optic technologies. These attributes have rendered NIRS an ideal candidate for several on-line applications in the pulp and paper industry.

Earlier studies have already demonstrated the potential usefulness of NIRS in pulping applications. Easty has reported correlations between intensities observed in second derivative transformations of NIR absorption spectra and the kappa number of unbleached loblolly pine kraft pulp and cotton linter mixtures (2). The same report also indicates a correlation between similar NIR intensities and the lignin content of larch kraft pulp handsheets. Birkett and Gambino have reported a correlation between untransformed NIR absorption intensities and the kappa number of kraft pulps prepared from a variety of species (3). Wright, et. al. have reported the ability to predict yield from the NIR absorption intensities measured from raw wood (4). Except for this most recent work by Wright, these studies were all limited to laboratory pulps that were cooked to typical kraft yield levels of approximately 50%. The effort summarized in this report is the first ever to use NIRS for the analysis of high-yield semi-chemical pulps.

Ultraviolet-visible Luminescence Spectroscopy

The luminescence phenomenon is initiated when a substance is "excited" by incident radiation at a characteristic frequency. The "excited" state is actually brought about by an absorption of photons that induces a momentary shift of vulnerable sample electrons to higher energy levels. Since this excitation is not self-sustaining, the electrons ultimately return to a ground state, dissipating energy in the process. Two principle pathways exist for the non-destructive dissipation of this energy: the generation of heat and the emission of light. The emission of light photons by an excited substance is called luminescence. Emitted radiation always occurs at a longer wavelength than the excitation radiation due to inherent inefficiencies in converting the excitation energy to emitted light.

The emitted radiation, or luminescence, is actually comprised of two different forms of emission: phosphorescence and fluorescence. Phosphorescence is distinguished from fluorescence by the long lived emission after extinction of the excitation source. Fluorescence generally occurs within $10^{-9}$ to $10^{-7}$ seconds of excitation while phosphorescence has a long lifetime varying from $10^{-4}$ to $10^{-2}$ seconds. Although the luminescence spectrometer used in this study offers the capability of detecting either phosphorescence or fluorescence, only the fluorescent behavior of pulps has been explored to date.

As in NIRS, UV-VIS fluorescence spectroscopy employs an excitation monochromator to sequentially irradiate a sample with bands of light energy having a narrow wavelength range.
Unlike the NIRS instrument, however, the fluorescence spectrometer is equipped with a second monochromator on the emission side of the sample. This optical arrangement provides the capability of acquiring three distinctly different types of spectral information.

By scanning the excitation monochromator and fixing the emission monochromator at an appropriate pre-selected wavelength, excitation spectra can be acquired. An excitation spectrum is therefore a plot of the intensity of the emitted fluorescence, detected at a specific wavelength, as a function of excitation wavelength.

The converse of this acquisition geometry is to scan the emission monochromator while holding the excitation monochromator stationary, and thus, the excitation wavelength constant. This approach generates what is known as an emission spectrum, which is a plot of the intensity of emitted fluorescence as a function of emission wavelength.

Yet a third approach to fluorescence spectral acquisition is possible if both monochromators are scanned synchronously with a selected wavelength difference between them. The result, a "fingerprint" spectrum, is a plot of the intensity of emitted fluorescence detected at x nanometers beyond the excitation wavelength, as a function of excitation wavelength. Typically, in this type of experiment, x has a value of 15 to 35 nanometers.

As in the case of near-infrared absorption spectra, fluorescence spectra exhibit primarily broad spectral features. However, features generally appear sharper and more distinctive in the "fingerprint" spectra, a fact that has led to the usefulness of these spectra in facilitating the identification of many organic compounds, especially complex mixtures, such as crude oils. All of the same attributes that have rendered NIRS an ideal candidate for potential on-line applicability also hold true for fluorescence spectroscopy.

Other researchers have explored the potential usefulness of fluorescence spectroscopy as an indicator of the extent of pulping reactions (5-8). None of this earlier work, however, has investigated its applicability to the analysis of pulps or spent liquors from high-yield processes. The technique has instead been applied exclusively to diluted pulping liquors that were generated in mill and laboratory trials under a variety of low-yield conditions (e.g. kraft, sulfite, and ASAQ). Generally, good correlations have been reported between fluorescence intensity and lignin concentration, although data obtained from mill samples did not always corroborate laboratory results.

The problems encountered with some of the mill data were attributed to poor overall control of several pulping parameters, such as liquor-to-wood ratio, white liquor strength, and chip charge. Despite these difficulties, the technique is still regarded as having high potential for the monitoring of pulping processes. However, this technique, as well as all others being evaluated in this study, can be rendered totally ineffectual in this capacity if the basic process parameters are not under reasonably good control.
EXPERIMENTAL APPROACH:

Chestnut oak chips were cooked under neutral sulfite semi-chemical (NSSC) conditions in a multi-unit digester to eight different yield levels that varied over the range of 74.7% to 82.7%. Samples at the two extremes of the range were extensively washed, fiberized, fluffed, and analyzed using near-infrared and fluorescence spectroscopy. For NIRS analysis, the samples were presented in three different conditions: 1) dried handsheet form; 2) dried fluff form; and 3) moist fluff form. Two reloads of each sample were scanned from 1100 to 2500 nm using a NIRSystems Model 6250 spectrophotometer in the reflectance mode with a ceramic standard as reference.

For the UV-VIS fluorescence analysis, only dried fluff and wet fluff samples were used. An extensive series of fluorescence excitation spectra were acquired from one particular pulp sample to characterize the fluorescence behavior that can be expected of pulp. The wavelength settings that produced the most dramatic spectral features were selected for use in the subsequent preliminary search for yield-related spectral differences.

RESULTS AND DISCUSSION:

Near-infrared Spectroscopy

Figure 1 shows NIR spectra acquired from two different high yield pulp samples. One sample was a pulp that was cooked to a yield of 82.7% and the other was a pulp cooked to a 74.7% yield. The spectra in Figure 1 were recorded from samples that were presented in air-dried handsheet form. Two sheets were made from each sample and one spectrum was recorded from each sheet.

Differences appear to be significant between spectra acquired from two different handsheets made from the same sample. Possible contributing factors include instrument variability, handsheet variability (such as formation differences), and inherent sample inhomogeneity. Future efforts should aim to identify, or at least quantify, the effects that these, or other factors, have on data variability associated with a single sample. Despite the interfering single-sample variability described above, a spectral difference between the two samples is readily apparent in Figure 1 and in Figure 2 where the paired spectra from each sample were averaged to give a single representative spectrum. The observed difference is primarily a baseline shift, greater in magnitude, but yet, similar to the difference that is attributed to single-sample variability.

Because baseline shift can also be caused, at least in part, by a variety of sampling-related factors, the feature is virtually useless as a predictor of a specific sample characteristic. It therefore becomes desirable to compensate for baseline differences so that differences in other spectral features may be enhanced. A convenient way of accomplishing this is to mathematically transform raw spectral data into second derivative spectra. The second derivative inverts absorption maxima to minima and increases the apparent resolution in a spectrum.
Second derivative spectra obtained from the raw spectral data shown in Figure 1 are depicted in Figure 3. Single-sample variability appears significantly reduced in the transformed spectra while narrow-band differences between the two samples are enhanced.

Selecting spectral regions that are known to be devoid of water absorption bands (1500-1800 nm and 2000-2400 nm), we can expand along the wavelength-axis and further magnify sample differences, as seen in Figures 4 and 5. Both regions exhibit spectral differences between samples that are potentially indicative of sample yield. The most notable differences involve features centered at approximately 1527, 1635, 1717, 1748, 2015, and 2226 nm.

When the same pulp samples were mechanically fluffed and presented for NIRS analysis, the spectra shown in Figure 6 were obtained. With fluffed pulp, differences between samples were considerably less pronounced than what was observed in the case of the handsheets. In fact, it is difficult to distinguish sample differences from single-sample variations. The significance of these differences remains questionable even though they are made more apparent when the paired spectra in Figure 6 (spectra acquired from two reloads of each sample) are averaged (Figure 7). Further enhancement by second derivative transformation is shown in Figures 8 and 9. The overall shape of the transformed fluff spectra is very similar to that observed in the transformed handsheet spectra. Some sample-to-sample differences are also consistent: the intensities at 1635, 1748 and 2226 increase with yield; the intensity of the shoulder at 1670 decreases with yield; and the minimum at 1717 exhibits a shift to lower wavelength as yield decreases.

Near-infrared spectra were also recorded on portions of the same two samples that were fluffed but not allowed to completely air dry (Figure 10). The moisture content of these samples, estimated at approximately 60-70%, significantly alters gross spectral features. As in the case of the dry fluff, sample-to-sample differences are largely obscured by single-sample variations.

Some potentially significant differences stand out, however, in the averaged spectra shown in Figure 11. The transformed and expanded spectral regions shown in Figures 12 and 13 reveal sample-to-sample differences consistent with those observed in the corresponding spectra obtained from the handsheet and dry fluff sample forms. This observed consistency suggests that the presence of moisture does not interfere with the most prominent sample-to-sample spectral differences. If this finding is upheld in future experiments, sample drying may not be required prior to NIR analysis.

**Ultraviolet-Visible Fluorescence Spectroscopy**

Figure 14 shows UV-VIS fluorescence excitation spectra acquired from two fluffed, air-dried pulps having different yield levels. In the acquisition of this data, fluorescence intensity was detected at a wavelength setting of 490 nm while the excitation wavelength was varied continually from 260 nm to 470 nm. Prominent differences are evident between the two spectra. The broad peak centered at 400 nm and the sharper feature at approximately 430 nm exhibit significantly decreased intensity in the lower yield sample.
As with the NIRS data, it is possible that the observed spectral differences are not entirely attributable to yield differences. Instrument variability, sample variability, and surface effects (such as particle size distribution) may be contributing. In light of this uncertainty, however, these preliminary results remain encouraging because of the magnitude of the observed differences.

An indication of the effect of moisture content on fluorescence activity is evident in Figure 15. A substantial decrease in fluorescence intensity occurs when an air-dried sample is diluted to approximately 20% consistency. This may be due to the decreased concentration of fluorescent material at the lower consistency. It may also be a result of the fluorescence quenching capability of water. Consequently, the fluorescence technique may turn out to be inapplicable to the analysis of wet pulps if this effect persists during the acquisition of the other types of fluorescence spectra.

CONCLUSIONS:

Significant differences are evident in the transformed near-infrared absorption spectra recorded from laboratory pulps that have been cooked under semi-chemical conditions to different yields. Differences are also observed in the fluorescence excitation spectra acquired from the same pulps. This represents the first direct evidence that these two techniques are potentially useful for yield estimation in high-yield pulps.

In NIRS, spectral differences between samples are most pronounced when the samples are presented for analysis in air-dried handsheet form. If the samples are presented in a fluffed form that still contains an appreciable amount of moisture, spectral differences are reduced. The differences remain significant, however, and may justify the elimination of a drying step in the sample preparation procedure, thereby simplifying the NIRS analysis.

Fluorescence spectroscopy has been applied so far only to fluffed pulp and no conclusions regarding the effect of sample form can be made at this time. However, there are indications that the technique may not be suitable for wet pulp analysis.

These conclusions should be regarded as somewhat tentative because the data base at this time is minimal in size. Future work should focus on the analysis of samples that have yields intermediate to that of the samples reported on here. The plan will be to quantify the effects of yield, sample form, moisture content, and sample presentation.

EXPERIMENTAL:

Sample Preparation

Chestnut oak chips were kindly supplied by the Willamette Industries pulp mill located Hawesville, Kentucky. Prior to use, the chips were hand-sorted to isolate approximately 900 grams of chips (oven-dried basis) that were roughly uniform in size. After overnight moisture equilibration, nine samples, with a combined weight of over 200 grams (oven-dried basis), were removed for consistency determination (TAPPI Test Method:
T258 om-89). These samples were placed in drying tins and dried in a 105°C oven for at least 24 hours. The resulting consistency measurements gave an average of 0.619 with the standard deviation \((S_w)\) equal to \(\pm 0.003\).

A chip charge of 96.93 grams at 61.9% consistency (equivalent to 60 grams on an oven-dried basis) was placed in each of two 500 ml stainless steel digesters. Cooking conditions were as follows:

- Liquor to wood ratio: 4:1
- \(\text{Na}_2\text{SO}_3\): 10% (as \(\text{Na}_2\text{SO}_3\) on o.d. wood)
- \(\text{Na}_2\text{CO}_3\): 3% (as \(\text{Na}_2\text{CO}_3\) on o.d. wood)
- Temperature: 170°C

The digesters were placed in a circulating oil bath and were heated from room temperature up to the reaction temperature over a period of 75 minutes. At a point 66 minutes into the heat up, the first digester was removed and the reaction quenched by rapid cooling. The other sample used in this study came from a digester that was removed approximately 45 minutes later. The contents of both were separately washed in a 4 liter sintered glass funnel, each with approximately 20 liters of deionized water. After refrigerated storage overnight, the samples were again washed, this time with about 10 liters of deionized water each.

Following this extensive washing, the samples were fiberized in a Waring blender for a period of 15 minutes and then washed again, using approximately another 8 liters of deionized water. After breaking up the final washed pad by hand, the pulp was allowed to equilibrate overnight in cold storage. Consistency was then determined in duplicate for each pulp sample using Tappi Method T240 om-88. The method involves forming a weighed amount of pulp into a pad on a sheet of filter paper, followed by thorough drying and subsequent reweighing. The pooled standard deviation of the pulp consistency measurements \((S_p)\) was less than \(\pm 0.001\).

Pulp yield was calculated as follows:

\[
\% \text{ Yield} = \frac{\text{weight of pulp} \times \text{pulp consistency}}{\text{weight of wood} \times \text{wood consistency}} \times 100
\]
The approximate error associated with a given pulp yield value is \( \pm 0.7 \). The limits on the range of error were calculated as:

\[
\frac{W_p (C_p + S_p)}{W_w (C_w - S_w)} \quad \text{and} \quad \frac{W_p (C_p - S_p)}{W_w (C_w + S_w)}
\]

After consistency determination, the samples were formed into thick pads and pressed for 1 minute at 10 psi followed by another minute at 15 psi to give a consistency of about 25%. The pulps were then fluffed using a narrow diameter dual-impeller benchtop device. After a few hours of exposure to forced air currents, a portion of each sample was presented for analysis as moist fluff. The remainder of the fluff from each sample was left exposed to air overnight and then analyzed as dry fluff. The sample pads that were formed on filter paper to determine consistency served as the air-dried pads that were analyzed.

Visual inspection of the dried consistency pads revealed that pulp fiberization was extensive but also that shive content was high. Uneven formation had resulted in poor uniformity across the sample pads, especially in the higher yield sample. It was possible, however, to avoid those areas of the pad that exhibited the poorest quality because only a 4 cm X 5 cm piece was used for the NIRS analysis.

It should be noted that the consistency pad pieces were analyzed while still attached to the filter paper upon which they were formed. It is not known to what extent this filter paper backing contributed to the reflectance measurements. It is possible, however, that this effect would be the same for each sample and would not contribute to the differences observed between samples. At any rate, this added source of uncertainty will be eliminated in future experiments by separating the pads from their filter paper backing immediately after formation.

**Instrumentation**

The instrument used for NIRS was a NIRSystems Model 6250 spectrophotometer controlled by an IBM PS/2 personal computer. It is a fully scanning instrument that utilizes an oscillating concave holographic grating as a dispersing element. In this study, the instrument was used exclusively in the reflectance mode. The diffusely reflected radiation from a sample is detected by an array of lead sulfide detectors that are positioned to exclude specular radiation.

All spectra reported here were acquired from samples mounted in a quartz-windowed stationary sample cell. With this sampling arrangement, the area of sample exposed to incident radiation was approximately 2 cm X 4 cm. To compensate for variations in light source energy output and detector response over the wavelength range covered, sample data were corrected by subtracting data acquired from an internal ceramic reference.
The instrument used for fluorescence spectroscopy was a Perkin-Elmer LS-5B luminescence spectrometer controlled by a PC's Limited System 200 personal computer. The excitation monochromator covers the range from 230 to 720 nm and the emission monochromator can range from 250 to 800 nm. The instrument utilizes a stroboscopic (60Hz) xenon light source and a standard photomultiplier detector.

As in NIRS, spectra were acquired from samples contained in a stationary, quartz-windowed cell. The area of sample exposed to incident radiation was on the order of 0.5 cm X 1.0 cm. All excitation spectra reported herein have been corrected for variations in light source energy output by electronic compensation circuitry.

FUTURE WORK

Near-infrared Spectroscopy

In future work, the original experimental approach will be expanded in scope to accommodate more detailed analyses of a greater number of pulp samples. Two separate sample sets will be prepared and analyzed. One set (which includes the two samples discussed here) is known as the calibration set and will be used to establish a quantitative correlation between NIRS data and laboratory yield determinations. A second, independent sample set, the validation set, will then be used to test how accurately the instrument can estimate yield. Each sample set will consist of eight samples cooked to different yield levels. The targeted yield range will be from approximately 70 to 85% with yield differences between samples achieved by varying individual retention times.

Laboratory determinations of yield will be conducted gravimetrically, keeping in mind that the non-homogeneous nature of the wood and pulp necessitates extensive sampling if a high degree of accuracy is desired. Since the gravimetric yield determinations are to be conducted in only one laboratory, it is not possible to quantify the accuracy of the laboratory method. An estimate of laboratory precision is possible, however, and will allow a comparison between the laboratory and instrumental precision.

Aside from yield, other sample-related variables will be examined in terms of their effect on spectroscopic features. These will include sample presentation form, the moisture content of the sample, and sample loading. The goal here, from the standpoint of simplifying eventual on-line implementation, is to identify the analysis procedure that involves the least sample preparation, yet gives an adequate correlation between yield and spectroscopic data. For example, the ability to obtain meaningful results from pulp that is wet and compacted would render the method ideally suited to the analysis of pulp as it exits a washer.

The different analysis procedures can be evaluated by monitoring the degree of correlation, in the calibration set, between NIRS yield estimations and laboratory yield measurements. The degree of correlation can be assessed via the standard statistical techniques described below.
In evaluating the effect of sample presentation form, three different forms will be used: sheet, fluffed, and unfluffed. The results obtained from these sample forms will provide an indication of the importance of surface homogeneity in the analysis of reflectance. The unfluffed pulp is to be prepared by hand-disintegrating the final washed pulp pad. It contains many, relatively large fiber clumps, or knots. The prevalence of the clumps is significantly decreased by applying the fluffing treatment, and almost completely eliminated in a good quality handsheet. It should be relatively straightforward to quantify surface homogeneity by applying image analysis routines to low magnification optical or electron micrographs of the samples as packed for analysis.

Over the yield range being investigated, unscreened pulps are expected to exhibit an increase in average particle size as yield levels increase. If significant spectral differences are observed between samples, and if near-infrared reflectance is found to be influenced by particle size, then it may become difficult to separate the effects of yield and particle size. To avoid this complication, it might be necessary to include some type of grinding procedure prior to NIRS analysis so that all samples have a similar particle size distribution.

When analyzing pulps in handsheet form, the effect of sample thickness on spectral data will also need to be evaluated. Knowledge of this effect will allow the determination of adequate sample thickness, thus ensuring that all reflected radiation detected during a NIRS analysis emanates exclusively from the sample and does not include radiation reflected from sample backing materials.

Different sample thicknesses will be achieved by varying the number of handsheet pieces that are layered together in the sample cell. Variability associated with inhomogeneity across an individual handsheet will be explored by acquiring several spectra from the layered pieces, each time shifting one piece from the bottom to the top of the layered stack. In addition, more than one handsheet will be prepared from some samples so that it will be possible to assess variability between different handsheets from the same pulp.

The influence of pulp moisture levels on acquired spectral data will be assessed by analyzing all forms of all samples at two widely different moisture contents. Specifically, samples will be analyzed in an air-dried state and in a condition in which they contain 60-70% water. It will also be necessary to characterize the effect of more subtle variations in moisture content since it is not feasible to hold moisture levels constant within the wet sample set.

Variability attributed to sample loading can be quantified by applying statistical analysis to data acquired from several reloads of each sample. There is also a quantifiable variability associated with the rotational orientation of a sample when the circular, cup-shaped cell is used. The effect of sample cell type will also be explored by using a large rectangular cell that slowly moves past the incident radiation during spectral acquisition, thus greatly increasing the sample area analyzed.

Raw absorption data is rarely used to develop a calibration equation because the results can be much improved if the raw data is enhanced by mathematical transformation. For this reason, several math options are available in the NIRSystems software including a variety of smoothing
algorithms, first, second, third, and fourth derivatives and a Kubelka-Munk transformation. Although a second derivative transformation is recommended for inhomogeneous samples with broad particle size distribution, the other transformations should be explored. If it turns out that one of the derivative transformations is most useful, the transform algorithm may be further optimized by adjusting specific derivation parameters (i.e. gap size and segment size).

Once the spectral data acquired from the calibration samples is mathematically transformed, a calibration equation will be generated by a stepwise linear regression program that is also resident in the instrument software. The program searches a specified wavelength range for the single wavelength that gives the best correlation between absorption and laboratory determined yield. Additional software capabilities allow the user to assess the reliability of the selected wavelength and its associated calibration equation. Options exist to modify the selected wavelength (e.g. dividing the data at the selected wavelength by the data at another wavelength), to replace the selected wavelength by another wavelength, or to add additional wavelength terms to the equation. The determination of reliability is aided by inspecting plots of the correlation coefficient and K1 magnitude as a function of wavelength (the variable K1 being a designator for the coefficient of the first term in the calibration equation). The reliability of the selected wavelength is compromised if the K1 value is unreasonably large or if the shape of the correlation curve is sharp or jagged at that particular wavelength.

Other statistical indicators that will be used to evaluate how well a given regression equation fits the calibration data include: the standard deviation of the residuals (standard error of calibration), the value of the squared correlation coefficient ($R^2$), a plot of residuals vs. calculated values, a plot of laboratory values vs. calculated values, and a plot of the average residual and the range of residuals for each data set (control chart).

With the exception of $R^2$, all of the above statistical indicators will also be used to evaluate the performance of a given calibration equation as it is used to predict yield in an independent data set (the validation set).

**Ultraviolet-Visible Fluorescence Spectroscopy**

A statistical study of the variability associated with the fluorescence method will be conducted much along the lines of the corresponding study of the NIRS technique that has been outlined above. With the fluorescence spectrometer, however, only one sample cell will be used. This will simplify, somewhat, the analysis of sample presentation variability.

One factor that may further limit our options in the case of the fluorescence work, at least temporarily, is that the operating software lacks derivative transformation capabilities. Since these capabilities appear to be crucial in the analysis of the NIRS data, it may be desirable to develop the appropriate software in order to evaluate any potential benefit that may be realized in applying the transformations to the fluorescence spectra.
Another capability that is missing from the fluorescence software is the automated stepwise linear regression that searches a spectrum and identifies the single wavelength that gives the best correlation between spectral intensity and yield. This should not present a problem, however, because a quick visual inspection of the fluorescence spectra, and the NIR spectra for that matter, reveals, fairly obviously, those wavelengths that offer the best yield correlation potential.

REFERENCES


- YIELD = 82.7%

- YIELD = 74.7%

FIGURE 2
AIR-DRIED FLUFF

YIELD = 82.7%
YIELD = 74.4%

LOG 1/R

WAVELENGTH (NANOMETERS)

FIGURE 6
AIR-DRIED FLUFF

YIELD = 62.7%
YIELD = 74.7%

WAVELENGTH (NANOMETERS)

FIGURE 7
AIR-DRIED FLUFF

YIELD = 82.7%
YIELD = 74.7%

FIGURE 9
MOIST FLUFF

- YIELD = 82.7%
- YIELD = 74.7%

FIGURE 10
MOIST FLUFF

**Figure 11**

YIELD = 82.7%

YIELD = 74.7%
MOIST FLUFF

SECOND DERIVATIVE (LOG 1/R)

- YIELD = 82.7%
- YIELD = 74.7%

WAVELENGTH (NANOMETERS)

0.244
0.104
0.036
0.0176
0.0316

2057
2200
2283
2226
2170
2113

FIGURE 13
Excitation Spectra

Fluorescence Intensity

Em λ = 490 nm

Excitation Wavelength (nm)

0 200 400 500 600

-76-
Excitation Spectra

Wet vs. Dry

74.7% Yield
Em_λ = 490 nm

FIGURE 15
PROJECT 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

RESEARCH REVIEW

April 3, 1991

Arthur J. Ragauskas
PROJECT SUMMARY FORM

Project Title: FUNDAMENTALS OF BRIGHTNESS STABILITY
Division: Chemical and Biological Sciences
Project No.: 3524
Project Leader: Arthur J. Ragauskas
FY 90-91 Budget: $135,000

IPST GOAL:
Increase the usefulness of high yield fibers

OBJECTIVE:
Research activities will be directed at investigating the fundamental chemical reactions which are initiated when high yield pulps are photolyzed. As our knowledge of the photooxidation of mechanical pulp increases, methods to stop or significantly retard the yellowing process will follow.

RESULTS:
Quinones appear to be produced during photoyellowing. Their photochemical behavior on a solid matrix may account for color development and is, therefore, being studied in this project. Mono and dimethoxybenzoquinone were synthesized by a unique route in good yield. Both quinones have been absorbed onto a solid support and photolyzed. Dimethoxybenzoquinone was relatively stable to the photolysis conditions. Photolysis of monomethoxybenzoquinone yielded several products, with the predominant compound being the hydroquinone. Apparently, a photo-reduction occurred which suggests that the cellulose is in turn oxidized during the photo-chemical reaction.
OBJECTIVES

The aim of this research is to investigate the fundamental chemical reactions which are initiated when high yield pulps are photolyzed and to apply this knowledge to stop or significantly retard the yellowing process. To accomplish this goal research efforts will focus on three important aspects of the brightness reversion phenomena: the photo-formation of chromophoric structures; the photo-reactivity of chromophoric structures; the design of novel photostabilization techniques for mechanical pulp. This goal will be accomplished by employing both model compounds and by examining the brightness reversion phenomenon as it occurs with TMP.

INTRODUCTION

The photo yellowing of mechanical pulp is most frequently attributed to the photo-formation of ortho and para quinones from lignin\textsuperscript{1}. Recent research efforts at IPST have clearly demonstrated the presence of ortho-quinones in irradiated mechanical pulp samples\textsuperscript{2}. The presence of para-quinones has been suggested by a variety of investigators\textsuperscript{3}.

Although the presence of quinones has been detected in mechanical pulp it remains undetermined if these are the final products in the brightness reversion phenomena or if these types of compounds may undergo further thermal and/or photolytic reactions. A review of solution phase photochemistry clearly suggests that a variety of ortho and para quinones should be photo-reactive\textsuperscript{4} although it is well known that distinct differences in solid and solution phase photochemistry often occur\textsuperscript{5}.

Clearly it would be beneficial to understand the ultimate fate of quinoid structures in mechanical pulp, under the brightness reversion phenomena. It is anticipated that this knowledge would aid in the design of novel systems aimed at retarding or stopping the photo-yellowing of high yield pulp.
RESULTS FROM PHOTOLYSIS STUDIES

Initial photochemical studies were focused on the photoreactivity of dimethoxybenzoquinone (DMBQ) and monomethoxybenzoquinone (MMBQ). Both of these compounds have been suggested to contribute to the yellowing process. These compounds were also selected as a starting point in this investigation since it was known that their reactivity and ease of preparation would permit facile development of the techniques needed to study the more reactive ortho-quinones.

To study the photo-reactivity of DMBQ and MMBQ as it applies to the brightness reversion conditions all studies were performed in the solid state and employed a photochemical reactor with a spectral distribution of 300-410 nm. All studies were performed under atmospheric conditions.

Due to the chemical complexity of mechanical pulp the initial photochemical studies were performed on extracted cotton linter fibers (i.e., cotton linters fibers which were washed with distilled water and then exhaustively extracted with methanol followed by dichloromethane). Para-quinones were applied onto the cotton linters, by preparing a slurry of cotton linters, para-quinone and dichloromethane. Samples were then dried under high vacuum. The resulting mixture was irradiated under atmospheric conditions, with vigorous mechanical stirring. Samples of the irradiated material were then periodically removed from the photoreactor, extracted and analyzed by GC and/or GC-MS.

The photolysis of DMBQ on cotton linters for periods of up to 8 h gave essentially only starting material.

<table>
<thead>
<tr>
<th>Period of Irradiation (h)</th>
<th>% DMBQ Recovered (GC Yields)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>69</td>
</tr>
<tr>
<td>8</td>
<td>76</td>
</tr>
</tbody>
</table>

Prolonged irradiation for > 24 h did result in the formation of a variety of minor components (< 10% of product mixture) but GC-MS analysis suggested that these compounds were dimeric in structure. Given the low concentration of quinones present in yellowed mechanical pulp these latter products were not considered significant.

The results of these photolysis studies suggested that DMBQ was not photo-reactive under the brightness reversion conditions. This was confirmed by spiking sheets of cotton linters with DMBQ, irradiating and monitoring the changes in brightness by TAPPI brightness measurements.

-85-
The slight increase in brightness was attributed to a volatilization of some of the DMBQ during irradiation.

Since it has been suggested that para-quinones could act either as singlet oxygen generator or undergo photochemical reactions with lignin itself a sample of DMBQ, and a dimeric lignin model compound were applied onto cotton linter fibers and photolyzed for 5 h. Tlc and GC analysis both indicated that the product mixture contained almost solely starting material. Clearly these results suggested that any DMBQ formed under the brightness reversion conditions is photostable and will not initiate any further reactions.

This conclusion was further verified by irradiating samples of DMBQ adsorbed onto TMP. Following the usual procedure, samples were irradiated, extracted and analyzed by GC. As the data clearly indicates, DMBQ is photostable under these conditions also.

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<table>
<thead>
<tr>
<th>Period of Irradiation (h)</th>
<th>Sample</th>
<th>TAPPI Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Cotton Linter</td>
<td>89</td>
</tr>
<tr>
<td>0</td>
<td>Cotton Linter\DMBQ</td>
<td>38</td>
</tr>
<tr>
<td>1</td>
<td>Cotton Linter</td>
<td>88</td>
</tr>
<tr>
<td>1</td>
<td>Cotton Linter\DMBQ</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Cotton Linter</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>Cotton Linter\DMBQ</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>Cotton Linter</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>Cotton Linter\DMBQ</td>
<td>56</td>
</tr>
</tbody>
</table>

The results for the 2 and 8 h samples gave greater than 100% yield since the samples were not completely homogeneous.

To explore the photoreactivity of MMBQ in the solid state, samples were applied onto cotton linters fibers and were irradiated in much the same manner as described above for DMBQ. GC-MS analysis of the product mixture indicated that the reactivity of MMBQ in the solid state was distinctly different than that reported for the solution phase. The photolysis of MMBQ, adsorbed onto cotton linters gave largely a product mixture containing MMBQ and monomethoxyhydroquinone (MMHQ).
The presence of MMHQ was not expected and repetition of the experiments confirmed its formation. The exact ratio of MMBQ:MMHQ did vary and was shown to be dependent upon the effectiveness of stirring. The formation of MMHQ was attributed to a photo-reduction, which suggests that the cellulose was undergoing an oxidation. This process is accompanied by a distinctive change in color of the starting material from bright yellow to a dark brown/purple color for the product. Samples of MMBQ were applied to sheets of cotton linters, irradiated and the color change was monitored by TAPPI brightness measurements.

Although the source of the increase in "color" has not been identified, an attractive possibility is the formation of a charge transfer complex between MMBQ and MMHQ. These types of structures are known to form intensely colored complexes and may well occur under the experimental conditions. Further studies are currently under way to pursue this proposal.

To determine if MMBQ would be photo-reactive to lignin, samples of MMBQ and a lignin model were adsorbed onto cotton linters and irradiated for 4 h. TLC and GC analysis of the product mixture indicated the presence of MMBQ, MMHQ and several unidentified products. Based upon GC retention times these latter compounds appear to be oxidized derivatives of the lignin model compound. Attempts at separating and characterizing these structures is currently underway. The photolysis reaction is accompanied by a intense darkening of the reaction material and this change will be quantified.

The photolytic behavior of MMBQ adsorbed onto TMP has also been explored. In contrast to the cotton linter studies it appears that after 4 h of irradiation very little quinone remains on the surface of the fibers.
The fate of MMBQ on TMP currently remains uncertain but these results clearly suggest that MMBQ is not a final photochemical product in the brightness reversion phenomena. Instead it appears that MMBQ is a reactive intermediate which oxidatively attacks lignin, generates other chromophoric structures and initiates a photo-degradation reaction of mechanical pulp.

These results clearly suggest that MMBQ is photo-reactive under the brightness reversion conditions. The nature of the photochemical reactions which occur are dependent if the reactions are occurring in the solution phase or the solid state. Furthermore the nature of the solid support also appears to influence the reaction outcome.

The lignin model compounds employed in these studies were prepared at IPST as part of this project. Current synthetic research efforts are directed at preparing stereochemical pure oligomers of B-O guaiacyl ether structure. The preparation of these compounds will provide a means of investigating photo-initiated intramolecular degradation of lignin like structures. Although these types of reactions have been shown to occur in a variety of polymers, to-date this type of reaction mechanism has not been investigated in lignin chemistry.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

Research efforts will be directed at completing the photochemical studies of MMBQ and initiating the photochemical studies of 4-methyl ortho-quinone. All of these studies will be performed in the solid state using either cotton linters and/or TMP as a solid support. Synthetic efforts will be continued to provide required lignin model compounds.

Attempts will also be directed at developing novel methods of retarding the brightness reversion process. The use of Birch Reduced aromatic systems (see below) to act as an antioxidants in the brightness reversion phenomena will be explored.

\[
\begin{align*}
\text{[Structures]} & \quad \text{[Structures]}
\end{align*}
\]

If these types of structures show any activity at retarding the rate of yellowing then the electrolytic generation of these types of structures from lignin will be pursued.
POTENTIAL FUTURE ACTIVITY:

Future research studies are to be directed at preparing and photolyzing other lignin model compounds (i.e., conjugated olefinic compounds, catechol derivatives, ...) believed to be involved in the brightness reversion process. Novel and efficient synthetic methods of preparing these structures will be examined when required.

The photoreactivity of ortho-quinones, under the brightness reversion conditions, will be further explored. A careful examination of the literature provides extensive examples of the tendency of quinones to undergo solution phase polymerization and photochemical reactions. The extent to which the solid matrix of mechanical pulp could mediate the photochemical reactivity of quinones is currently unknown. The above proposed studies will therefore extend our knowledge of the chemical reactivity of the quinones formed in mechanical pulp.

Previous IPST research efforts demonstrated that derivatization of ortho-quinones with trialkyl phosphites could be employed as a means of detecting ortho-quinones in mechanical pulp, by means of $^{31}$P NMR. This technique will be employed in this proposed study. The use of solid-state $^{13}$C CP-MAS NMR will also be explored to investigate the chemical structure of mechanical pulps and its relevancy to the photo-yellowing phenomena.

It is anticipated that the results of the modelling studies will further refine our understanding of the brightness reversion process. These results will then be corroborated with accelerated brightness reversion studies on mechanical pulp handsheets.

Collectively, these investigations will provide fundamental information as to what is occurring in the chemically complex structure of mechanical pulp when it is irradiated. Based upon these studies, novel methods of retarding or stopping the brightness reversion process will be proposed and investigated.
REFERENCES


