ANNUAL RESEARCH REVIEW

CHEMICAL PULPING AND BLEACHING

March 22, 1995

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Institute of Paper Science and Technology
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CLOSED MILL OPERATIONS

PROJECT F017

Subtask: Control of Nonprocess Element

ANNUAL RESEARCH REVIEW

March 22, 1995

Patrick Bryant

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TECHNICAL PROGRAM REVIEW

Project Title:	Closed Mill Operations
Project Code:	CLDMIL
Project Number:	F017
Division:	Chemical and Biological Sciences
Project Staff:	P.Bryant, JY.Zhu
FY 94-95 Budget:	$487,500

PROGRAM OBJECTIVE:

Develop technology required to move toward closed mill operation.

Subtask Goals:

The goal of this subtask are as follows:

- Develop a scientific understanding of the material balance and partitioning of non-process elements (NPE) in pulp and paper mill process streams.
- Provide member companies with mathematical models which predict the behavior of NPE's in pulp and paper mills with different process configurations and operating conditions.
- Determine the impact of NPE's on mill operations.
- Develop NPE control techniques and technologies.

SUMMARY

Work began in August 1994 on the first two goals of the project. The research plan includes mill sampling, laboratory experiments, full-mill simulation, predictive model development and model verification.

We are working with three member companies to develop three bleached kraft mill NPE material balances. This work involves sampling and analyzing process streams at each mill for NPE's and developing a full-mill process simulation for each mill. The sampling and full-mill simulation is complete for one mill and analysis of the mill samples is in progress. Work with the other two mills is in the planning stage. This portion of the project is scheduled to be complete by September 1995.

Laboratory experiments have been completed to characterize the behavior of NPE's with three different pulps using different chelants at different pH's. Experiments on the impact of primary and secondary fines on NPE behavior have been completed. Initial experiments exploring the effects of dissolved organics on NPE behavior has been completed. Analysis of samples from these experiments is in progress.

A functional specification has been completed for the development of a NPE equilibrium module (version 1.0) which will run in the WinMAPPS/WinGEMS environment. Programming of the module will be by a third party contractor.

BACKGROUND

The EPA has recently proposed a set of regulations for the pulp and paper industry which are commonly referred to as the *cluster rules*. Achieving the proposed effluent limitations will require significant process modifications and capital investment by the industry. Improved kraft pulp bleaching technology is key to meeting or exceeding the proposed regulations. One of the best long term solutions for reducing effluent pollutants from bleached kraft pulp mills is to move towards closure of the bleach plant.

Internally recycling effluent waste streams into the process for further processing or use (closed-cycle operations) reduces both the water makeup and the effluent discharge of the mill. Current bleaching technology is designed around open bleach plants, which wash out residual dissolved organics and inorganics from each bleach stage. The bleach plant washer filtrates are sent through waste treatment prior to discharge to the environment. Closing the bleach plant entails using bleach washer filtrates in a counter-current fashion as wash water for the pulping operation. Residual bleach plant organics make their way to the recovery boiler where they are burned as fuel along with organics from the pulping operation. Residual bleaching inorganics either serve as makeup chemical (Na and S) for the pulping operation or must be purged from the chemical recovery system.

Closure of operating bleach plants would dramatically reduce both the volume and the pollutant concentration of pulp mill effluents. However, closing the mill creates many operational problems. The biggest problem associated with closing the bleach plant is the concentration build-up of non-process elements (NPE) in process streams. NPE usually enter the pulp process as trace constituents of wood. The acidic open filtrates of conventional bleach plants provide a significant purge for the NPE, keeping their concentration in the process low.

Recycle of chlorine-based or totally chlorine free (TCF) based bleach plant filtrates leads to increased NPE concentrations. TCF bleaching technologies such as O_2, O_3 and H_2O_2 require control of NPE such as Mn, Fe, Mg and Ca. Process equipment scaling, corrosion and plugging can result from high concentrations of NPE such as Cl, K, Al, Si and Ca.

Water use and effluent discharge from unbleached chemical pulping, mechanical pulping, secondary fiber pulping and paper making are not currently receiving the attention that effluents of chemical bleached pulp mills are receiving. However, in the future, water use (and the accompanying effluent discharge) at all pulp and paper mills will likely become an issue. Developing low-effluent mills using closed-cycle technology will impact all segments of the industry.

MILL BASE-LINE STUDIES

The purpose of conducting mill-base line studies is to develop a better understanding of the partitioning of NPE's in *open* bleached kraft mills, to develop NPE material balances for mills from different geographical areas which have different process configurations and to develop full-mill simulations that can be used to validate NPE predictive models.

Three member company mills are participating in the NPE material balance base-line studies. The first mill (A) is a Southern single line market kraft pulp mill with conventional kraft cooking and ECF bleaching. The mill campaigns runs of hardwood and softwood for periods of 1-2 weeks. The mill has white liquor pressure filters in place of conventional white liquor clarifiers.

The second mill (B) is a Southern dual line (SW and HW) integrated kraft pulp mill with conventional kraft cooking, medium consistency O_2 delignification and conventional C/D bleaching.

The third mill (C) is a Northern dual line (SW and HW) integrated kraft pulp mill with medium consistency O_2 delignification.

Previous studies[1-3] have focused on the fiberline and did not track Si or Cl. The current base-line studies include sampling in the liquor recovery cycle and analysis for Si and Cl. Figures 1 and 2 show where samples where taken at Mill A to develop a NPE base-line material balance. Sampling has been completed for both a softwood and a hardwood run at Mill A. Samples were taken over two separate three day periods. Morning and afternoon composite samples were gathered from each sample location. Sample analysis is in progress.

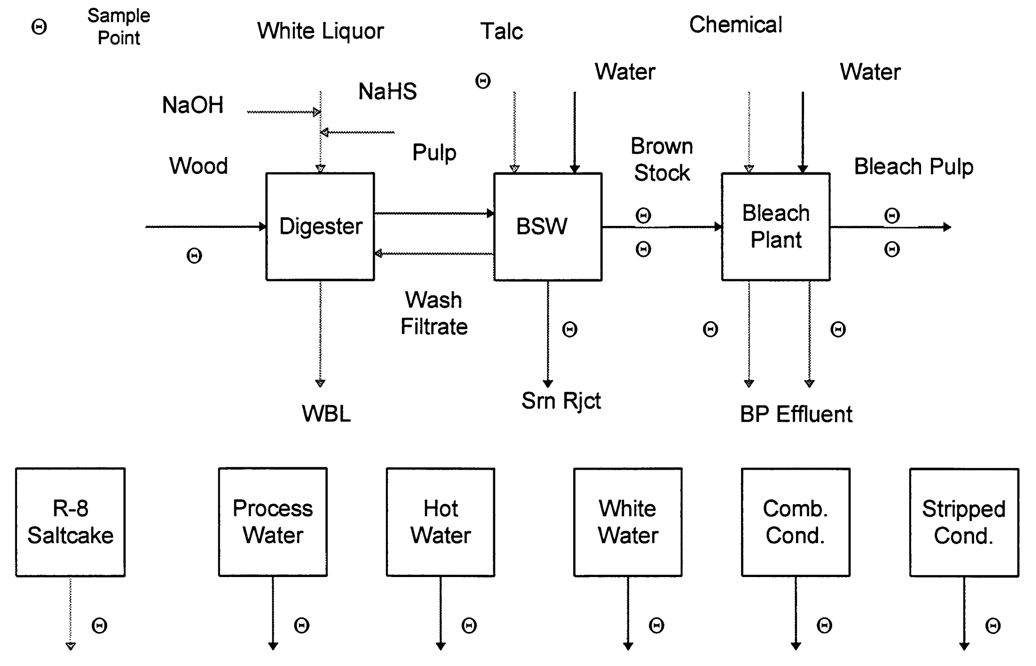

Figure 1. NPE base-line study sample locations for Mill A fiberline .

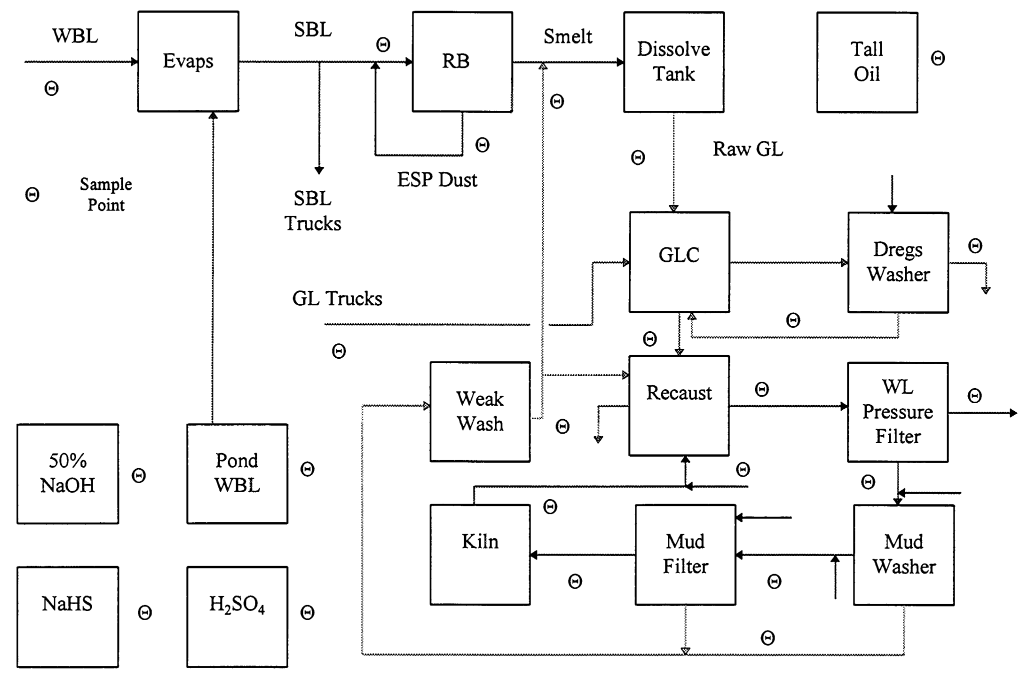

Figure 2. NPE base-line study sample locations for Mill A recovery.

LABORATORY EQUILIBRIUM STUDIES

Laboratory experiments have been conducted to characterize the binding of NPE's to kraft pulps over a range of pH's both with and without chelants (EDTA and DTPA) presents. A previous study characterized a Douglas Fir 14 Kappa oxygen delignified pulp.[4,5] The three pulps investigated were: 1) a Southern Pine kraft pulp ≈ 30 Kappa; 2) a Southern Pine O_2 delignified kraft pulp ≈ 18 Kappa; 3) a Southern Hardwood O_2 delignified kraft pulp ≈ 13 Kappa.

Experiments to evaluate the binding capacity of primary and secondary fines relative to average pulp fibers were conducted for each pulp.

Sample analysis for most experimental runs is currently in progress using Inductively Coupled Plasma Spectrometry Chromatography (ICP). Samples are wet ashed using a hydrofluoric acid digestion. Sample and data analysis should be complete by May, 1995.

Figures 3-5 give results from one experimental run on the 18 Kappa softwood with 0.3% EDTA applied on an o.d. pulp basis. The starting pulp consistency for all experiments was approximately 30%. Pulp was diluted to 1% consistency with nano-pure water. Pulp slurry pH's were adjusted with either H_2SO_4 (EM Science TracePur Plus) or NaOH (EM Science ACS reagent grade). Pulp slurries were mixed for 30 minutes with a 2.5 inch diameter polypropylene paddle at 200-300 rpm in a 2 liter glass tempering beaker with circulating water in the shell to maintain a temperature of 75° C. The pulp slurry was then vacuum dewatered across a Buchner funnel to approximately 25% consistency. The pulp was further dewatered by pressing to approximately 50% consistency.

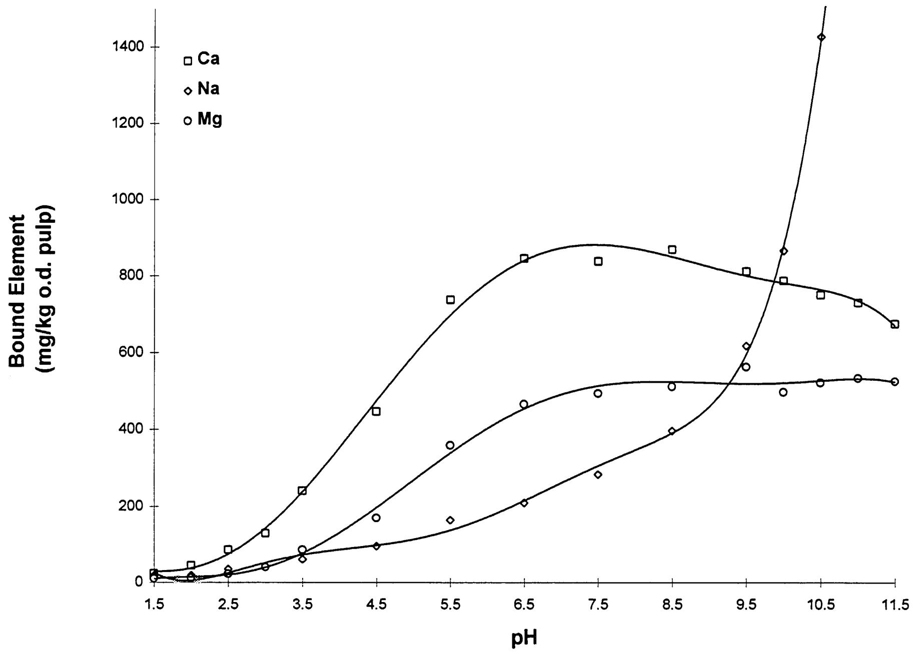

Figure 3. Fiber bound Ca, Na and Mg as a function of pH. Temperature 75° C, 0.3% EDTA, 1% consistency slurry, 30 minutes mixing.

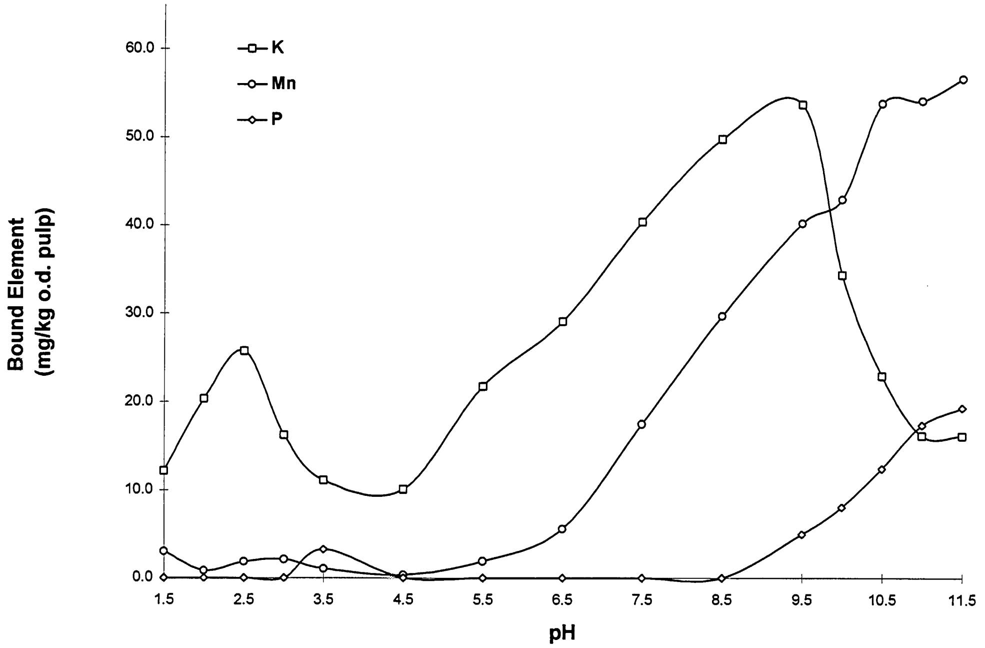

Figure 4. Fiber bound K, Mn and P as a function of pH. Temperature 75° C, 0.3% EDTA, 1% consistency slurry, 30 minutes mixing.

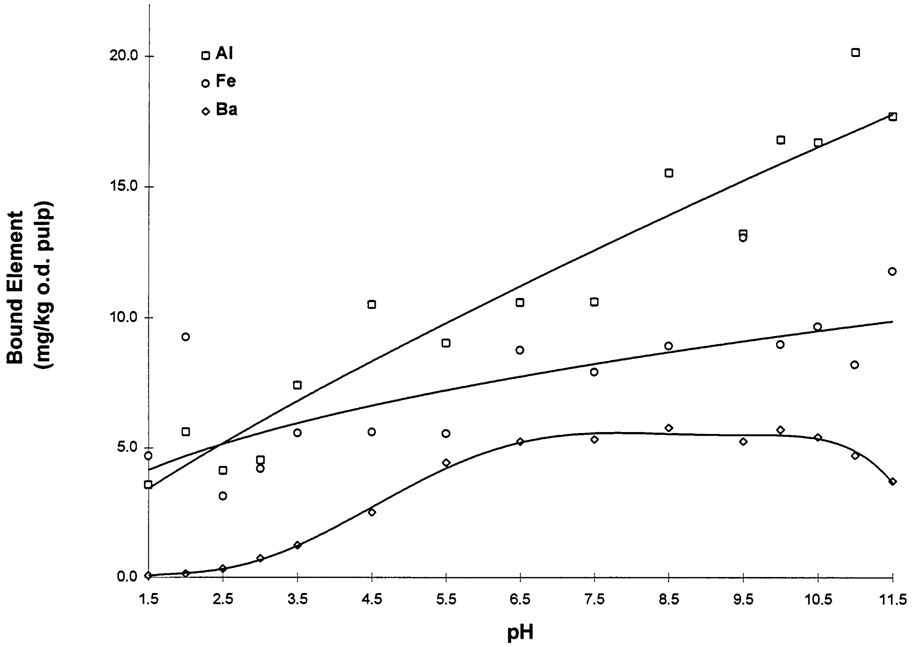

Figure 5. Fiber bound Al, Fe and Ba as a function of pH. Temperature 75° C, 0.3% EDTA, 1% consistency slurry, 30 minutes mixing.

NPE PREDICTIVE MODEL

There are a number of important splits which occur in pulp and paper processing in which the partitioning of electrolytes are important. As mills move towards closed water systems, predicting these splits becomes critical to good process design and operations.

The sorption of cations onto fiber can be modeled with Langmuir isotherms or other empirical models[6]. However, this approach is not easily applied in general for all pulp and paper processing conditions and requires development of sorption constants for each pH and mix of cations in the system. A more general approach of modeling cellulose as a cation exchange medium with or without competing ligands (e.g. chelating agents) has been developed.[7] This approach requires only one set of formation constants for each cation/ligand pair independent of the pH or concentration of competing cations.

A simulation block, EQUIL01, is being developed for use with either WinMAPPS or WinGEMS process simulators. EQUIL01 solves general electrolyte equilibrium problems encountered in the pulp and paper industry.

Two general approaches are commonly used to develop and solve multiple-component chemical equilibrium problems:

1. minimization of the system free energy under mass balance constrains. This approach is taken by the programs SOLGASMIX and GIBBS[8].
2. simultaneous solution of the nonlinear mass action expressions and linear mass balance relationships. This is the approach taken in EQUIL01 and follows many of the techniques used in the EPA program MINTEQA2[9] which derived its approach from Dr. John Westall's work at MIT and Oregon State University. [10]

For EQUIL01, electrolytes partition into one of three phases; dissolved solids, suspended free solids or suspended pulp bound solids. Gas phase partitioning (e.g. recovery boiler, lime kiln, etc.) is not predicted.

A modified version of the MINTEQA2's thermodynamic database is used for EQUIL01. The database is user configurable and can be extended to include additional thermodynamic data in the future (e.g. heat capacities, diffusion coefficients, etc.).

Version 1.0 of EQUIL01 has the following restrictions:

- all streams are considered well mixed equilibrium stages with fixed temperature, pressure and total electrolyte concentrations.
- concentration gradients through pulp mats are not included (washer mats).
- the pH of the equilibrium stage must be set by the user and is not predicted.
- activity coefficient prediction for moderate to high ionic strength solutions is limited by the available data on the species in the defined system.
- gas phase concentrations are not considered.
- reaction kinetics are not incorporated and all systems are assumed at equilibrium.
- redox reactions are not utilized and the system pE is irrelevant to the system.

Primary Species and Formed Species Definitions

All electrolytes which take part in the chemical equilibrium reactions are defined as either primary or formed species.

Primary Species

Primary species are the basic building-blocks from which all species in the equilibrium system are built. In most cases, primary species are the dissolved cations and anions in the system. In general the only restriction on primary species is that they linearly combine to form all formed species in the system. and that formation of a primary species from other primary species is not allowed. There are five defined types for primary species:

0. Electrons (currently not supported)
1. Water
2. Inorganic Cation
3. Inorganic Anion
4. Inorganic uncharged
5. Organic (charged or uncharged)

Each primary species is defined by a primary species number, name, type, molecular weight, charge, extended Debye-Huckel constants *a* and *b* (not available for all). Approximately 100 primary species have been initially defined.

Formed Species

Formed species are formed from a linear combination of primary species. Each formed species is defined by a formed species number, name, type, heat of formation, LogK formation constant, charge, extended Debye-Huckel constants *a* and *b* (not available for all), molecular weight and a primary species number and stoichiometric coefficient for each primary species used to make up the formed species (up to six primary species allowed).

Formed species are defined to exist in one of five types:

1. Aqueous phase (dissolved) solid
2. Non-pulp suspended (precipitated) solid
3. Pulp bound solid
4. Gas (currently not supported)
5. Redox (currently not supported)

Hydrogen and hydroxide concentrations are fixed by a user specified pH and a temperature dependent K_w. Other primary species may be given fixed activities.

Pulp bound species behave as dissolved solids from an equilibrium calculation point of view. Therefore, the activity of pulp bound solids is proportional to its concentration on a liquid basis.

Suspended solids have an activity of 1.0 by definition. Suspended solids are only formed when the solubility product is exceeded. If the solution becomes over-saturated with respect to a particular solid, and if that solid is more over-saturated than any other possible solid composed of the same primary species, then EQUIL01 precipitates that solid reducing the aqueous phase concentrations of the primary species. Conversely, under saturated solutions will dissolve solid phase formed species if they are present.

Problem Formulation

A system of *n* independent primary species that can combine to form *m* formed species (including the non-reacted primary species as a special case) is represented mathematically by a set of mass action expressions of the form

$$a_i = K_i \prod_{j=1}^{n} X_j^{v_{ij}} \quad for \;\; i = 1 \ldots m \tag{1}$$

Where:

K_i = equilibrium constant for the formation of species i
a_i = activity of formed species i
X_j = activity of primary species j
v_{ij} = stoichiometric coefficient of primary species j in formed species i

The activity of species i (a_i), is related to the molal concentration (C_i) by the activity coefficient, γ_i.

$$a_i = \gamma_i \, C_i \tag{2}$$

Defining K'_i such that

$$K_i' = \frac{K^i}{\gamma_i} \tag{3}$$

then

$$C_i = K_i' \prod_{j=1}^{n} X_j^{v_{ij}} \quad for \;\; i = 1 \ldots m \tag{4}$$

A mass balance on primary species yields

$$Y_j = \sum_{i=1}^{m} v_{ij} C_i - T_j \quad for \; j = 1 \ldots n \tag{5}$$

The mathematical solution is the set of primary species activities, X_j*'s*, which give rise to all Y_j*'s* being approximately zero. A numerical solution to the set of non-linear equations can be found by guessing each primary species' activity and iterating by Newton's method to convergence.

The set of linear equations created by guessing the primary species' activities are solved by Gaussian elimination. The partial derivatives of equation **(5)** with respect to each primary species are taken to create the Jacobian Matrix used in the Gaussian elimination.

$$\frac{\partial Y_j}{\partial X_k} = \sum_{i=1}^{m} v_{ij} v_{ik} \frac{C_i}{X_k} \quad for \quad k = 1 \ldots n \tag{6}$$

A FORTRAN program designed to solve for Y_j uses a modification of NLSYST presented by Gerald and Wheatley[11].

Activity Coefficient Estimations

There are four options for estimating activity coefficients for each species:

1. Activity coefficients are set equal to a user defined constant. Default value is 1.0.
2. Activity coefficients are calculated with user defined functions. The function is an algebraic expression which can use temperature, ionic strength and the current species molality to estimate the activity coefficient.
3. Activity coefficients are calculated using the Davies equation.
4. Activity coefficients are extended Debye-Huckel equation if constants are available, otherwise values are calculated using the Davies equation.

It is impossible to measure an individual ionic activity coefficient, but for estimation purposes, they can be calculated for each species. Keeping individual ionic activity coefficients simplifies inclusion of those coefficients into multi-component electrolyte system calculations. The more common method of using mean ionic activity coefficients, which can be measured, is more difficult to incorporate in to a general purpose electrolyte equilibrium equation solver.

Using either the Davies equation or the extended Debye-Huckel equations the activity coefficient estimations are calculated after every iteration based on the systems total ionic strength.

Davies Equation

$$Log\gamma_i = -A \cdot Z_i^2 \left[\frac{\sqrt{I}}{1+\sqrt{I}} - .24I \right] \qquad \textbf{(7)}$$

Extended Debye-Huckel

$$Log\gamma_i = -A \cdot a_i \cdot Z_i^2 \frac{\sqrt{I}}{1+B \cdot b_i \sqrt{I}} + b_i \cdot I \qquad \textbf{(8)}$$

Where

a_i = ion size parameter of species *i*
b_i = ion specific parameter *i*
A,B = temperature dependent constants
Z_i = charge on species *i*
I = ionic strength of solution
γ_I= activity coefficient of species *i*

The Davies equations and Extended Debye-Huckel equations are implemented following the methods used in MINTEQA2[9]. The calculation of the temperature dependent constants *A* and *B* used in both equations follows the development of Truesdell and Jones[12] and the implementation of Ball et. al.[13]

The activity coefficients of neutral species are estimated with a simple empirical relation developed by Helgeson[14],

$$Log\gamma_i = \alpha \cdot I \qquad \textbf{(9)}$$

where

α = global user defined constant with a default value of 0.1
I = ionic strength of solution
γ_I.= activity coefficient of species i

Solution Ionic Strength

The ionic strength is calculated prior to each iteration with the following equation

$$I = \frac{1}{2}\sum_{i=1}^{m} Z_i^2 C_i \qquad \textbf{(10)}$$

where

C_i = concentration of ion species
m = number of charged species
Z_i = charge on each species

The ionic strength, I, is constrained to $0 < I < 4.0$.

Equilibrium Constant Temperature Correction

The equilibrium constants in the thermodynamic database are at a reference temperature of 25° C. The values must be corrected temperature before the start of the equilibrium calculations. The van't Hoff correction is used as follows:

$$Log\,K(T) = Log\,K_{25^\circ C} - \frac{\Delta H_r^\circ}{2.303 \cdot R}\left[\frac{1}{T} - \frac{1}{298.16}\right] \qquad \mathbf{(11)}$$

Where

$K(T)$ = temperature corrected equilibrium constant
$K_{25^\circ C}$ = equilibrium constant at the reference temperature of 25° C
ΔH_r° = standard enthalpy change of reaction at 25° C, Kcal/g-mole
R = molar gas constant, 1.987×10^{-3} Kcal/(Mole °K)
T = temperature of system in Kelvin

The van't Hoff equation assumes the enthalpy of reaction is constant with temperature, which is a good approximation for temperatures below 100° C.

Precipitated Suspended Solids

A user defined global switch determines if precipitation of suspended solids (type 2 formed species in the data base) is allowed. The precipitation of a single formed species can be prohibited by not including the solid phase formed species in the local data base configuration.

A saturation index is calculated for each "possible" suspended solid in the system and is defined as follows:

$$SI_i = \log \frac{\prod_{j=1}^{n} X_j^{v_{ij}}}{K_i} \quad for \;\; i = m+1 \ldots m' \qquad \textbf{(12)}$$

Where

m' = the number of suspended solids configured for the system
SI_i = saturation index for suspended formed species i
K_i = equilibrium constant (solubility product) for the formation of solid species i
a_i = activity of formed species i
X_j = activity of primary species j
v_{ij} = stoichiometric coefficient of primary species j in formed species i

If the index is negative for a particular suspended solid, then the system is under saturated with respect to that solid species. If the index is positive (> 0.001), the solution is supersaturated in that solid species. If the user has configured that solid species should precipitate if possible, then a correction must be applied to the aqueous phase solution for supersaturated solids to allow them to precipitate.

This is done in a stepwise fashion by starting with the suspended solid species with the highest saturation index. The activity of a solid is defined as unity which allows equation **(4)** to be rewritten as follows:

$$1 = K_j' \prod_{i=1}^{n} X_i^{v_{ji}} \quad for \;\; j = m+1 \ldots m'' \qquad \textbf{(13)}$$

Where

K_i' = equilibrium constant (solubility product) for the formation the suspended solid

n = the number of primary species

m'' = the number of actual (precipitated) suspended solids, created by the stepwise precipitation of those possible solids with the highest saturation index

X_i= activity of primary species i

v_{ji} = stoichiometric coefficient of primary species i in formed solid species j

One additional equation and one additional unknown are added to the system of simultaneous equations in a stepwise fashion for each solid precipitated. The species with the highest *SI* is allowed to precipitate and a new solution for all species calculated. The *SI*'s for other possible solids are recalculated and if any are supersaturated the species with the highest *SI* is added to the system of equations and allowed to precipitate. The process continues in a stepwise fashion until all possible solids are under-saturated.

The new unknown variable is the mass of the solid species precipitated (in terms of concentration on solvent basis) rather than a primary species activity (which are what all the unknowns in the aqueous portion of the system represent). The additional equation results from rearranging equation **(13)** in terms of residual:

$$Y_j^* = K_j' \prod_{i=1}^{n} X_i^{v_{ji}} - 1.0 \quad for \quad j = m+1 \ldots m'' \qquad \textbf{(14)}$$

The partial derivatives for the new rows in Jacobian matrix can be calculated as follows:

$$\frac{\partial \ Y^*_j}{\partial X_k} = K_j \prod_{i=1}^{n} v_{jk} \frac{X_i^{v_{ji}}}{X_k} \ for \ \ j,k = n+1 \ldots m'' \qquad \textbf{(15)}$$

The mass balance on each primary species given by equation **(5)** must be modified to include the suspended solid species:

$$Y_j = \sum_{i=1}^{m} v_{ij} C_i - T_j + \sum_{n+1}^{n+1+m''} v_{ij} X_i \quad for\ j = 1 \ldots n \tag{16}$$

The partial derivatives in the Jacobian matrix for rows and columns *n* x *n* are calculated as before using equation **(6)**. The partials for the new solid phase unknowns in columns *n+1...m′′* of the Jacobian matrix are calculate using equation **(17)**.

$$\frac{\partial\ Y_j}{\partial X_k} = v_{kj}\ for\ \ k = n + 1 \ldots m'' \tag{17}$$

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CLOSED MILL OPERATIONS

PROJECT F017

Subtask: VOC Control

ANNUAL RESEARCH REVIEW

March 22, 1995

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Project Title:	Closed Mill Operations - VOC Prediction and Modeling
Project Code:	CLDMIL
Project Number:	F017
Division:	Chemical and Biological Sciences
Project Staff:	J.Y. Zhu and Pat Bryant

OBJECTIVE

To develop general predictive models for VOC partitioning in pulp and paper mills.

GOALS

The goals of the project are as follows:

- Develop a scientific understanding of the thermodynamic phase equilibrium (liquid/gas partitioning) of VOC in pulp and paper mill process streams.
- Provide member companies with mathematical models which predict the behavior of VOC's in pulp and paper mills with different process configurations and operating conditions.

SUMMARY

Conceptual work on this project began in the fall of 1994. Significant funding for this project will likely be obtained from external research grants. A proposal will be submitted to external agencies this year in cooperation with other Universities.

The project will focus on modeling the partitioning of methanol in liquid and gas process streams with known initial methanol inputs or generation rates. Experimental work is required to develop liquid phase activity coefficients and gas/liquid phase distribution coefficients.

Predictive models will be developed from experimental data. The models will be incorporated into simulation modules capable of running with either WinMAPPS or WinGEMS process simulators.

The predictive models will be validated using mill data collected in recent NCASI studies.

Longer term work will include the prediction of VOC generation rates in pulping and bleaching reactions.

STATUS REPORT

VOC Calculation Sub-Model

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To model closed mill operation processes, it is required to be able to model the amount of vaporized organic compounds (VOCs) in brown stock washing operations. The present study proposed a research approach for the calculation of VOCs using thermodynamic phase equilibrium principles. The proposed method use the ideal mixture assumption in which the vapor is assumed as a ideal gas while the liquid is treated as an non-ideal solution, and the poynting correction is neglected.

1. Thermodynamic Phase Equilibrium Principles

Thermodynamic phase equilibrium among N components and 2 phases with uniform temperature and pressure requires the satisfaction of the Gibbs phase rule:

$$\mu_i^V = \mu_i^L \tag{1}$$

where μ_i denotes the chemical potential of the *ith* component and superscript V and L denote the vapor and the liquid phase, respectively. The chemical potential is an intensive property. It can be expressed in terms of mole fractions of the components involved. For a two phase system involving N components under giving temperature and pressure, there are 2N variables in eqs. (1). The mole fractions add up to unity, therefore, there are only 2(N-1) independent variables. With N equations in (1), the number of free variables of the giving system is therefore:

$$2(N-1) - N = N - 2 \tag{2}$$

To satisfy eqs (1), we often require the uniformity of the fugacity of each phase for each component:

$$f_i^V = f_i^L \tag{3}$$

The fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. For vapor phase, the fugacity can be related to the vapor mole fraction by introducing the fugacity coefficient ϕ_i

$$\phi_i = \frac{f_i^V(T,P,\mathbf{y})}{y_i P} \tag{4}$$

where y_i is the vapor mole fraction of component i and P is the total vapor pressure. For a mixture of ideal gas $\phi_i = 1$.

The calculation of liquid phase fugacity is not trivial. The common approach involves the quantities of standard state fugacity of the activity coefficient. The fugacity of liquid component i can be expressed as:

$$f_i^L(T,P,\mathbf{x}) = x_i \gamma_i(T,\mathbf{x}) f_i^{pureL}(T) \exp\left[\int_{P_i^o}^{P} \left(\frac{\bar{v}_i^L[T,P,\mathbf{x}]}{RT}\right)_{T,\mathbf{x}} dP\right] \tag{5}$$

where $\bar{v}_i^L$ is molar liquid volume which equals to the ratio of the molecular weight to the density, x_i is the liquid mole fraction, γ_i is the liquid activity coefficient, and the exponential term is the Poynting correction and is only important at high pressures. In equation (5), f_i^{pureL} is the pure liquid fugacity at the "standard state" of T, P_i^s. The standard state is chosen such that a value of $f_i^{pureL}(T)$ can actually be found. A cleaver choice of P_i^s is the saturation (or vapor) pressure of pure liquid i. In this state, the liquid and the saturated vapor is in equilibrium. Therefore,

$$f_i^V(T,P_i^s,y_i = 1) = f_i^{pureL}(T) \tag{6}$$

Substitute eq. (4) into above equation,

$$P_i^s(T)\phi_i^s(T) = f_i^{pureL}(T) \tag{7}$$

The liquid fugacity now can be calculated as,

$$f_i^L(T,P,\mathbf{x}) = x_i \gamma_i(T,\mathbf{x}) P_i^s(T)\phi_i^s(T) \exp\left[\int_{P_i^o}^{P} \left(\frac{\bar{v}_i^L[T,P,\mathbf{x}]}{RT}\right)_{T,\mathbf{x}} dP\right] \tag{8}$$

Substitute eqs. (4) and (8) into eq. (3), we have

$$y_i P = \gamma_i(T,\mathbf{x}) x_i P_i^s \Im_i \tag{9}$$

where $\Im_i = \frac{\phi_i^s}{\phi_i} \exp\left[\int_{P_i^o}^{P} \left(\frac{\bar{v}_i^L[T,P,\mathbf{x}]}{RT}\right)_{T,\mathbf{x}} dP\right]$ is the Poynting correction factor. For subcritical components, $\Im_i$ is near unity when the total pressure P is not very high. Therefore equation (9) can be simplified as,

$$y_i P = \gamma_i(T,\mathbf{x}) x_i P_i^s \tag{10}$$

Equations (10) are often used for the calculation of phase equilibrium of multiphase systems, along the two additional equations of mole fractions adding to unity,

$$\begin{aligned} \sum_i x_i &= 1 \\ \sum_i y_i &= 1 \end{aligned} \tag{11}$$

For a given temperature, P_i^s in eq. (10) is the vapor pressure of pure liquid *i* at this temperature. The unknowns are x_i and y_i.. The difficulty in the calculation of phase equilibrium using eqs. (10) and (11) is that the finding of the liquid activity coefficient γ_i is often not trivial. We will discuss this in the next section.

For a binary two phase system, we can find that the problem is uniquely defined by equations (10) and (11) given that the activity coefficients are known. For a ternary system, however, we will have one degree of freedom according to eq. (2). The solution of the problem will involve iterations.

2. Liquid Activity Coefficient

Equation (10) indicate that the liquid activity coefficient plays a key role in the calculation of vapor-liquid equilibrium. Limited thermodynamic knowledge about the activity coefficient is available. The Gibbs-Duhem equation is the only available relation allows us to effectively use experimental data to determine the activity coefficient. For practical work, the utility of the Gibbs-Duhem equation is best realized through the concept of excess Gibbs energy. For a binary system, the Gibbs excess energy of an non-ideal solution is defined by

$$g^E = RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \qquad (12)$$

Through differentiation, we are able to relate the individual activity coefficientsγ_1 or γ_2 to Gibbs energy g^E

$$RT\ln\gamma_1 = \left(\frac{\partial g^E}{\partial x_1}\right)_{T,P,x_2} \qquad (13a)$$

$$RT\ln\gamma_2 = \left(\frac{\partial g^E}{\partial x_2}\right)_{T,P,x_1} \qquad (13b)$$

If we can find some mathematical correlation of excess Gibbs energy g^E, we can calculate the activity coefficient from eqs. (13). There are several Gibbs energy correlation equations in the literature. Table I lists several commonly used correlation for excess Gibbs energy along with the activity coefficients for binary systems. These correlation contains one or more constant parameters which can be determined from experiments. The Van Laar equation is frequently used for its linearity and the Wilson's equation is also commonly used for its good approximation and simplicity.

The determination of the constant parameters in excess Gibbs energy correlation requires some experimental data in order for the correlation to accurately predict the liquid activity coefficients. The following procedure describes how the activity coefficients can be determined from experimental data.

Let us first consider an isothermal binary system at some constant temperature T, we need to construct two diagrams; y vs. x and P vs. x.

1. Fine the pure liquid vapor pressure P_1^s and P_2^s at temperature T.

2. Suppose a few experimental data points for the mixture are available at temperature T. For example, given five values of x there are five corresponding experimental equilibrium values of y and P. Calculate γ_1 and γ_2 according to

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^s} \qquad (14a)$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^s} \qquad (14b)$$

Table I Some models for Excess Gibbs Energy and Subsequent Activity Coefficient for Binary Systems

Name	g^E	Binary parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Two-suffix[b] Margules	$g^E = Ax_1x_2$	A	$RT \ln \gamma_1 = Ax_2^2$
			$RT \ln \gamma_2 = Ax_1^2$
Three-suffix[b] Margules	$g^E = x_1x_2[A + B(x_1 - x_2)]$	A, B	$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3$
			$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$
van Laar	$g^E = \dfrac{Ax_1x_2}{x_1(A/B) + x_2}$	A, B	$RT \ln \gamma_1 = A\left(1 + \dfrac{A}{B}\dfrac{x_1}{x_2}\right)^{-2}$
			$RT \ln \gamma_2 = B\left(1 + \dfrac{B}{A}\dfrac{x_2}{x_1}\right)^{-2}$
Wilson	$\dfrac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$
			$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$
Four-suffix[b] Margules	$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	A, B, C	$RT \ln \gamma_1 = (A + 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12Cx_2^4$
			$RT \ln \gamma_2 = (A - 3B + 5C)x_1^2 + 4(B - 4C)x_1^3 + 12Cx_1^4$
NRTL[c]	$\dfrac{g^E}{RT} = x_1x_2\left(\dfrac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \dfrac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$ where $\tau_{12} = \dfrac{\Delta g_{12}}{RT}$ $\tau_{21} = \dfrac{\Delta g_{21}}{RT}$ $\ln G_{12} = -\alpha_{12}\tau_{12}$ $\ln G_{21} = -\alpha_{12}\tau_{21}$	$\Delta g_{12}, \Delta g_{21}, \alpha_{12}$[d]	$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\dfrac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \dfrac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$
			$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\dfrac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \dfrac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$
UNIQUAC[e]	$g^E = g^E \text{ (combinatorial)} + g^E \text{ (residual)}$ $\dfrac{g^E \text{ (combinatorial)}}{RT} = x_1 \ln \dfrac{\Phi_1}{x_1} + x_2 \ln \dfrac{\Phi_2}{x_2} + \dfrac{z}{2}\left(q_1x_1 \ln \dfrac{\theta_1}{\Phi_1} + q_2x_2 \ln \dfrac{\theta_2}{\Phi_2}\right)$ $\dfrac{g^E \text{ (residual)}}{RT} = -q_1x_1 \ln[\theta_1 + \theta_2\tau_{21}] - q_2x_2 \ln[\theta_2 + \theta_1\tau_{12}]$ $\Phi_1 = \dfrac{x_1r_1}{x_1r_1 + x_2r_2}$ $\theta_1 = \dfrac{x_1q_1}{x_1q_1 + x_2q_2}$ $\ln \tau_{21} = -\dfrac{\Delta u_{21}}{RT}$ $\ln \tau_{12} = -\dfrac{\Delta u_{12}}{RT}$ r and q are pure-component parameters and coordination number $z = 10$	Δu_{12} and Δu_{21}	$\ln \gamma_i = \ln \dfrac{\Phi_i}{x_i} + \dfrac{z}{2} q_i \ln \dfrac{\theta_i}{\Phi_i} + \Phi_j\left(\ell_i - \dfrac{r_i}{r_j}\ell_j\right) - q_i \ln(\theta_i + \theta_j\tau_{ji}) + \theta_jq_i\left(\dfrac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \dfrac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right)$ where $i = 1$ $j = 2$ or $i = 2$ $j = 1$ $\ell_i = \dfrac{z}{2}(r_i - q_i) - (r_i - 1)$ $\ell_j = \dfrac{z}{2}(r_j - q_j) - (r_j - 1)$

[a] Reference 97 discusses the Margules, van Laar, Wilson, UNIQUAC, and NRTL equations. The UNIQUAC equation is also discussed in Ref. 4.

[b] Two-suffix signifies that the expansion for g^E is quadratic in mole fraction. Three-suffix signifies a third-order, and four-suffix signifies a fourth-order equation.

[c] NRTL = Non Random Two Liquid.

[d] $\Delta g_{12} = g_{12} - g_{22}$; $\Delta g_{21} = g_{21} - g_{11}$.

[e] UNIQUAC = *Uni*versal *Qua*si *C*hemical. Parameters q and r can be calculated from Eq. (8-10.52').

[f] $\Delta u_{12} = u_{12} - u_{22}$; $\Delta u_{21} = u_{21} - u_{11}$.

3. For each of the five points, calculate the molar excess Gibbs energy

$$g^E = RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \qquad (12)$$

4. Choose one of the equations for g^E given in table 1. Use a least square fit or iterations to find the constants in the equation chosen with the data calculated from step 3.

5. Once the constants are found, then activity coefficient can be calculated using equations 13.

6. Using equations (10) and (11) to solve the problem with the activity coefficient calculated from step 5.

3. Experimental Plan

For the present project, we are interested in the methanol and water vapor release in brown stock washing process. In order to simplify the problem, the following assumptions are made:

1. The vapor phase is assumed as ideal gas.
2. The process are under fairly low pressures (about 1 atmosphere).
3. The liquid phase is not an ideal solution. The components of the liquid mixture are water and black liquor which contains dissolved solids (organics and inorganics).

With these assumptions, all the derivations discussed in the previous sections can be used for the present project. However, we need to obtain some experimental data to determine the constant parameters in excess Gibbs energy equation for the calculation of the activity coefficients.

The experimental facility required includes a mixing cell which will be maintained at a fixed temperature during the experiment, a methanol, and a water vapor sensor. The parameters need to be measured are: water and methanol vapor concentration, the water and black liquor florates.

The experiments need to be carried out under several black liquor sample conditions. The purpose is to find the activity coefficient under various dissolved solids and organic/inorganic ratios.

The detailed design of the experiments wuill be reported in the next meeting.

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1. Reid, R. C., Prausnitz, J.M., and Poling, B.E., (1987), in *"The Properties of Gases and Liquids"*. 4th Ed., McGraw-Hill, Inc.

2. O'Connell, J.P., (1981), in AIChE Modular Instruction, Series D, Volume 3, Thermodynamic Properties of Multicomponent Systems, Multiphase Equilibria and Chemical Equilibria,"Vapor-Liquid Equilibrium for Miscible Systems of Subcritical Componets".

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

PROJECT F013

ANNUAL RESEARCH REVIEW

March 22, 1995

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TECHNICAL PROGRAM REVIEW

Project Title:	ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP
Project Code:	BLECH
Project Number:	F013
Project Staff:	T.J. McDonough, C.E. Courchene, B. Carter, T. Ard, T. Schwantes, C. Walker, C. Woitkovich
Budget (FY 94-95):	$484,000

OBJECTIVE:

Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

GOALS:

A. Totally Chlorine-Free Bleaching

1. Identify residual lignin structural features likely to be of importance in defining bleachability.
2. Determine the rate laws governing the kinetics of delignification and cellulose degradation by ozone, as a route to improved selectivity in ozone bleaching.
3. Establish effects of delignification with kraft pulping liquor, oxygen and ozone on cellulose characteristics (viscosity, carboxyl content, etc.), pulp refining behavior and papermaking properties, and compare with corresponding effects of delignification with chlorine and chlorine dioxide.
4. Evaluate novel chlorine-free bleaching agents.
5. Evaluate sulfite-anthraquinone-nonchlorine routes to high- brightness, kraftlike pulps.

B. Environmentally Compatible Bleaching with Chlorine Compounds

1. Develop techniques for characterizing the AOX in (DC)E_O and DE_O partial bleach sequences and use them to determine bleaching conditions that minimize the potential for environmental effects (Ph.D. Thesis Research - T. Schwantes).

2. Compare toxicity of effluents from chlorine dioxide delignification with that of effluents from delignification with chlorine (Ph.D. Thesis Research - T. Ard).

SUMMARY:

Research has included investigations of both chlorine compound free and chlorine and chlorine dioxide based systems.

Ozone Bleaching Kinetics

Selectivity often limits the use of ozone for delignifying chemical pulps. Our approach to optimizing selectivity is to study the kinetics of the reactions of ozone with cellulose and lignin, both independently and in each other's presence, in a flow reactor. The rates of reaction of ozone with both cotton linters were studied in earlier work. Since the last report, emphasis has been on oxygen delignified kraft pulp. Activity has been limited, however, as a result of unusual administrative demands on the principal investigator's time. A new, special purpose ozone monitoring system has been installed to free up the general purpose spectrophotometer which had been used previously. This introduced a number of experimental difficulties which have now been largely resolved.

Ozone Bleaching Fundamentals

Investigations of fundamental aspects of ozone bleaching and interactions between oxygen delignification and subsequent ozone bleaching stages have been a joint activity of this project and Project F015. Results of this activity are described in the report for that project.

Rapid, Low-Impact ECF Delignification

Earlier, it was shown that, in an OD(EO) sequence, a one-minute D stage achieved 84% of the delignification of a 30-minute stage while generating only 42% of the AOX. Furthermore, the AOX generated is of a type that is more likely to be innocuous than the AOX produced under conventional conditions. This is because it occurs in compounds that are not as highly chlorinated, having a chlorine-to-carbon ratio that is, on the average, only one-half that found in conventional ECF effluents. Recent work in this area has sought to expand these conclusions to the entire bleach sequence and to examine the interaction between kappa factor and D stage reaction time. The impact on delignification of decreasing the reaction time has been shown to be smaller at lower kappa factors, allowing very rapid D stages to be employed with little or no penalty in low kappa factor bleaching. When a rapid D stage is employed the kappa factor can be reduced from 0.25 to 0.1 without significant brightness penalty by adding peroxide to the extraction stage. Effluent data from the more recent studies indicate a 30% reduction in AOX and a 20% reduction in chlorine-to-carbon ratio when the D-stage reaction time is decreased from 30 minutes to 1 minute at 0.1 kappa factor. At higher kappa factor, however, the advantage of decreasing the D stage reaction time was not as apparent as in our earlier studies. This has been attributed to the fact that the effluents from the present study were stored for approximately one month before being analyzed.

Characterization of Effluents from Chlorine Dioxide Delignification

Effluents from OC(EO), OD(EO) and D(EO) sequences were characterized with respect to their molecular weight distributions. The amount of low molecular weight chlorinated organic material formed during bleaching is of concern because this fraction may contain materials that adversely affect the environment. Complete substitution of ClO_2 for Cl_2 decreased the proportion of low (<960) molecular weight material in the bleaching effluents by 14-18%. Smaller effects result from changes in D stage initial pH and reaction time. Oxygen delignification prior to 100% ClO_2 slightly decreased the proportion of low molecular weight material in the (EO) stage effluent.

Polysulfide-Anthraquinone Pulping

Work was begun on a study of polysulfide-anthraquinone (PSAQ) pulping as a means of reducing the kappa number of unbleached pulp. Yield improvements reported by others have been reproduced in our laboratory and we have demonstrated the capability of producing polysulfide liquors in the laboratory that simulate liquors produced in a commercial white liquor oxidation reactor. Additional work in the form of a systematic study is needed to determine the effect of all the process variables on the extent of the yield improvement that can be expected.

OZONE BLEACHING KINETICS

The heart of the experimental system used for these experiments is a continuous stirred tank reactor operated in semibatch mode. In a typical run, ozone is predissolved in buffer solution (0.4M acetic acid/0.0072M sodium acetate, pH 3) and the solution then flows, at constant rate and concentration, to the reactor vessel. The ultraviolet absorbance at 260 nm of the effluent stream from the reactor vessel is continuously monitored. The resulting data are stored and converted to ozone concentration by a computer-based data acquisition system. After steady state is established, a sample of pulp is added to the reactor. The pulp sample is prevented from leaving the reactor by a fine mesh plastic screen at its outlet.

Upon addition of a pulp sample to the reactor, the ozone concentration in the reactor (as measured downstream of the outlet) undergoes a sudden drop due to consumption of ozone by the sample. Because the reactor is continuously fed with fresh ozone solution (at the same rate that liquid leaves the reactor), and because the sample has a limited capacity to react with ozone, the concentration passes through a minimum and begins to rise.

The mass balance around this type of semibatch reactor is

$$\frac{dc}{dt} = \frac{c_o - c}{\tau} + r$$

The data from the entire concentration time curve is analyzed by numerically differentiating the curve and solving the mass balance equation for *r* at all points on the curve. This gives many (rate, ozone concentration) data pairs that can be used to derive the rate law. Stoichiometric coefficients are needed to allow calculation of the concentration of remaining lignin from the available ozone consumption data. They will be obtained by conducting runs of varied duration and measuring both ozone consumption and kappa number decrease.

Unusual circumstances related to personnel changes have limited activity in this area in recent months. A new, special purpose ozone monitoring system has been installed to free up the general purpose spectrophotometer which had been used previously. This introduced a number of experimental difficulties which have now been largely resolved. Experiments in progress will yield stoichiometric coefficients and delignification rate laws.

RAPID, LOW-IMPACT ECF DELIGNIFICATION

Earlier, it was shown that, in an OD(EO) sequence, a one-minute D stage achieved 84% of the delignification of a 30-minute stage while generating only 42% of the AOX. Furthermore, the AOX generated is of a type that is more likely to be innocuous than the AOX produced under conventional conditions. This is because it occurs in compounds that are not as highly chlorinated, having a chlorine-to-carbon ratio that is, on the average, only one-half that found in conventional ECF effluents. Recent work in this area has sought to expand these conclusions to the entire bleach sequence and to examine the interaction between kappa factor and D stage reaction time. The objectives were (1) to demonstrate that fully bleached brightness could be achieved after a shortened ClO_2 delignification stage, (2) to evaluate the effect of shortening the ClO_2 delignification stage on the AOX generated downstream in the necessarily more vigorous ClO_2 brightening stage and (3) to determine whether the beneficial effects observed earlier persisted when the kappa factor is decreased. The last determination was needed because of the possibility that the observed effect was simply due to the decrease in reaction time limiting the amount of ClO_2 that can react with the pulp. If so, it would be indistinguishable from the effect of decreasing the kappa factor at longer retention time.

Figure 1 shows the effects on brightness development of decreasing the kappa factor at a D_0 retention time of one minute (controlled by quenching with Na_2SO_3). When the extraction stage was reinforced only with oxygen (4.8 kg/t, 70min, 70°C, 10% consistency), reducing the kappa factor from 0.25 to 0.15 decreased the brightness ceiling to a value below 82, making it impossible to reach our target of 85. Additional reinforcement of the extraction stage with hydrogen peroxide (8 kg/t, 60 psig oxygen for 10 min., total time 60 min., 24 kg/t NaOH, 80°C, 10% consistency) had little effect on brightness development when the kappa factor was 0.25, but markedly improved it at lower kappa factors. As a result, brightness development in the $OD_0(EOP)D_1$ sequence was only slightly affected by reducing the kappa factor from 0.25 to 0.10.

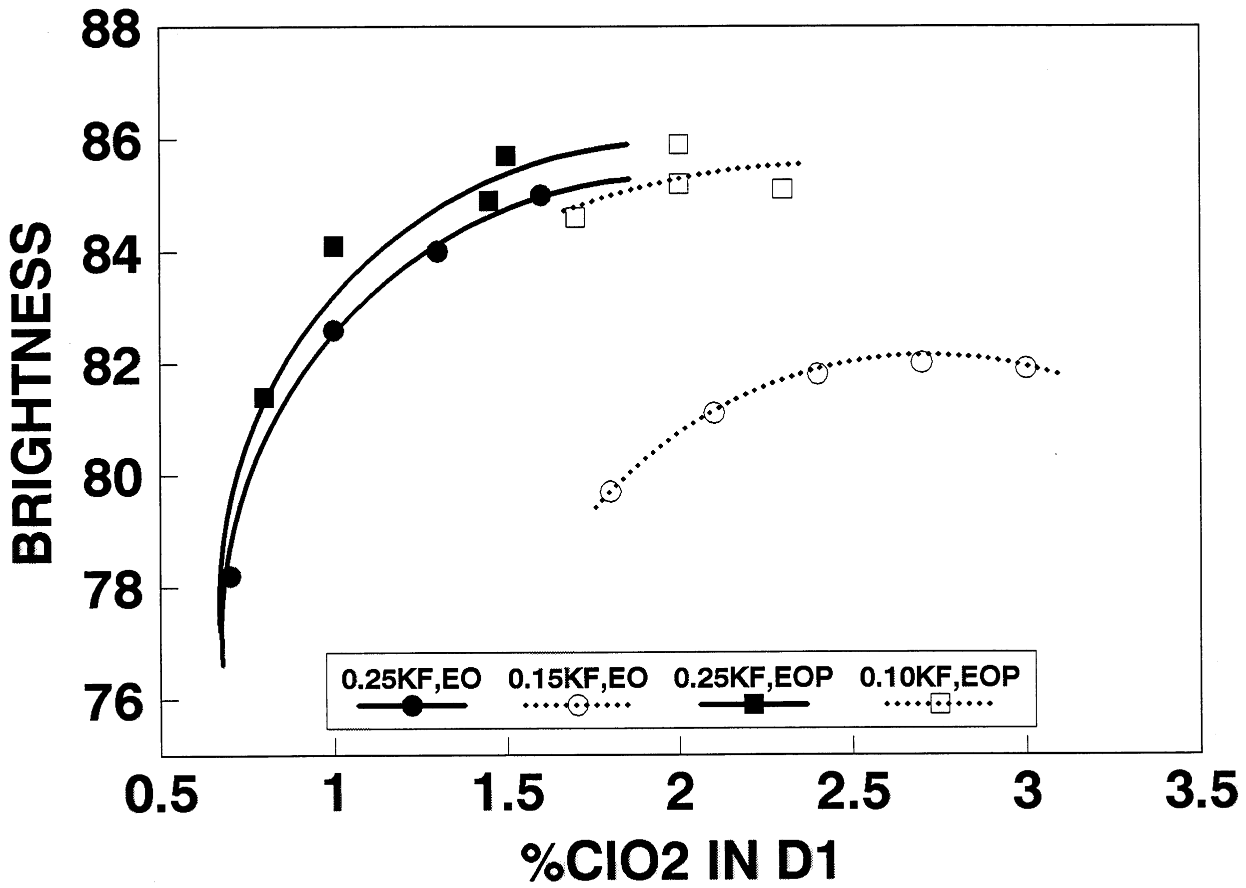

Fig. 1. Effects of kappa factor at a D_0 retention time of one minute.

The effects on brightness development of changes in D_0 retention time and kappa factor are compared in Figure 2. At 0.25 kappa factor, decreasing the D_0 retention from 30 min. to 1 min. decreases fully bleached brightness by about 3 points at the same D_1 charge. In contrast, the corresponding effect at 0.10 kappa factor is less than one point. It is also apparent from Figure 2 that, when the retention time is one minute, fully bleached brightness is almost independent of kappa factor over the range 0.10 to 0.25. It may be concluded that there is no need for a D_0 bleach tower in low kappa factor ECF bleaching!

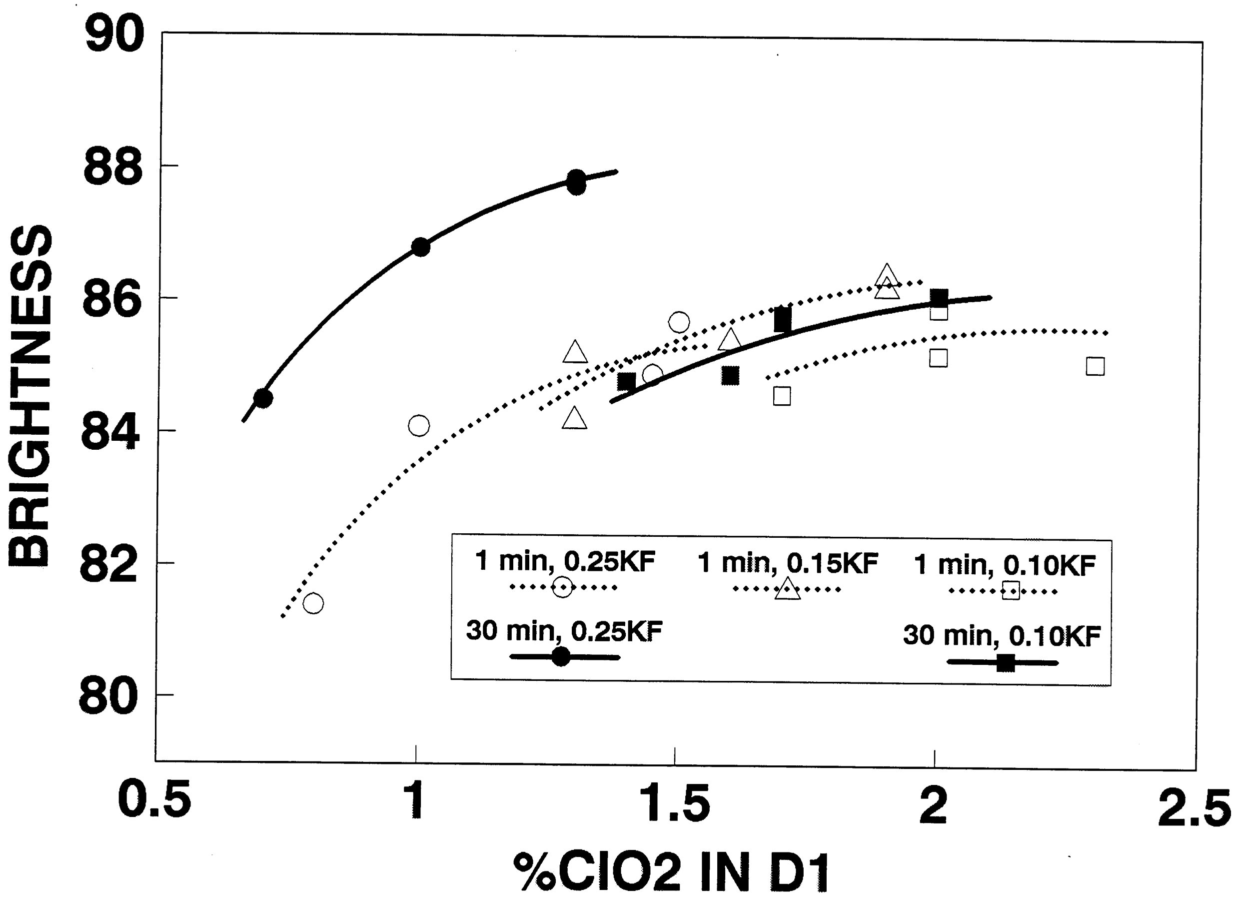

Fig. 2. Effects of kappa factor and D_O retention time.

Figure 3 shows the effects of the above variables on extracted kappa number. The greater effect of peroxide at low kappa factor is apparent from the convergence of the upper two curves at high kappa factor. The increase in extracted kappa number that accompanies a shortening of the D_0 stage at low kappa factor, however, is not reflected in a correspondingly large decrease in fully bleached brightness, as discussed above in reference to Fig. 2.

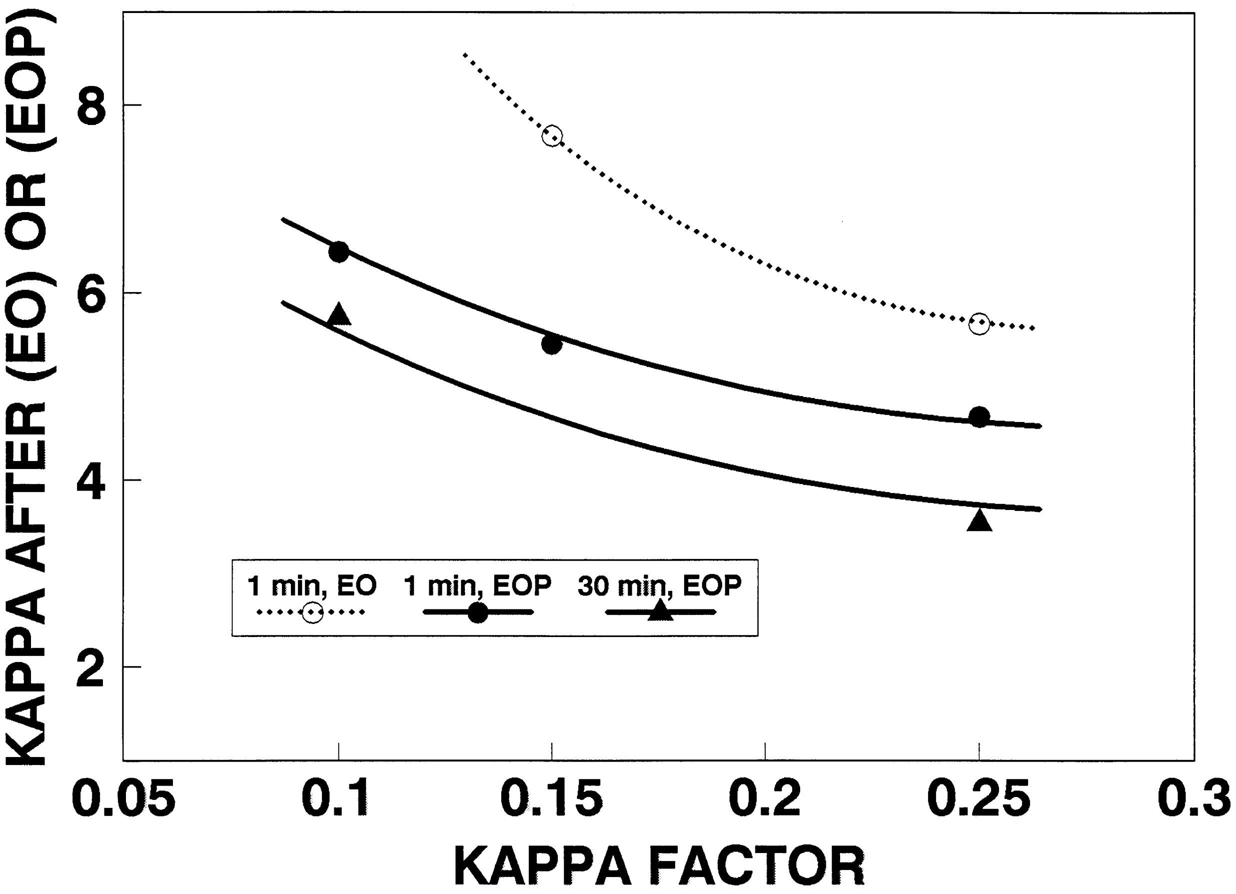

Fig. 3. Effects of kappa factor and retention time on extracted kappa numbers.

Characteristics of the effluents are contained in Table 1. It does not appear to be possible to interpret these data unambiguously, since the marked effect of retention time on AOX and chlorine-to-carbon ratio (CL/C_{100}) seen earlier is not present. We attribute this to the fact that the effluents were stored for more than one month before being analyzed, possibly providing an opportunity for occurrence of reactions leading to organic binding of chlorine. Nevertheless, a significant effect was observed at low kappa factor, where decreasing the D_0 retention time from 30 min. to 1 min. decreased AOX by 30% and CL/C_{100} by 20%.

Sequence		$OD_0(EO)D_1$	$OD_0(EO)D_1$	$OD_0(EOP)D_1$	$OD_0(EOP)D_1$	$OD_0(EOP)D_1$	$OD_0(EOP)D_1$	$OD_0(EOP)D_1$
D0 Time	min.	1	1	1	1	1	30	30
Kappa Factor		0.15	0.25	0.1	0.15	0.25	0.1	0.25
Extr. Kappa		7.67	5.68	6.43	5.46	4.68	5.74	3.54
ClO2 in D1	%	3	1.6	2	1.9	1.5	1.7	1.3
Brightness		81.9	85.1	85.9	86.2	85.7	85.7	87.8
Viscosity	mPa.s		17.4	11.9	12	12.7	12.3	11.8
AOX, kg/t	D0	0.153	0.161	0.135	0.159	0.337	0.23	0.309
	(EO) or (EOP)	0.039	0.037	0.038	0.045	0.062	0.039	0.076
	D1		0.032	0.081	0.075	0.059	0.077	0.064
	Total		0.23	0.254	0.279	0.458	0.346	0.449
TOC, kg/t	D0	5.21	2.32	5.56	5.66	6.2	6.54	9.16
	(EO) or (EOP)	6.44	8.99	10.19	11.75	11.23	10.51	13.54
	D1		2.52	2.91	2.68	2.42	2.98	2.35
	Total		13.83	18.66	20.09	19.85	20.03	25.05
Cl/C100	D0	0.99	2.35	0.82	0.95	1.84	1.19	1.14
	(EO) or (EOP)	0.20	0.14	0.13	0.13	0.19	0.13	0.19
	D1		0.43	0.94	0.95	0.82	0.87	0.92
	Total		0.56	0.46	0.47	0.78	0.58	0.61

Table 1. Experimental bleaching data and effluent characteristics.

CHARACTERIZATION OF EFFLUENTS FROM CHLORINE DIOXIDE DELIGNIFICATION

Effluents from OC(EO), OD(EO) and D(EO) sequences were characterized with respect to their molecular weight distributions. The amount of low molecular weight chlorinated organic material formed during bleaching is of concern because this fraction may contain materials that adversely affect the environment. Complete substitution of ClO_2 for Cl_2 decreased the proportion of low (<960) molecular weight material in the bleaching effluents by 14-18%. Smaller effects result from changes in D stage initial pH and reaction time. Oxygen delignification prior to 100% ClO_2 slightly decreased the proportion of low molecular weight material. A full report, in the form of a paper presented at the 1994 TAPPI Pulping Conference, is appended as Attachment 1.

GOALS FOR 1995-96:

A. Totally Chlorine-Free Bleaching

1. Identify residual lignin structural features likely to be of importance in defining bleachability. These are to be chosen from among a list that includes carboxyl groups, phonemic hydroxyl groups, alpha carbonyl groups and lignin-carbohydrate bonds.

2. Determine the rate laws governing the kinetics of cellulose and lignin degradation by ozone and use them to effect improvements in the selectivity of ozone bleaching.

3. Establish effects of delignification with kraft pulping liquor, oxygen and ozone on cellulose characteristics (viscosity, carboxyl content, etc.), pulp refining behavior and papermaking properties, and compare with corresponding effects of delignification with chlorine and chlorine dioxide.

4. Evaluate the toxicity's of chlorine dioxide and chlorine bleaching effluents in comparison with one another.

B. Environmentally Compatible Bleaching with Chlorine Compounds

1. Develop technology for environmentally acceptable chlorine dioxide based bleaching sequences by applying the information and methods developed to date in studies of D stage effluent characteristics and their dependence on bleaching conditions.

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

PROJECT F013

Subtask: Extended Delignification

ANNUAL RESEARCH REVIEW

March 22, 1995

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Extended Delignification

Polysulfide-Anthraquinone Pulping

Efforts at reducing the Kappa no. going to the bleach plant concentrated on the known process of combining polysulfide and anthraquinone with Kraft liquors. The synergistic effect of polysulfide and anthraquinone (PSAQ) for increasing Kraft pulping yields has been previously documented. PSAQ pulping has received increasing attention as a way to provide for extended delignification and acceptable yield retention with a low capital investment . Our interest in PSAQ pulping was initiated by private contract work. As an extension of that work, additional experiments were done as part of our dues-funded effort and these are reported here.

A series of pulping experiments were done in a laboratory digester with a single source of southern pine wood chips. The cooks included baseline Kraft, Kraft plus AQ, and Kraft-PSAQ. The total time and active alkali were held constant for all cooks. The H-factor was varied by changing the final pulping temperature within the range of 167-176°C. For the baseline Kraft and Kraft-AQ cooks, the active alkali was 18.8% and the sulfidity was 30%. The AQ addition was 0.1%. Polysulfide liquor was simulated to represent a liquor that can be produced from a commercial white liquor oxidation reactor. Since the conversion of a white liquor to a polysulfide liquor involves the oxidation of a portion of the sulfide to polysulfide, the measured white liquor sulfidity is necessarily reduced. The polysulfide liquors were made in the laboratory to result in 18.8% active alkali, 12% sulfidity, and 1.22% polysulfide. For each cook, the Kappa no., viscosity, total yield and screened yield were determined. The effect of the independent variables on the dependent variables, yield and Kappa no., were determined by separate multiple regressions. The two regressions for yield and Kappa no. were combined to produce the yield-Kappa no. relationship shown in Figure 1.

The regression curves plotted in Figure 1 show that at a Kappa no. of 30, the addition of 0.1% AQ results in a yield increase of approximately 0.5%. The addition of 1.22% polysulfide plus AQ results in a yield increase over the base case of almost 1.5%. If the objective is to lower the Kappa no. without a yield loss penalty, then PSAQ pulping at these conditions would permit a reduction in the Kappa no. from 30 to 21-22.

With the work done to date, we have demonstrated the capability of producing polysulfide liquors in the laboratory that simulate liquors produced in a commercial white liquor oxidation reactor. The yield improvements seen for both AQ and PSAQ have also been reported by others. Additional work in the form of a systematic study is needed to determine the effect of all the process variables on the extent of the yield improvement that can be expected.

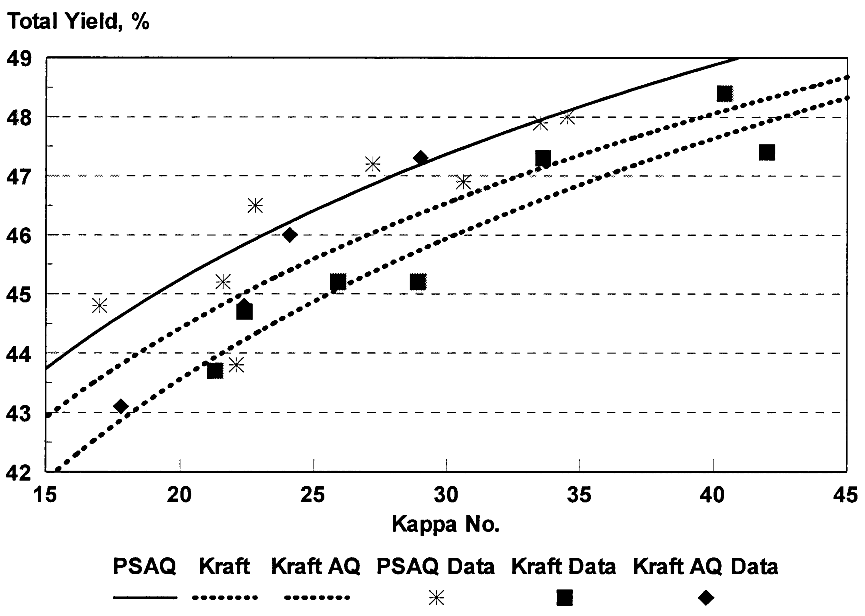

Figure 1. Total Yield vs. Kappa no.

Student Research

Measurement of Delignification Diversity Within Kraft Pulping

Brian S. Boyer
Advisor: Dr. Alan Rudie

This project is attempting to measure the variation in lignin content on a fiber to fiber basis for Kraft pulps and determine if a lack of uniformity has a measurable impact on pulp strength. The initial effort has used the two solvent density gradient technique in an attempt to separate pulps by lignin content and to measure the variation in lignin content. Efforts are now underway to validate this technique with specially prepared, highly uniform pulps and with infrared spectroscopy on individual fibers. Future efforts will include preparing pulps with a high lignin variability from mixtures of uniformly delignified pulps. These will be used to evaluate the impact of lignin content uniformity on pulp strength.

Evaluation of the Physical Chemical Mechanisms by Which Residual Cooking Liquor Retards Kraft Delignification

Jeffrey A. Frazier
Advisor: Dr. Alan W. Rudie

This project will evaluate the significance of the following phenomena:

- Lignin fragment trapping as fiber swelling is reduced in the later stages of a Kraft cook.
- Chemical (lignin and carbohydrate models) adsorption on fibers.
- Chemical (lignin and carbohydrate models) effects on fiber swelling.
- The effect of residual alkalinity and lignin molecular weight on solubility.

Current work is attempting to determine the influence of lignin and carbohydrate models on fiber swelling and the fiber pore size distribution with changes in alkalinity.

Attachment #1
Molecular Weight Distributions of Effluents from Chlorine Dioxide Delignification

Todd A. Schwantes
Thomas J. McDonough

ATTACHMENT #1

MOLECULAR WEIGHT DISTRIBUTIONS OF EFFLUENTS FROM CHLORINE DIOXIDE DELIGNIFICATION

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ABSTRACT

The amount of low molecular weight chlorinated organic material formed during bleaching is a concern because this material has the potential to adversely affect the environment. To study the extent of the formation of low molecular weight material during elemental chlorine free (ECF) bleaching, a method of aqueous gel permeation chromatography (GPC) was developed for the determination of bleaching effluent molecular weight distributions. It employs Sephadex gels, aqueous LiCl eluents, and total organic carbon (TOC) detection.

Softwood kraft pulp was delignified with ClO_2, NaOH, and O_2 and the molecular weight distributions for both the D and (EO) stage effluents were determined. Complete substitution of ClO_2 for Cl_2 decreased the proportion of low (< 960) molecular weight material in the bleaching effluents by 14-18%. Smaller effects result from changes in D stage initial pH and reaction time. Oxygen delignification prior to 100% chlorine dioxide bleaching slightly decreased the proportion of low molecular weight material in the (EO) stage effluent.

INTRODUCTION

The molecular weight distribution of bleaching effluents is important from an environmental perspective, because high molecular weight material is not biologically active and may therefore be innocuous. High (> 1000) molecular weight effluent material has been shown to be either non-toxic (1) or less toxic (2) than the low molecular weight fraction, which contains the majority of the effluent's acute toxicity (3). However, low molecular weight material is more readily degraded in biological treatment systems than high molecular weight material (4, 5).

Molecular weight distributions of bleaching effluents have been determined by both ultrafiltration (6-11) and gel permeation chromatography (GPC) (1, 11, 12). The two methods give widely differing results, with GPC detecting more low molecular weight material than ultrafiltration (11). Both methods indicate considerably more high molecular weight material in E stage effluents than in C or D stage effluents (1, 6-9, 12). Several studies have determined the effect of bleaching variables, such as chlorine dioxide substitution (7, 13) or oxygen bleaching (8, 9, 14) on the molecular weight distributions of effluents. It is difficult to draw conclusions from these limited results however, due to the lack of reliability of ultrafiltration which has most often been used in such studies. Ultrafiltration may indicate more high molecular weight material than GPC because of the concentration dependent association that occurs in ultrafiltration (11). Such association can be controlled with GPC. However, GPC has not often been used to investigate the effects of bleaching process variables on the molecular weight distribution of effluents.

A method of aqueous GPC was developed in this laboratory, as described elsewhere (12). The method employs Sephadex gels, aqueous LiCl eluent, and total organic carbon (TOC) detection. This method has several advantages over other GPC methods, including greater resolution, control of association, and a universal detection system. TOC detection is more appropriate than ultraviolet (UV) detection for GPC of bleaching effluents, since effluents may contain carbohydrates and other materials, not detected by UV.

In the present investigation, this method was used to determine the molecular weight distributions of bleaching effluents produced in the laboratory under well controlled bleaching conditions. The effects of 100% ClO_2 substitution, oxygen bleaching, D stage initial pH, and D stage reaction time were studied.

EXPERIMENTAL APPROACH

Distributions of D and (EO) stage effluents were determined individually. Gel permeation was done using 2 Sephadex columns in series. The first contained G-50 gel and the second contained G-15 gel. The 2-column system was used to achieve improved low molecular weight separation (12). Polyethylene glycol standards of known molecular weight were used to calibrate the system, and all distributions were transformed to a relative retention volume scale based on high and low molecular weight standards

(12). Relative retention volume is calculated as follows:

$$\text{Relative Retention Volume} = R_s - R_h / R_l - R_h$$

where

R_s = retention volume of sample.
R_l = retention volume of low molecular weight standard.
R_h = retention volume of high molecular weight standard.

TOC Detection

The eluent passes from the columns through a 1 ml flow cell, from which TOC samples are drawn. At each sampling interval, the instrument draws 5 250 µl samples and injects them to the waste stream. This essentially empties the flow cell, and allows it to fill with fresh column eluent containing a new sample. Immediately after the injections to waste, the sample for TOC determination is drawn and analyzed. This process is automatically repeated as often as the TOC instrument can achieve a baseline after TOC measurement (usually every 3-4 minutes). The eluent flow rate was 0.6 ml/minute and total column volume was 200 ml or less. Therefore, a typical experiment lasted 300 minutes or more and consisted of more than 85 individual TOC determinations.

Molecular Weight Distributions

The GPC chromatograms, as originally collected, consist of pairs of time and TOC data. The data were transformed to the relative retention volume scale, the baseline corrected to zero TOC, the chromatograms integrated to determine eluted TOC, the curves normalized to 1000 µg TOC, and the area between the mean elution values of the standards determined.

This information was used to construct cumulative molecular weight distributions. Such distributions provide an approximate numerical measure of the percentage of effluent TOC below a given molecular weight level. All standards exhibit retention volumes with approximately normal distributions and the center of the distribution was used in determining the cumulative distributions of the effluents. Therefore it is not strictly correct to state that these curves indicate the percentage of material with a molecular weight less than the corresponding molecular weight, since material of a particular molecular weight actually elutes both before and after the mean retention volume of the standard. However, these cumulative distribution curves remain valuable for comparing effluent distributions. They allow quantitative analysis rather than the purely qualitative analysis usually done with this type of data.

Statistical Analysis

Quantitative results allow statistical analysis and determination of significant differences between effluents. A total of 32 samples were analyzed. The D and (EO) stage effluents were produced under 8 different sets of bleaching conditions. Each bleaching sequence was performed twice. In one case, a replicate effluent sample was not available. In this case, the identical sample was run twice. The variation was not distinguishable from that attained with the replicate effluent samples and therefore this replicate chromatogram of the identical sample was used in the analysis. A 2-way analysis of variance was performed on the percentage of material with a molecular weight of less than 960 for each set of bleaching conditions and for both stages. Duncan's multiple range test (15) was used to determine which differences were statistically significant.

RESULTS AND DISCUSSION

The reproducibility of both the bleaching experiments and GPC runs was very good as illustrated in Figure 1. This shows the normalized D and (EO) stage effluent distributions for the OD(EO) bleaching sequence. The D stage distributions represent the 2 replicate chromatograms for the identical effluent, while the (EO) stage distributions represent a single GPC chromatogram for each of 2 replicate effluents.

The relative retention volume scale, which serves as the x-axis for the chromatograms, was determined using high and low molecular weight standards. The relative retention volumes for all molecular weight standards are given in Table I, and the corresponding calibration curve is shown in Figure 2.

The cumulative molecular weight distribution curves given here are based on the mean results of the 2 replicates per set of bleaching conditions. Figure 3 shows replicate cumulative D stage molecular weight distribution data for 5 minute and 3 second D stage reaction times. This figure makes clear how reproducible the cumulative data are, particularly at molecular weight levels of greater than 300. The figure shows that small significant differences can be detected, due to precise data.

The cumulative molecular weight distributions were interpreted principally in terms of the proportion of material with a molecular weight of less than 960, since this is the environmentally significant portion of the effluent. Throughout this paper, the material with a molecular weight of less than 960 will be referred to as "low" molecular weight material.

The Effect of 100% ClO_2 and O_2 Bleaching

Effluents from OC(EO), OD(EO), and D(EO) bleaching of softwood kraft pulps were previously generated (16). The cumulative molecular weight distributions for D or C, and for (EO) stage bleaching effluents from these partial sequences are shown in Figures 4 and 5.

For all 3 sequences, the D or C stage effluents contained a significantly greater proportion of low molecular weight material than the (EO) stage effluents. For example, within the OC(EO) sequence, about 94% of the C stage material was low molecular weight, while only 85% of the (EO) stage material was low molecular weight.

Use of chlorine dioxide to completely replace chlorine decreased the proportion of low molecular weight material in the effluents from both stages. Use of 100% chlorine resulted in about 94% low molecular weight material in the D or C stage compared to about 81% when chlorine dioxide was used. Similarly within the (EO) stage, use of 100% chlorine dioxide decreased the proportion of low molecular weight material from about 85% to 70%. On the basis of these molecular weight distributions, it may be concluded that the environmental benefits of ClO_2 delignification include formation of a decreased proportion of low molecular weight material.

The effect of oxygen bleaching on the effluent molecular weight distribution was not nearly as large but was nevertheless statistically significant. Oxygen delignification preceding 100% chlorine dioxide bleaching increased the proportion of low molecular weight material in the (EO) stage effluent (70 vs. 67%). Although a greater proportion of low molecular weight material was formed in the OD(EO) sequence, on an absolute basis the D(EO) sequence produced more low molecular weight material since about half of the lignin was removed during oxygen bleaching.

The Effect of D Stage pH

Cumulative molecular weight distributions for effluents from the OD(EO) bleaching sequence utilizing 2 initial D stage pH levels (17), are presented in Figures 6 and 7. As previously observed for different bleaching sequences, the D stage effluents contained an increased proportion of low molecular weight material than the (EO) stage effluents.

In the case of the D stage effluents, the D stage begun at pH 2 resulted in 81% low molecular weight material, while the D stage begun at pH 4 resulted in 78% low molecular weight material. However, in the (EO) stage effluents the trend was reversed, with the D stage begun at pH 2 resulting in 70% low molecular weight material and the D stage begun at pH 4 resulting in 74% low molecular weight material. Overall, changing the D stage initial pH over the range of 2 to 4 had little effect on effluent molecular weight distribution.

The Effect of D Stage Reaction Time

Using a specially designed D stage bleaching reactor, effluents were produced by using the OD(EO) bleaching sequence, with D stage reaction times of between 3 seconds and 30 minutes (18). The cumulative molecular weight distributions for the effluents are presented in Figures 8 and 9. Like D stage pH level, D stage reaction time has little effect. Again, the D stage effluents consist of a greater proportion of low molecular weight material than the (EO) stage effluents.

In the case of the D stage effluents (Figure 8), 30 minute and 3 second D stage bleaching times resulted in a significantly greater proportion of low molecular weight material than D stage bleaching times of 5 minutes and 1 minute. The 30 minute and 3 second D stages resulted in about 80% low molecular weight material. The 5 minute and 1 minute D stages resulted in about 75% low molecular weight material. It is reasonable to suppose that in the first 3 seconds of bleaching the most accessible lignin end units are preferentially affected, resulting in an increased proportion of low molecular weight material. Subsequently, higher molecular weight material is removed, while the removed material is simultaneously degraded in solution.

In the case of the (EO) stage effluents (Figure 9), no simple time trend is observed. Although a 30 minute D stage significantly increased the level of low molecular weight material compared to 5 minutes or 3 seconds, it was not significantly different from the proportion of low molecular weight material produced in the 1 minute D stage. The absence of a time trend suggests that the process of making lignin alkali soluble occurs within the first 3 seconds of the D stage. This is consistent with work (18) that showed that the entire amount of TOC that could be released during caustic extraction, was released after only a 3 second D stage.

Recovery of Effluent TOC

An advantage of GPC with TOC detection is that it allows a determination of effluent recovery from the columns, by comparison of the integrated chromatogram TOC level with the actual measured TOC of the effluent. Any additional TOC due to column degradation or loss of TOC due to adsorption are apparent using TOC detection but would be unnoticed with other types of detection. Table II presents the average recovery for each bleaching sequence and for each stage. TOC losses were generally less than 25%.

EXPERIMENTAL METHODS

Sample Preparation

Effluent samples were stored in the dark, under highly acidic conditions (< pH 2), and at 4°C. Prior to storage, samples were sparged under acidic conditions to remove carbonates. LiCl was added to the samples to adjust its concentration to 0.1 M and the pH was adjusted to 5.0-5.5 prior to chromatography.

Gel Preparation and Column Packing

Sephadex G-type gels, made of crosslinked dextran, were used for GPC work. The gels were purchased in a powdered state and were swelled in 0.1 M LiCl before column packing. Pharmacia HR 16/50 columns were used for GPC work, and a HR 16 column packing reservoir used during the packing process. Each column was packed individually. The swelled gel was added to the column and the packing reservoir and the gel was packed into the column using flow rates and pressures in excess of those used during chromatography experiments. At least 2 column volumes of eluent (200 ml) was passed through the columns under these conditions to stabilize the gel bed. Once the bed was stable, the column top adapter was attached, and the columns used for chromatography.

Gel Permeation Chromatography

Chromatography was done using a Sephadex G-50 column followed by a G-15 column. Eluent flow was maintained through the chromatography system with an Alltech Model 300 LC pump and an attached pulse dampener. Total organic carbon (TOC) detection was done using a Shimadzu Model TOC-5050 total organic carbon analyzer.

SUMMARY AND CONCLUSIONS

Gel permeation chromatography, utilizing aqueous LiCl eluent, Sephadex G-type gels, and TOC detection was used to determine the molecular weight distributions of a series of laboratory produced effluents.

Use of 100% chlorine dioxide rather than 100% chlorine to bleach oxygen delignified pulp, decreased the proportion of low molecular weight material in the bleaching effluents by 14-18%. The decreased proportion of low molecular weight material formed by ClO_2 is significant from an environmental viewpoint, particularly since this material is also much less chlorinated.

Oxygen delignification before 100% ClO_2 bleaching had a significant effect on the proportion of low molecular weight material formed only in the case of the (EO) stage effluent. However, the effect was much smaller, with only about 3% more low molecular weight material formed when oxygen bleaching preceded chlorine dioxide. Although the OD(EO) sequence resulted in a larger proportion of (EO) stage low molecular weight material, on an absolute basis it still produced about half the low molecular weight material as the D(EO) sequence because oxygen bleaching achieved about 50% delignification prior to the D stage.

D stage initial pH had only a small effect on the proportion of low molecular weight material formed. An initial D stage pH of 2 increased the proportion of low molecular weight D stage material, but decreased the proportion of low molecular weight (EO) stage material, compared to a D stage begun at pH 4.

The D stage reaction time also had only a small effect on the proportion of low molecular weight material. Within the D stage, low molecular weight material was removed at short reaction times, followed by the removal of higher molecular weight material. At longer times, the material was possibly degraded, resulting again in a greater proportion of low molecular weight material. On the other hand, the (EO) stage effluent distribution was independent of D stage reaction time.

ACKNOWLEDGMENTS

The authors thank Dr. Earl Malcolm and Dr. Lucy Sonnenberg for technical advice and guidance, and the Institute of Paper Science and Technology and its member companies for supporting this research. Thanks also to Clark Woitkovich for considerable assistance in data transformation. This work will be used by T. S. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.

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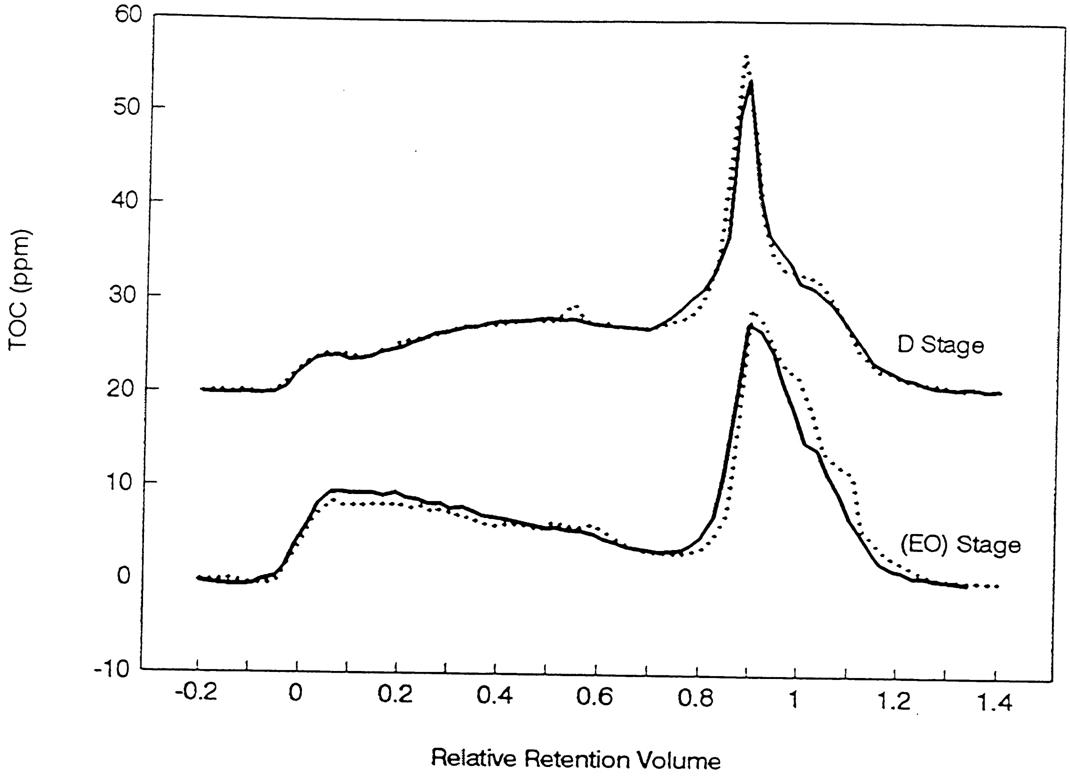

Figure 1. Reproducibility of Chromatograms.

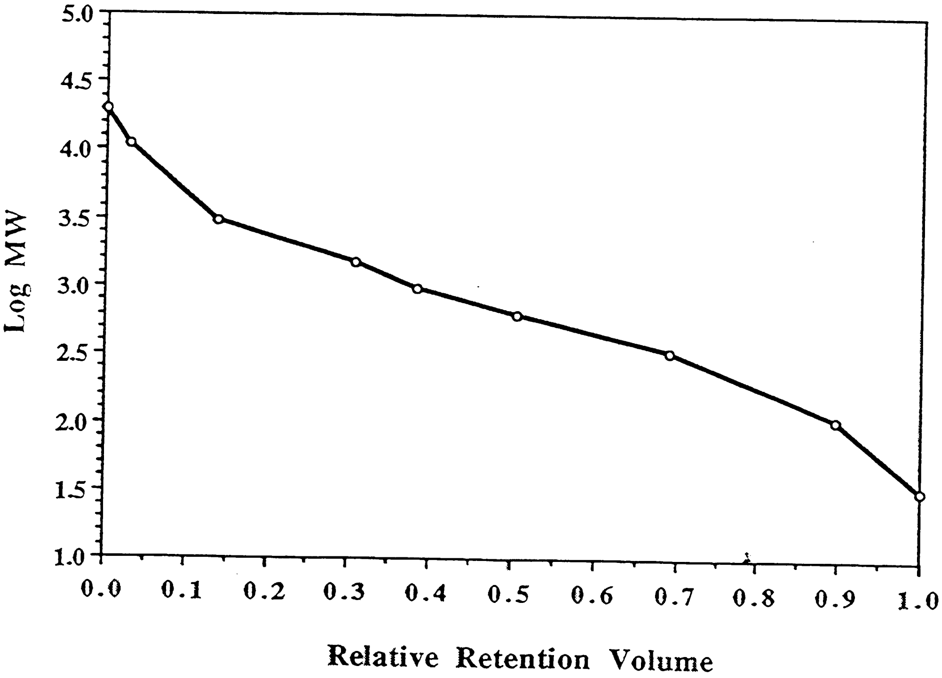

Figure 2. GPC Calibration Curve.

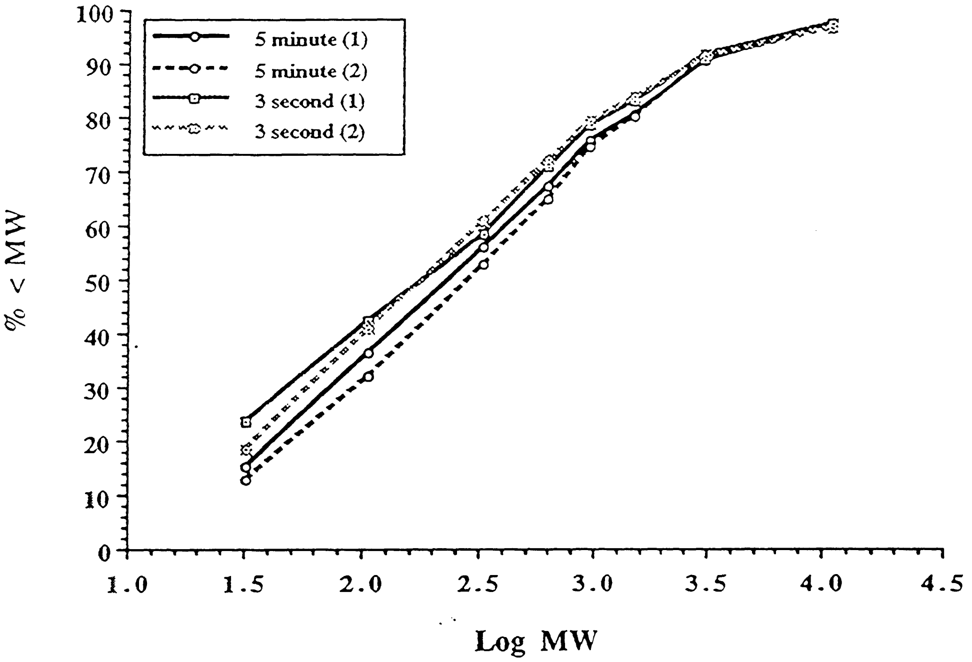

Figure 3. Reproducibility of D Stage Cumulative Molecular Weight Distributions.

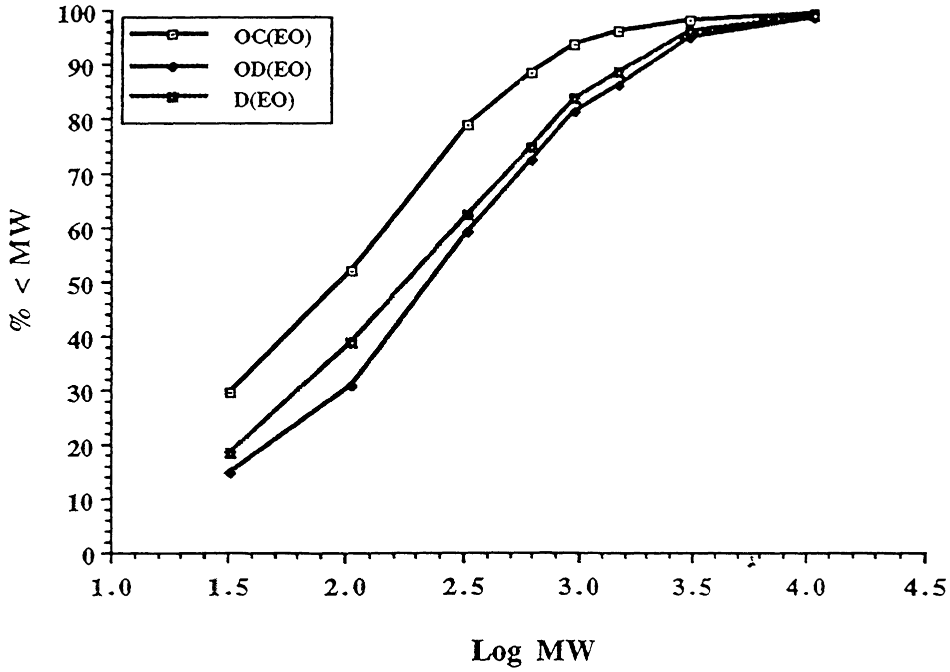

Figure 4. D or C Stage Effluent Cumulative Molecular Weight Distributions.

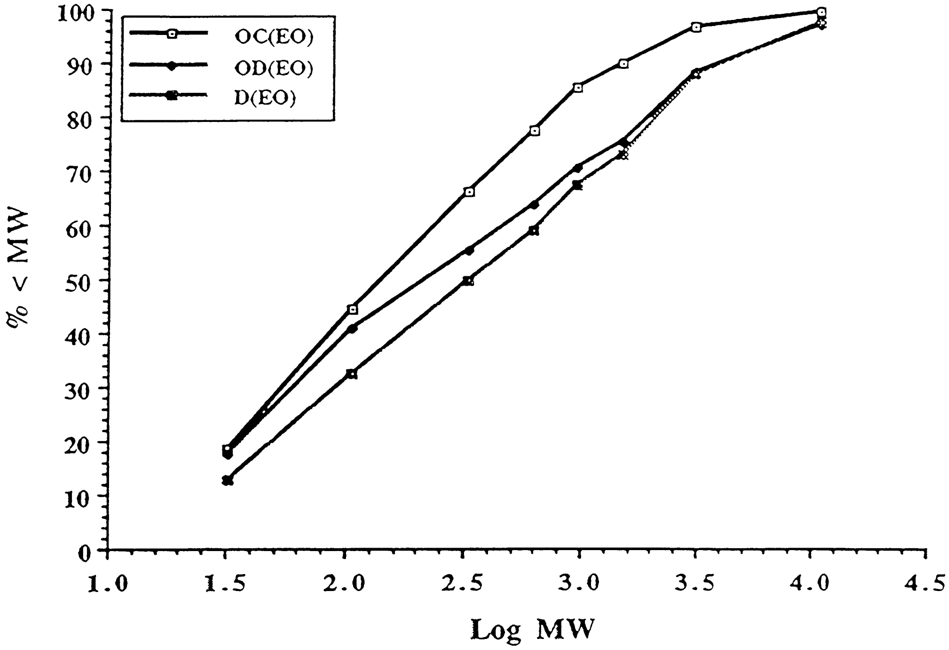

Figure 5. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

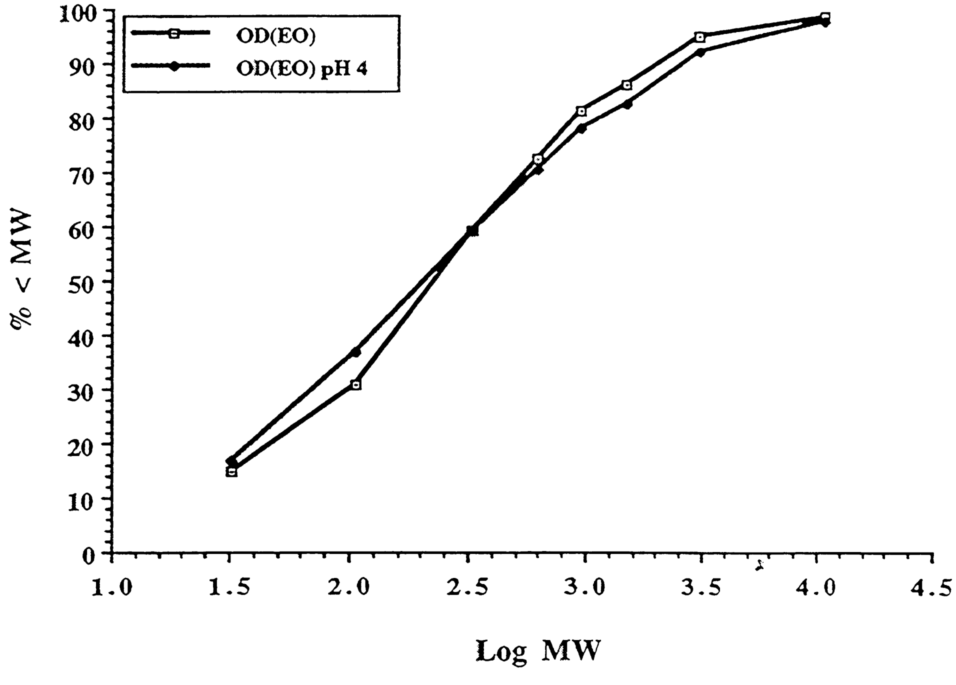

Figure 6. D Stage Effluent Cumulative Molecular Weight Distributions.

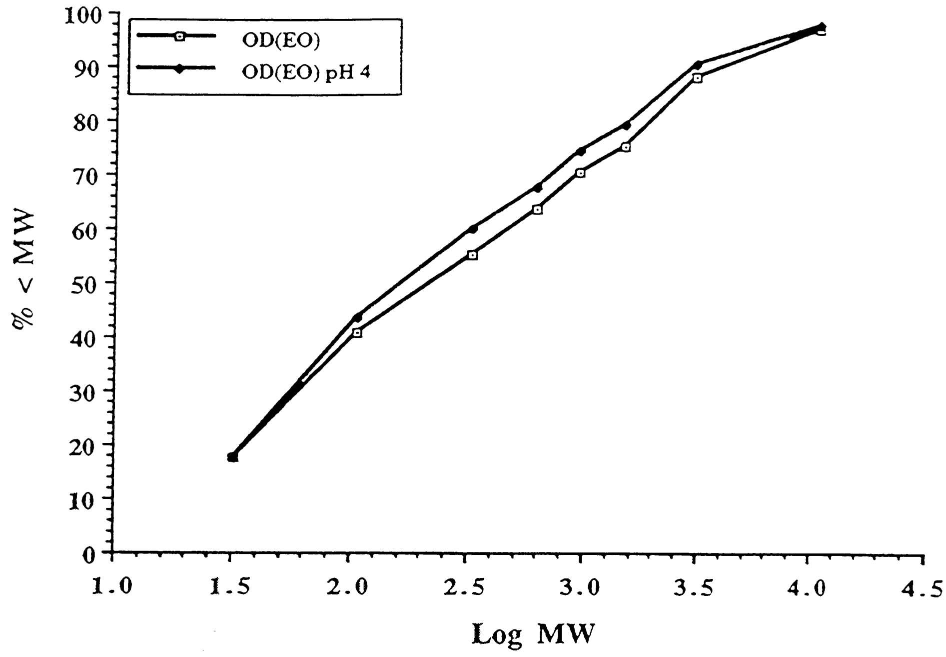

Figure 7. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

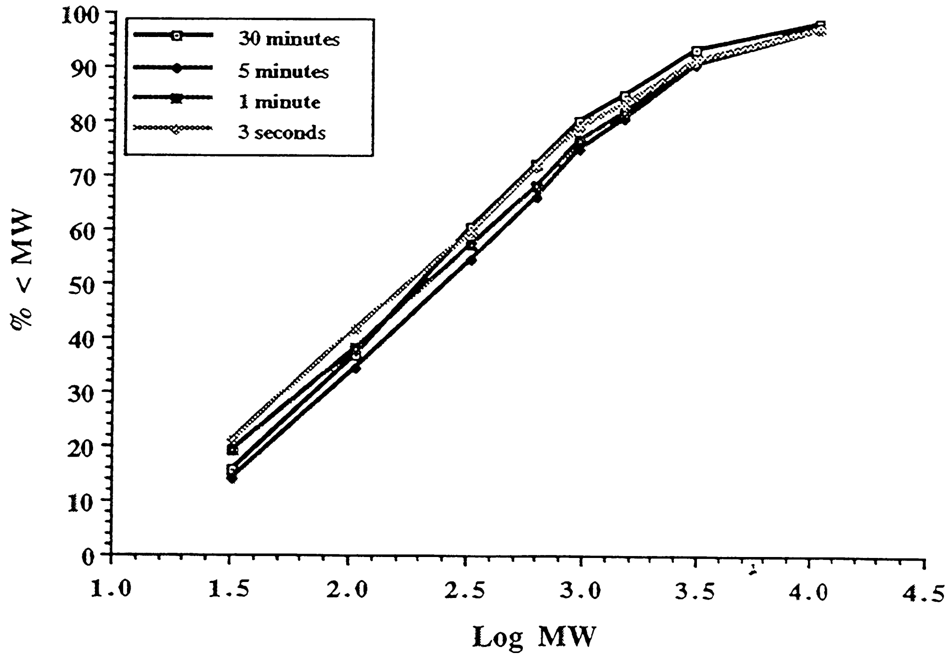

Figure 8. D Stage Effluent Cumulative Molecular Weight Distributions.

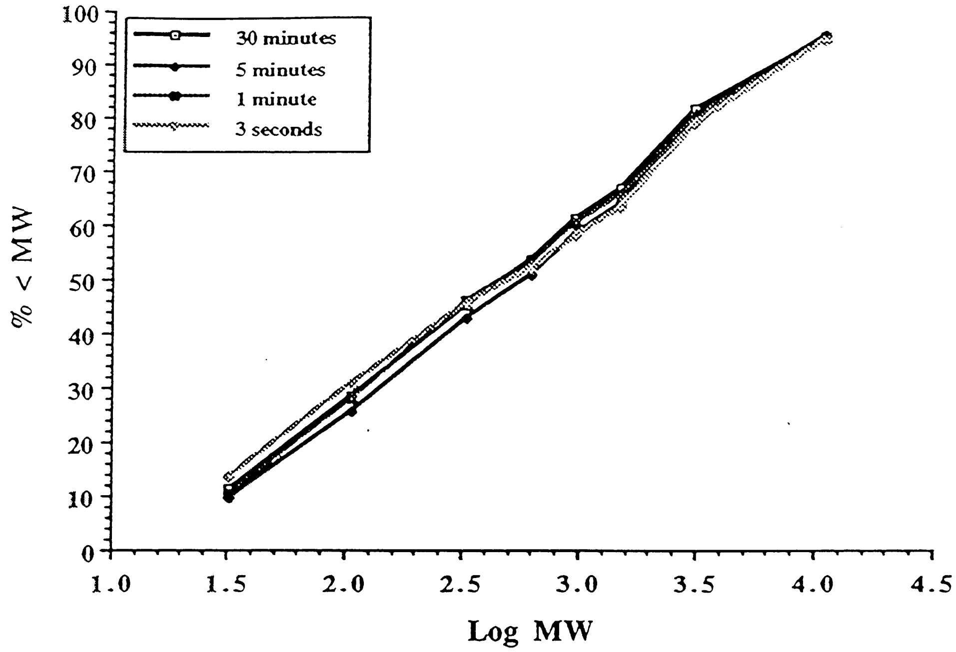

Figure 9. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

Table I. Relative Retention Volume of PEG Standards and Methanol.

Molecular Weight	Relative Retention Volume
19,700	0.000
10,900	0.028
3,070	0.138
1,490	0.308
960	0.383
629	0.506
331	0.691
106	0.897
32	1.000

Table II. Recovery of Effluent TOC.

Bleaching Sequence	D or C Stage Recovery (%)	(EO) Stage Recovery (%)
OC(EO)	75.6	75.7
OD(EO)	85.2	71.7
D(EO)	81.9	76.1
OD(EO)-pH 4 D Stage	78.0	70.3
OD(EO)-30 min D Stage	96.8	77.1
OD(EO)-5 min D Stage	111.8	76.3
OD(EO)-1 min D Stage	98.1	76.6
OD(EO)-3 sec D Stage	104.8	79.0

FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT F015

ANNUAL RESEARCH REVIEW

March 22, 1995

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TECHNICAL PROGRAM REVIEW

1Project Title:	FUNDAMENTALS OF BLEACHING CHEMISTRY
Project Code:	CHEMBL
Project Number:	F015
Division:	Chemical and Biological Sciences
Project Staff:	D.R. Dimmel, A.J. Ragauskas, L.B. Sonnenberg
FY 1995 Budget:	$217,000

Program Objective:

Provide a fundamental understanding of the physical and chemical reactions that control lignin removal and residual lignin structure. Understand the reasons for selectivity of reactions that occur in selected pulping and bleaching sequences. Work in concert with Project F 013 on bleach process technology.

IPST Goal: Improved bleaching processes.

Summary of Results Since Last Report:

Previous Results:

Introduction

Bleaching kraft pulps is undergoing profound technical changes as environmental and market forces have combined to substantially alter process. EPA's recently proposed "cluster rules" could substantially impact most chlorine/chlorine dioxide-based bleaching processes. Our research studies have been directed towards developing new technologies that could be utilized either for the development of low AOX bleaching protocols or towards the application new TCF bleaching technologies.

Biobleaching:

Previous research studies have demonstrated the application of xylanase as a pretreatment prior to ozone bleaching protocols. We have demonstrated that for conventional kraft pulps the application of xylanase prior to ozone bleaching provide clear benefits in terms of improved delignification, brightness and viscosity gains. For oxygen delignified, modified kraft pulps xylanase pretreatment followed either by Z(EO)D or Z(EO)P was shown to lead to higher brightness ceilings for the fully bleached pulp.

Activated Peroxide:

Research efforts have also been directed towards the development of new methods of activating the bleaching capabilities of hydrogen peroxide. Past research studies have demonstrated that the use of acetone and other keto-compounds could lead to substantial improvements in the bleaching properties of peroxymonosulfate. Employing acetone as a catalyst it was demonstrated that peroxymonosulfate could be catalytically converted into dimethyldioxirane and this reagent exhibited a very high oxidative selectivity towards lignin. The results of these studies suggested that dimethyldioxirane's bleaching properties were comparable to those of chlorine or ozone. Unfortunately, the implementation of this technology into existing mill processes was shown to be complicated by the need for specialized equipment and complicated chemical recovery technologies. Nonetheless, these studies validated the general concept that the activation of hydrogen peroxide can lead to new and improved bleaching agents. The technical challenge that now exists is to find new means of activating peroxide that can be readily installed into today's mill operations.

Ozone Fundamentals

Previous ozone bleaching studies examined the byproducts formed from pulp ozonation and focused on the role of secondary reactions during bleaching. There was some evidence that the soluble constituents in ozone filtrates exert an ozone demand and are further fragmented; however, the relative importance in ozone consumption is likely to be minimal. The primary low molecular weight byproducts were identified as small fatty acids, short-chain and long-chain aliphatic acids and diacids.

The effect of oxygen bleaching on the selectivity and efficiency of ozone bleaching was recently examined. A softwood kraft pulp was oxygen bleached to 30% and 50% delignification in the laboratory. The three high consistency pulps were ozonated at several ozone charges. Pulp properties, functional groups, and filtrate characteristics were measured.

The moderately oxygen delignified pulp exhibited superior selectivity during ozonation than the kraft pulp or the 50% delignified pulp. The carbohydrates appeared to benefit from the protecting effect of the residual lignin, such that loss of viscosity was similar to that of the kraft pulp. At low ozone charges, delignification efficiency was greater for the oxygen bleached pulps than for the kraft pulp, possibly due to the higher content of carboxylic acid groups in the oxygen residual lignin.

Oxidized, labile portions of both carbohydrates and lignin in unozonated pulp are readily removed at low ozone charges and produce soluble, acidic fragments. Concurrently, phenolic rings are cleaved and carboxylic acid groups are introduced onto rhe residual lignin. As ozone charge is increased, the ring fragments become solubilized, producing less acidic lignin fragments.

Current Results:

Biobleaching

Softwood and hardwood kraft pulps were pretreated with xylanase followed by treatment with hydrogen peroxide, dimethyldioxirane, or hydrogen peroxide reinforced with nitrilamine. The resulting pulps were then further bleached with a DEDED sequence. Bleaching studies demonstrated that the activation of peroxide was an effective method of reducing the total applied charge of chlorine dioxide while still achieving 90+ ISO brightness values. These bleaching studies also demonstrated that softwood kraft pulps responded linearly to the xylanase and peroxide treatments. In contrast, the hardwood pulps exhibited a cooperative interaction between the xylanase treatment and subsequent peroxide-based bleaching treatments. Under optimal conditions these studies suggested a 21% reduction in total applied chlorine dioxide (TAC) charges by pretreating kraft pulps with nitrilamine activated hydrogen peroxide.

Activated Peroxide

Research studies this past year have examined the use of nitrilamine to activate the delignification properties of hydrogen peroxide for kraft pulps. Bleaching studies demonstrated that low charges of nitrilamine could substantially improve the overall bleaching properties of hydrogen peroxide. Improved delignification and brightness were noted for southern softwood kraft pulps when treated with activated peroxide. The effects of temperature, charge, chelation, and time were investigated. Furthermore, the application of alternative activators was also explored. Subsequent chlorine dioxide bleaching sequence studies demonstrated that the use of activated peroxide as a first stage bleaching agent provide a means of achieving higher brightness values.

Ozone Fundamentals

Properties of oxygen delignified, ozone bleached pulps. It is important to relate the chemistry of ozone bleaching to paper properties. The zero-span tensile strength was measured for the unbeaten pulps described in the previous section to estimate the effects of oxygen and ozone on structural features that affect strength. There was little apparent relationship between strength and the drop in viscosity due to ozonation, possibly due to alkaline depolymerizatino of unstabilized ozonated pulps with the conventional viscosity test. Oxygen reduced strength more than ozone bleaching when ozone bleaching is carried out at low charges (<0.5%). Further work is needed in this area to ascertain the true effect of low oxygen and low ozone charges on strength.

Dissolved byproducts of oxygen and ozone bleaching. In order to fully understand the fundamental reactions taking place during delignification and carbohydrate degradation, it is important to characterize the dissolved products of bleaching as well as to characterize the bleached pulp. We compared the molecular weight distribution (MWD) of the dissolved byproducts from oxygen (55% delignification) and ozone bleaching (0.4% charge) of brownstock. Compared to the oxygen byproducts, the ozone byproducts had a more uniform distribution across the molecular weight ranges. Oxygen may depolymerize more effectively than ozone without introducing the same quantity of hydrophilic functional groups that ozone produces. The result is that smaller products are preferentially dissolved in the oxygen filtrate while the more oxidized components of all sizes are dissolved in the ozone filtrates.

Comparisons of ozone filtrates of oxygen delignified pulps showed that oxygen tranforms the residual lignin so that the depolymerized (but still insoluble) residual lignin readily dissolves upon exposure to an effective oxidant such as ozone. Oxygen delignification probably promotes ozone efficiency by producing residual lignin that is smaller in size and enriched in carboxylic acid groups compared to brownstock residual lignin.

Fundamentals of improved bleachability of oxygen bleached pulps. The Wood Chemistry and the Pulping and Bleaching Groups have initiated a series of experiments to further examine the bleachability of oxygen delignified pulps. The goal of these studies is to find optimal conditions for efficient and selective bleaching using our knowledge of fundamental reactions that occur during various processes. The general approach is to oxygen delignify three different brownstock pulps to a range of kappa numbers, and then to ozone bleach these pulps at 0.4% ozone charge. Both fundamental and applied aspects of the processes are being monitored by measuring functional groups, dissolved products, and pulp properties. The oxygen bleaching has been completed by the Pulping and Bleaching Group, and the ozone bleaching is in progress by the Wood Chemistry Group.

Tentative Goals For FY 1995 - 1996:

1. Ozone Fundamentals (Sonnenberg):

Completion of the extensive work in progress is a major goal for 1994-1995. When this series of studies is complete we will have generated a large database of information about the impact of different pulping and oxygen delignification processes on subsequent bleachability (also see item 4 below).

2. Physical Properties of "New" Pulps (Sonnenberg, Courchene):

Expand data base initiated under item 1. above to include physical properties of pulps produced by new pulping and bleaching sequences. This database will provide information about the chemistry of the processes coupled with data on pulp properties under controlled conditions. This approach will allow us to relate changes in chemical structures of pulp throughout pulping and bleaching processes to ultimate changes in bleached pulp properties.

3. Fundamentals of Selectivity (Dimmel):

Investigate selectivity factors in oxygen, ozone, and peroxide bleaching systems by using amorphones cellulose/lignin model combinations.

4. Biobleaching (Ragauskas):

Future biobleaching studies will examine the fundamental properties by which hemicellulases and oxo-reductase enzymes activate kraft pulps for subsequent chemical bleaching treatments. Research targets will include:

- Characterization of hemicellulase interactions with kraft pulps with a special emphasis on pore size determinations and nature of hemicellulase released during biobleaching stage.
- Explore use of laccase mediated reactions to actively delignify kraft pulps and examine delignification chemistry.

5. Activated Peroxide (Ragauskas):

Research studies will continue to examine the use of additives to improve the bleaching properties of hydrogen peroxide with a special emphasis on studying catalytic technologies. The interaction of activated peroxide stages with other bleaching agents, especially chlorine dioxide, will be examined. Research issues to be examined in this field include:

- The development of novel peroxide activators for kraft bleaching;
- Examine the interactions between activated peroxide and chlorine dioxide bleaching treatments to develop low AOX bleaching sequences;
- Determine the nature of residual lignin after activated peroxide bleaching stages.

FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT F015

Subtask: IMPROVEMENTS IN ECF BLEACHING: Use of Activated Oxygen Species and Xylanase

ANNUAL RESEARCH REVIEW

March 22, 1995

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Improvements in ECF Bleaching:
Use of Activated Oxygen Species and Xylanase

Changes in public policy *(1)* and new market demands *(2)* have increased the interest in developing low effluent AOX bleaching technologies for kraft pulps. In response to these demands, a variety of new pulping and bleaching technologies are being studied. Current solutions to these concerns include the use of extended pulping technologies,*(3)* oxygen deliginification, *(4)* and 100% chlorine dioxide substitution.*(5)* Xylanase pretreatments *(6)* and oxidative alkaline extraction stages *(7)* have also been shown to reduce the levels of AOX generated during the bleaching of kraft pulps. Alternatively the use of ozone as a replacement for chlorine-dioxide has also shown promising laboratory and mill experiences.*(8)*

Despite these significant advances in pulp bleaching technology, there remains a need to develop alternative bleaching protocols which could further reduce the levels of AOX generated from modern chlorine dioxide-based bleaching sequences. Our research interests have been directed towards developing new bleaching technologies which address these needs. Recently we reported that xylanase pretreatments were an effective method of improving the bleaching properties of several non-chlorine based bleaching agents including dimethyldioxirane *(9)* and ozone *(10)*. Xylanase pretreatment of hardwood kraft pulps was shown to enhance the delignification effects of DMD by 11% on kraft hardwoods and 2% on softwood kraft pulp. In this report we have examined the bleaching interactions between xylanase, activated peroxide, and chlorine dioxide for softwood and hardwood kraft pulps.

Experimental

Materials

Oxone^{TM} ($2KHSO_5.KHSO_4.K_2SO_4$), 30% hydrogen peroxide, nitrilamine, acetone, aqueous H_2SO_4, NaOH, and $NaHCO_3$ were all purchased from Aldrich and employed as received. Conventional kraft pulps were prepared in the laboratory from Eastern Canadian hardwood and softwood chips. The softwood kraft pulp had an unbleached kappa number 27.4 and viscosity 37.0 cP. The hardwood kraft pulp had an initial kappa number 18.0 and viscosity 49.5 cP.

A cellulase-free xylanase preparation, prepared by ICI Canada Inc., was employed for all enzymatic treatments. The microbial source for the enzyme was *Streptomyces lividans* [pIAF 20] for the DMD studies and Ecopulp X-200^R for the nitrilamine and hydrogen peroxide studies.

Xylanase and control treatments

Xylanase treatments (X-stage) were carried out on 300 grams (oven-dry weight) of pulp in a Mark II Quantum Mixer at 12% consistency and 50° C. After adjusting the pH of the pulp slurry to 6.0 - 7.0 with 1 N H_2SO_4 the enzyme was added (1 BXIU per gram oven dry pulp) and the mixture was stirred for 2 hour . Control experiments (W-stage) utilized the same experimental approach except that the enzyme was omitted.

DMD pretreatment (I-stage)

A 0.7% charge of DMD was added to the pulp at neutral pH as a 0.1 N DMD/acetone solution at room temperature and at 3.5% consistency. The mixture was stirred for one hour at room temperature before filtering and washing the pulp with water [Note: since the use of DMD for bleaching is currently experimental, all studies were performed following standard laboratory practices for handling peroxides (11)].

Nitrilamine activated peroxide treatment (Pnt-stage)

Pulp samples were placed in polyethylene bags and treated with a 0.9% charge of NaOH, 0.7% charge hydrogen peroxide, and 0.2% nitrilamine. The consistency of the pulp bleaching mixture was 10%. The sealed polyethylene bags were then placed in a 70° C water bath and kneaded every 15 minutes. After two hours the pulp samples were removed, filtered, and washed.

Hydrogen peroxide treatment

The P-stage was executed in the same manner as the Pnt-stage except that the nitrilamine was omitted.

Chlorine dioxide stages

Chlorine-free chlorine dioxide was prepared by calculating the amount of free chlorine in the solution and adding the stoichiometrically equivalent amount of sodium chlorite. All D stages were carried out in sealed glass Mason jars.

The experimental conditions for the 100% substitution stage (D_0) were as follows: consistency, 3.5%; temperature, 50° C; retention time, 30 minutes.
The kappa factors applied are listed below in Table 1.

D_1 charges of 1.2% were applied to pulp samples (20 g.,od weight) under the following conditions: 6% consistency; 70° C; 180 min retention time. D_2 charges of 0.2% were employed for the softwood kraft pulp samples and 0.4% charge for the hardwood kraft pulp samples. The experimental conditions were the same as the D_1 experimental conditions.

Table I. Kappa Factor Employed for Bleaching Softwood and Hardwood Kraft Pulps.

Pretreatment	Kappa Factor	
	Softwood	Hardwood
Control	0.18, 0.20, 0.23	0.16, 0.18, 0.20
Pnt, I, P	0.18, 0.20, 0.22	0.16, 0.18, 0.20
X	0.15, 0.18, 0.20	0.13, 0.16, 0.18, 0.20
XI, X(Pnt), XP	0.16, 0.18, 0.20	0.16, 0.18, 0.20

Caustic extractions:

Post DMD Stage: The E stage after each DMD treatment was accomplished employing a 1.5% charge of NaOH at 3.5% consistency for 3/4 hr at room temperature.

For DEDED: The E_1 and E_2 stages for the softwood kraft pulps employed 3% and 4% charges of NaOH, respectively. The caustic extractions were performed at 70° C, 60 min retention, and 10% consistency. For the hardwood kraft pulps E_1 and E_2 employed 2% and 0.5% charges of NaOH, respectively. The caustic extractions were performed for 60 min retention at 10% consistency. The E_1 stage was performed at 70° C and the E_2 stage was performed at 73° C.

Pulp properties

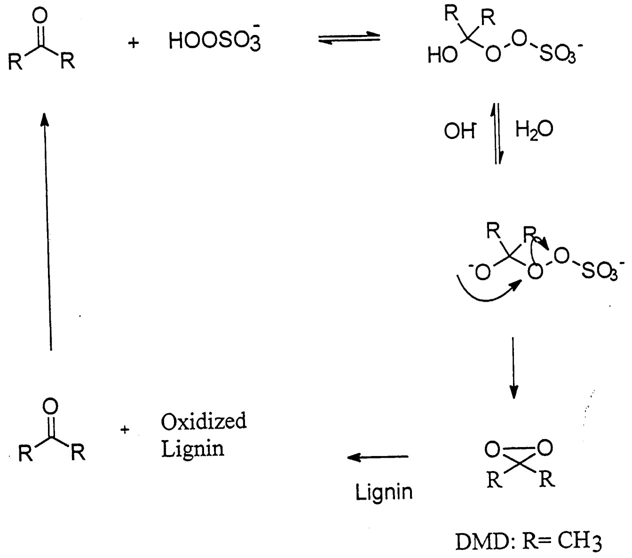
Brightness, Kappa #, and viscosity measurements of the pulp were determined using CPPA standard methods.

Results and discussion

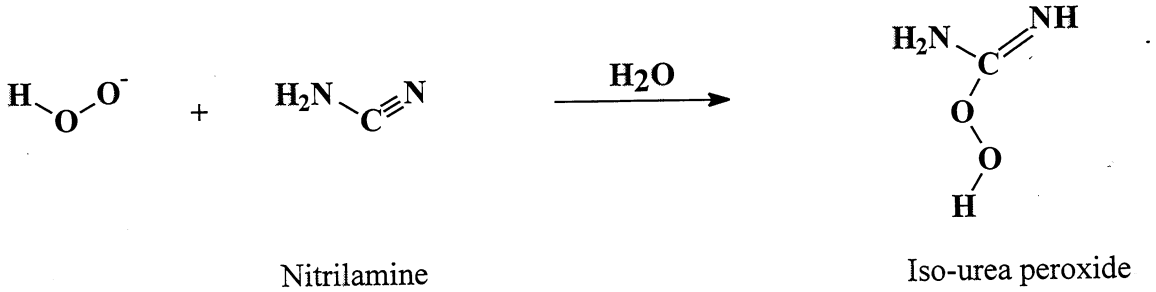
Xylanase/activated peroxide bleaching

Although the benefits of xylanase pretreatment for chlorine dioxide bleaching of kraft pulps are now well established, there application for oxygen-based bleaching protocols is still undergoing active investigation.*(10, 12)* Studies by Eriksson, (12) Joyce (13) and others (14) have clearly highlighted the potential benefits of xylanase pretreatments for ozone and hydrogen peroxide-based bleaching sequences. This report summarizes our preliminary studies directed at evaluating the interactions between xylanase and two forms of activated hydrogen peroxide, dimethyldioxirane and iso-ureaperoxide. The chemical pathways by which these reagents are generated are summarized below.

DMD Generation *(15)*.



Iso-ureaperoxide Generation *(16)*.



The bleaching chemistry of DMD has been explored by Ragauskas *(17)* and Lee et al. *(18)* These promising laboratory studies have been further advanced by a series of pilot-plant trials, which addressed many of the technical issues surrounding mill implementation of DMD. *(19)* Sturm *(16, 20)* and others *(21)* have recently published several articles highlighting the use of nitrilamine reinforced hydrogen peroxide as an improved kraft bleaching agent. These studies demonstrated that nitrilamine activation of hydrogen peroxide for the final stage of bleaching in TCF bleaching sequences resulted in higher brightness values for a given charge of hydrogen peroxide. Recent studies by Troughton have further examined the application of this agent to improve peroxide reinforced oxygen delignification of kraft pulps.(22)

These bleaching agents and other lignin oxidizing treatments will continue to provide new research avenues in the development of low AOX and/or TCF bleaching technologies. This paper describes our research efforts at improving the bleaching properties of DMD and nitrilamine reinforced peroxide by means of coupling their bleaching properties with xylanase pretreatment protocols.

The bio-boosting interactions between xylanase and activated peroxide were examined employing softwood and hardwood kraft pulps. Pulp samples were pretreated with xylanase following well established literature procedures.*(6)* As a control, a second series of pulps was treated in an analogous manner except that the enzyme itself was omitted. The resulting pulps were then bleached with a 0.7% charge of dimethyldioxirane or its molecular equivalence of hydrogen peroxide or hydrogen peroxide/nitrilamine. The results of these bleaching studies are summarized in Table 2. The bleaching results for DMD were reported after an alkaline extraction stage since the I-stage is performed at neutral pH whereas the P and Pnt stages are performed under alkaline conditions. Analysis of the bleaching data from various xylanase/ peroxide treatments indicates that the enzyme-treated hardwood pulps responded more favorably to either the I or Pnt-stages than the softwood pulps. Interestingly, the xylanase pretreatment prior to peroxide bleaching was beneficial to both the hardwood and softwood kraft pulps. A comparison of the bleaching results for WIE versus WPnt for the softwood and the hardwood kraft pulps suggest that the bleaching efficiency of these two agents at low charges is comparable. Indeed, in the case of the softwood kraft pulp it appears that the nitrilamine/peroxide treatment was slightly more effective at delignifying the kraft pulp at these relatively low charges of peroxide.

To explore the bleachability of these pulps each sample was subsequently treated with a DEDED bleach sequence. The kappa factor for the D_{100} stage ranged from 0.13 to 0.23 depending on the exact pulp and these values are summarized in Table 1. The D_1 stage employed a 1.2% charge of chlorine-free chlorine dioxide while the final D_2 stage employed a 0.2% charge of ClO_2 for the softwood pulps and 0.4% for the hardwood pulps. The brightness results for the xylanase/nitrilamine reinforced peroxide studies are summarized in Figures I and II. An examination of these results indicates that the enzymatic pretreatment, combined with the Pnt-stage, significantly raises the brightness ceiling of the pulps. For target brightness values of 89% ISO the use of XI reduces the totally applied chlorine dioxide stage (TAC) by approximately 15 - 23% and even greater reductions were observed at 90% ISO brightness values. A comparison of the nitrilamine-reinforced bleaching studies with the hydrogen peroxide bleaching experiments, summarized in Figures III and IV, further illustrates the benefits of activating hydrogen peroxide with nitrilamine. For both the hardwood and softwood kraft pulps the nitrilamine-reinforced bleaching sequences yielded higher brightness pulps while reducing the TAC employed.

The DMD-treated pulps also afforded higher brightness values at reduced TAC than comparable peroxide bleached pulps, as shown on Figures V and VI. Interestingly, a comparison of the Pnt and DMD treated pulps suggests that the nitrilamine/peroxide treated pulps respond slightly more favorably to the DEDED bleached sequence than the DMD treated pulps. Several factors may be contributing to these differences including the experimental methodology employed to generate DMD for I-stage and differing sensitivity to trace metals present in the pulp. Nonetheless, a comparison of the DMD bleached pulps with the hydrogen peroxide treated pulps demonstrates a clear advantage to activating peroxide prior to bleaching.

Conclusions

In conclusion, the use of activated peroxide species such as DMD or nitrilamine reinforced peroxide followed by DEDED allowed for 2 - 5% ISO brightness gains in hardwoods and 2 - 3% ISO brightness gains for softwood kraft pulps. The use of xylanase pretreatments also improved the delignification properties for all forms of peroxide studied. As previously noted for xylanase/chlorine dioxide bleaching studies, the hardwoods kraft pulps were more responsive to the xylanase treatments than the softwoods which have been attributed to differences in hemicellulose contents between hardwood and softwood kraft pulps.*(23)*

In light of the relative ease of incorporating nitrilamine reinforced peroxide stages in modern bleaching operations we plan to continue exploring the application of X(Pnt) stages as pretreatments for low AOX chlorine dioxide bleaching technologies.

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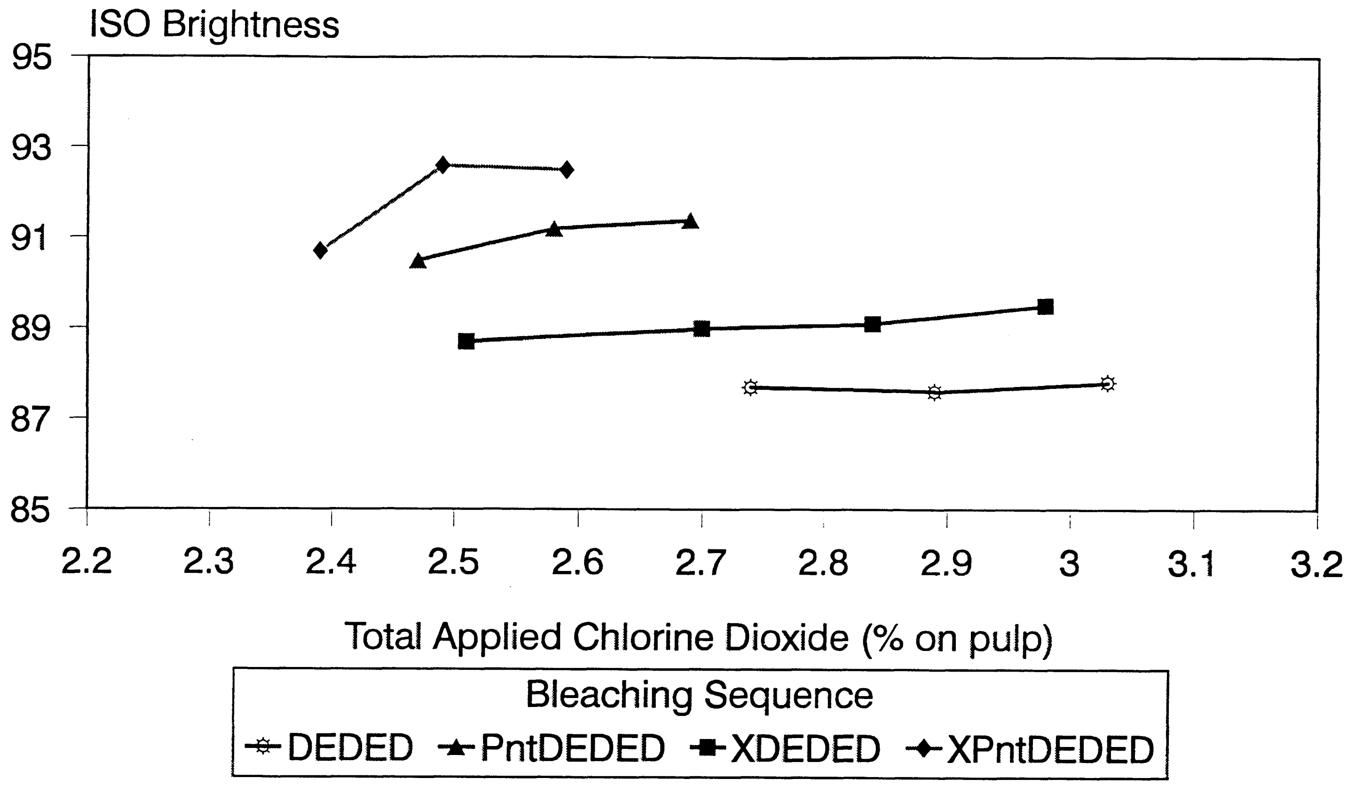
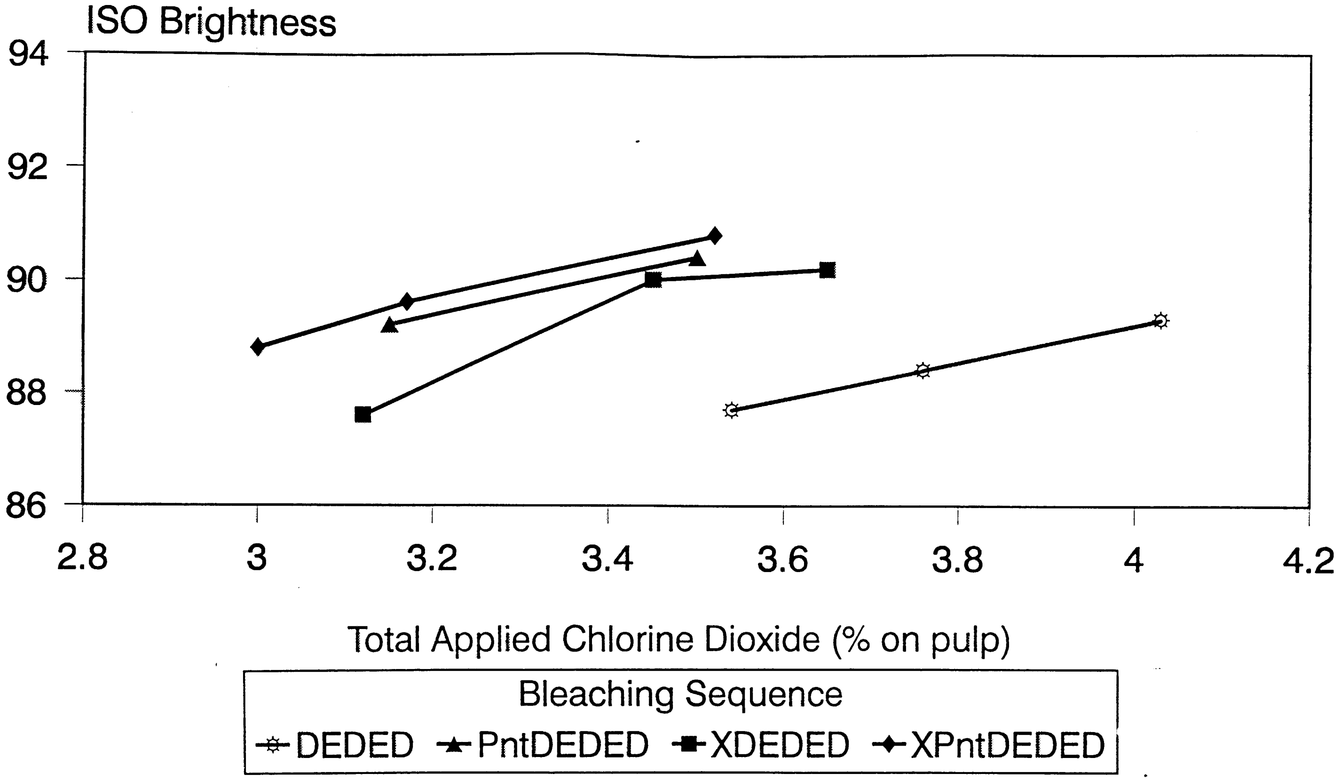
Table II. Characteristics of Pulp Samples Bleached with DMD, Hydrogen Peroxide, or Nitrilamine/Hydrogen Peroxide.

	Hardwood			Softwood		
Treatment	Brightness (% ISO)	Kappa #	Viscosity (cP)	Brightness (% ISO)	Kappa #	Viscosity (cP)
W	34.7	18.0	49.5	29.7	27.4	37.0
X	35.1	17.3	51.0	30.6	26.7	38.5
WIE	46.4	14.1	40.7	32.3	24.9	35.0
XIE	48.6	13.0	51.0	32.3	24.6	36.6
W(Pnt)	46.1	14.3	38.8	32.6	22.7	25.4
X(Pnt)	46.0	13.0	41.4	32.4	23.0	30.0
WP	41.6	16.0	--	32.9	24.1	--
XP	42.2	14.9	--	32.2	22.7	--

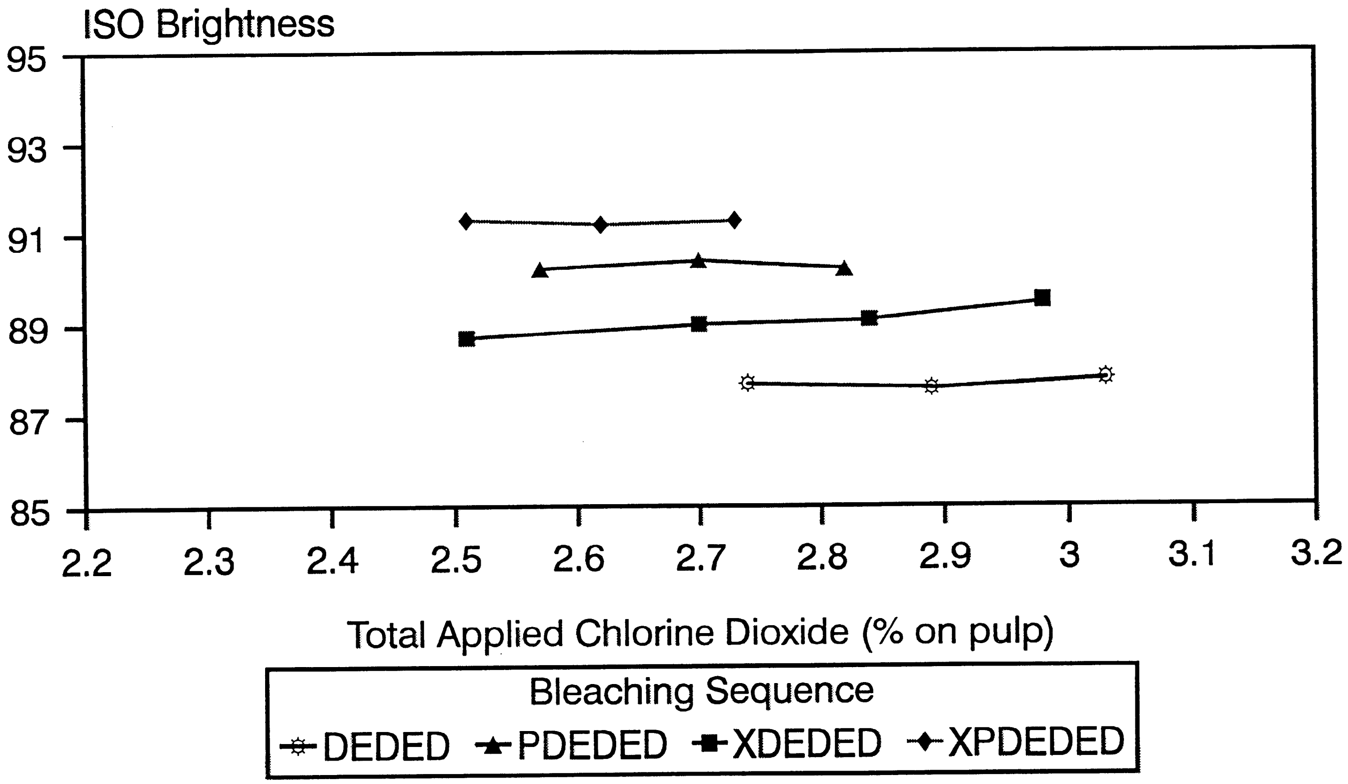
I. Effects of xylanase and nitrilamine-reinforced hydrogen peroxide treatments on DEDED bleaching properties for hardwood kraft pulp.



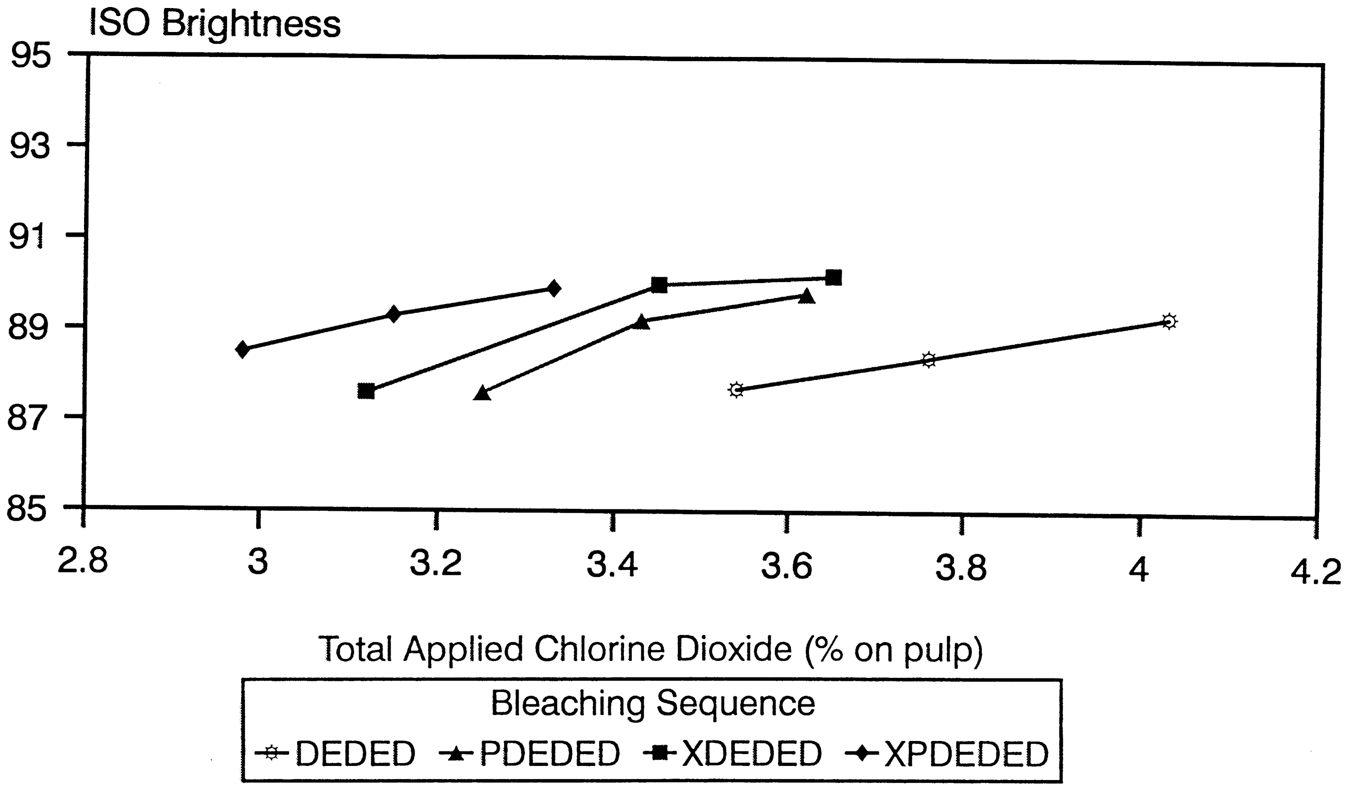
II. Effects of xylanase and nitrilamine-reinforced hydrogen peroxide treatment on DEDED bleaching properties for softwood kraft pulp.



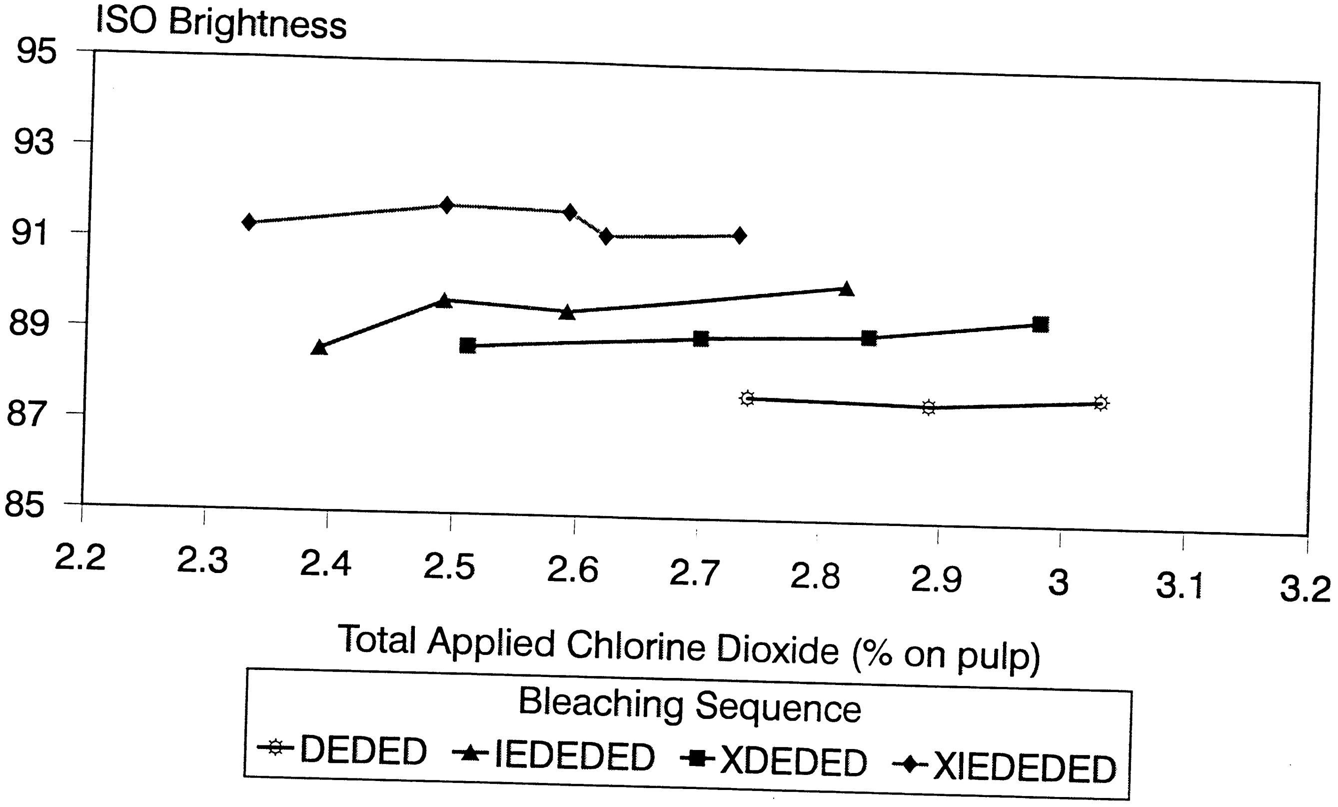
III. Effects of xylanase and hydrogen peroxide treatments on DEDED bleaching properties for hardwood kraft pulp.



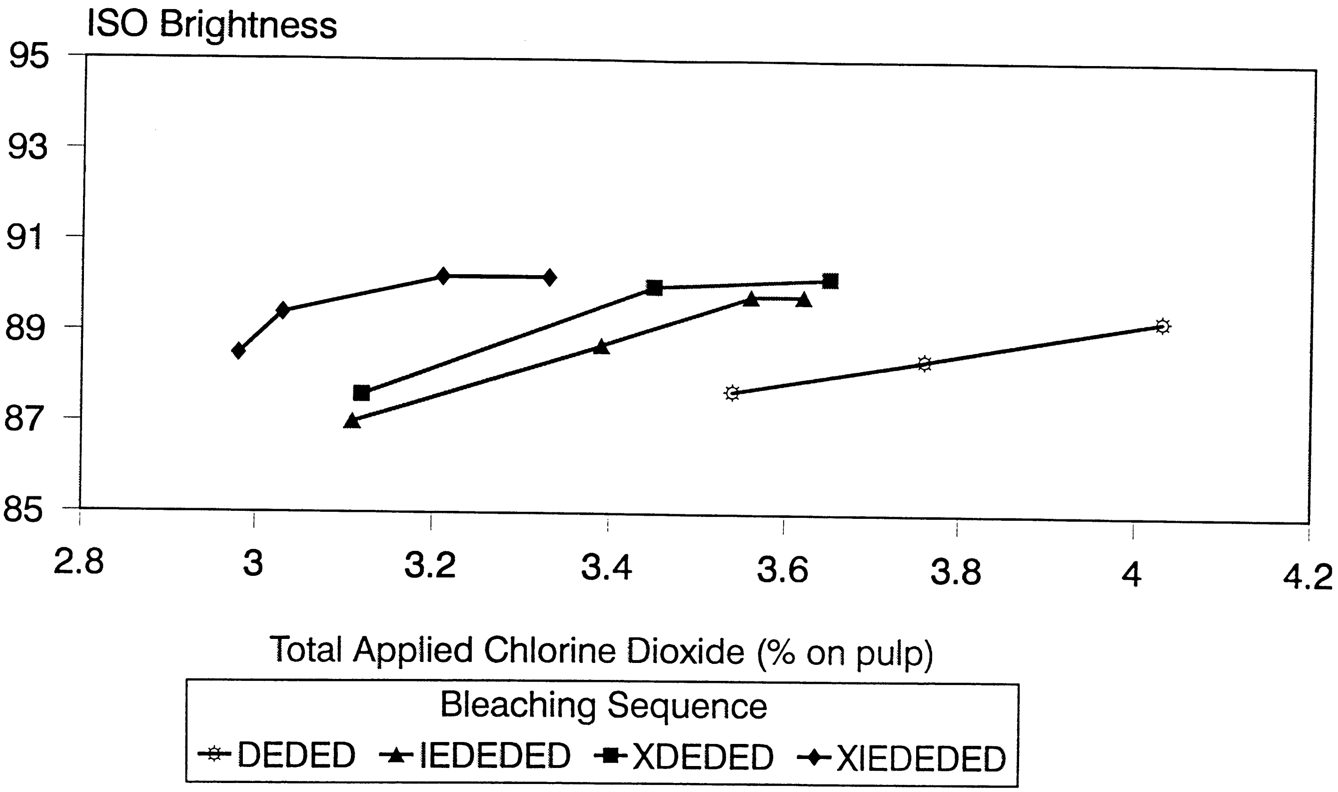
IV. Effects of xylanase and hydrogen peroxide treatments on DEDED bleaching properties for softwood kraft pulp.



V. Effects of xylanase and DMD treatments on DEDED bleaching properties for hardwood kraft pulp.



VI. Effects of xylanase and DMD treatments on DEDED bleaching properties for softwood kraft pulp.



FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT F015

Subtask: Fundamental Investigations Directed at Improving the Delignification Properties of Nitrilamine Reinforced Hydrogen Peroxide

ANNUAL RESEARCH REVIEW

March 22, 1995

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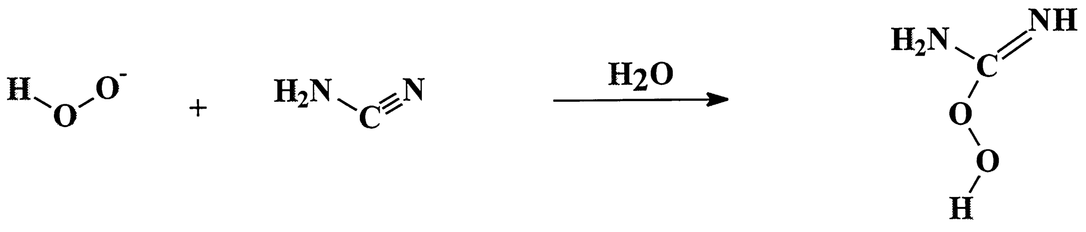
Fundamental Investigations Directed at Improving the Delignification Properties of Nitrilamine-Reinforced Hydrogen Peroxide

Considerable progress has been made over the past few years to enhance the environmental performance of kraft bleaching operations. Improved mill procedures and new bleaching technologies have substantially reduced the formation of chlorinated organic compounds in bleach plant effluents.[1] Nonetheless, EPA's recently proposed "cluster rules"[2] could pose a serious challenge to many of today's chlorine-based bleaching technologies. To address these issues and to develop new and improved kraft bleaching technologies, our research efforts have been directed towards the development of new oxygen-based bleaching agents. Previous studies from our laboratories have shown that the conversion of hydrogen peroxide into dimethyldioxirane[3] yields a highly selective bleaching agent for kraft pulps. Studies by Lee[4] and McDonough[5] further explored the bleaching potential of this reagent and examined its application in multistaged bleaching sequences. Despite the attractive bleaching properties of DMD, the need for specialized bleaching equipment and chemical recovery systems may limit future applications. Nonetheless, these research efforts demonstrated that chemical activation of hydrogen peroxide and its derivatives could yield more selective bleaching agents.

Recent studies by Sturm[6] demonstrated that the use of nitrilamine provides an attractive alternative method of activating hydrogen peroxide. The generally accepted chemical mechanism of activation is believed to come about due to the formation of an iso-urea peroxide,[7] as shown below.



Nitrilamine

Iso-urea peroxide

The nitrilamine/peroxide adduct has been shown to yield a stronger oxidizing agent than hydrogen peroxide, and this enhanced chemical reactivity presumably contributes to improved bleaching. Studies by Sturm[8] and Nelson[9] have demonstrated that the application of nitrilamine to an EOP or EP stage improved delignification and brightness gains of hydrogen peroxide both for TCF and ECF bleaching sequences. Reisner[10] has recently reported the use of nitrilamine-reinforced peroxide as a facile means of improving mill bleaching operations for spruce sulfite pulps.

In conjugation with the beneficial oxidative characteristics of iso-urea peroxide, its application into mill operations can be readily accomplished employing either a P or E-stage bleaching tower without substantial process modifications. In summary, preliminary studies have shown that nitrilamine provides an effective means of improving peroxide-based bleaching treatments. Our research interests in this additive have been directed toward the development of low AOX chlorine dioxide bleaching sequences for southern softwood kraft pulps. Specifically, we have been exploring the use of nitrilamine-reinforced peroxide as a first-stage bleaching treatment prior to a DED bleach sequence. Our initial studies have been focused on optimizing the delignification properties of nitrilamine-reinforced peroxide for southern softwood kraft pulp. This report examines the influence of several bleaching parameters on nitrilamine reinforced hydrogen peroxide treatments including H_2O_2:NH_2CN, temperature, and time.

Experimental

Materials

30% hydrogen peroxide, nitrilamine, NaOH, $MgSO_4$, N-hydroxynitrilamine, 1,3-dicyanobenzene, and 1,2-dicyanobenzene were purchased from Aldrich and employed as received. A commercial source of modified kraft pulp followed by oxygen delignification was employed for all of the studies described in this report. Pulp samples from the mill were taken at two different times, and this resulted in two differing pulps samples pulp A had a kappa number of 11.5, viscosity of 20.9 cP, and

TAPPI brightness of 34. Pulp B was determined to have a kappa number of 13.8, viscosity of 22 cP, and TAPPI Brightness of 39.

Hydrogen Peroxide and Nitrilamine-Reinforced Peroxide Treatments

All peroxide bleaching studies were performed at 10% consistency in sealed polyethylene bags. The addition sequence of bleaching reagents was first, the aqueous sodium hydroxide followed by hydrogen peroxide, and finally either $MgSO_4$ or nitrilamine. The pulp bags were then sealed, kneaded, and immersed in a water bath. The sealed bags were kneaded every 15 minutes, and after the appropriate time period, the pulp slurry was filtered, washed, and air dried. The bleached pulps were characterized according to kappa number, viscosity, and TAPPI brightness values following standard TAPPI test methods.

Preliminary Bleaching Studies: Initial bleaching studies were directed at assessing the delignification properties of hydrogen peroxide reinforced with nitrilamine. These preliminary studies were accomplished employing a commercial southern softwood kraft pulp after oxygen delignification. The initial results from bleaching the pulp with nitrilamine-reinforced peroxide versus peroxide are summarized in Figure 1. From these studies, it becomes readily apparent that nitrilamine addition to a P-stage is beneficial for the delignification of kraft pulps. A comparison of the extent of delignification after 1 hour at 70°C indicates that the addition of a 0.5% charge of nitrilamine improves peroxide delignification by 56%. Improved delignification also leads to slightly improved brightness values for the nitrilamine-reinforced peroxide treatment (Pnt-stage). The results from the 2 hour Pnt-stage with 0.5% NH_2CN were much the same as the 1 hour treatment suggesting that nitrilamine was rapidly consumed in the early portion of the bleaching reaction. Indeed, if the charge of nitrilamine is increased from 0.5% to 2%, we then observe an improved delignification effect as summarized in Figure 1. Based on these preliminary studies, it appears that for the pulp employed an optimal charge of nitrilamine is in the range of 0.5-1.0%. The changes in viscosity with differing peroxide treatments were also examined, and these results are presented in Figure 2. Although our initial peroxide studies omitted the use of $MgSO_4$, it was still promising to note that the nitrilamine-reinforced peroxide bleaching reactions yielded lower lignin-containing pulps at viscosity values higher than those observed for the peroxide-only treatments.

Following these promising preliminary studies our research efforts then examined the sensitivity of the Pnt-stage toward alkaline charge and the use of $MgSO_4$ as a viscosity protecting agent. To investigate the effects of varying the alkaline charge, bleaching conditions were maintained at 2.4% hydrogen peroxide, 70°C, 2 h, and 0.5% charge of NH_2CN while varying the charge of NaOH from 1.0% to 3.0%. Figure 3 summarizes the results of our bleaching studies with an oxygen delignified southern softwood kraft pulp, and these results suggest that a 2.5% charge of alkali is close to optimal for delignification. Finally, we have also explored the effects of adding $MgSO_4$ into the Pnt-stage; unfortunately, todate we have been unable to find a clear consistent trend with regards to the addition of $MgSO_4$ to a Pnt-stage. Our preliminary data suggest a minor benefit from adding $MgSO_4$ to the Pnt-stage for some applications.

Temperature and Chelation Effects: Among the many parameters which may influence peroxide delignification, Lierop[11] and others[12] have shown that metal chelation, bleaching time, and temperature are three effective means of optimizing the bleaching chemistry of peroxide. To explore the impact that these parameters have on a Pnt-stage we initially varied the bleaching temperature between 70-90°C and the bleaching time between 2-4 hours for an unchelated pulp. The results from peroxide and nitrilamine reinforced peroxide bleaching studies at 70° and 90°C are summarized in Figures 4a and 4b, respectively. The studies at 70°C illustrated a clear benefit for extending the bleaching time from 2 to 4 hours for the Pnt-stage. An additional 2 hours bleaching time provided sufficient time so as to allow for further delignification to occur. After 4 hours at 70°C, our results suggest that the use of 0.5% NH_2CN can enhance the delignification properties of hydrogen peroxide by a factor of two. In comparison, the differences in delignification are substantially reduced when the bleaching temperature is raised to 90°C for unchelated kraft pulp as shown in Figure 4b. Furthermore, the Pnt bleaching reactions at 90°C appear to hinder the development of brightness in comparison to the results achieved with hydrogen peroxide alone.

The effects of chelation on a Pnt-stage were explored with a second oxygen delignified softwood kraft pulp. Table 1 summarizes the metal profile of the pulp before and after treatment with an acidic EDTA stage. Following standard bleaching procedures, pulp samples were bleached with a 2.4% charge of peroxide and 2.5% charge of sodium hydroxide. For the P-stage, a 0.5% charge of $MgSO_4$ was added, whereas for the Pnt-stage, this reagent was replaced with a 0.5% charge of nitrilamine. Peroxide bleaching results for 2 and 4 hours at 70°, 80°, and 90°C are shown in Figures 5 and 6. The 2 and 4 hour studies clearly demonstrate improved delignification and brightness gains for the Pnt-treated pulps. Interestingly, we did not observe a detrimental influence of nitrilamine on brightness development at 90°C that was previously noted for the unchelated pulps. Furthermore, although the extent of delignification for the P- and Pnt-treated pulps narrows as the temperature is increased, there remains a noticeable benefit for the application of nitrilamine. After 2 hours at 90°C, the Pnt-treated pulps are 60% further delignified than the P-treated pulps, and after 4 hours, the Pnt-treated pulps still contain 24% less lignin than the P-treated pulps.

Table 1: Metals Profile of Oxygen Delignified Southern Softwood Kraft Pulp.

Pulp / Metal (mg/kg od pulp)	Cr	Cu	Fe	Mg	Mn	Ni
Unchelated	BDL[a]	61.0	13.5	4.44×10^3	46.0	BDL
Chelated	BDL	BDL	9.1	244.6	1.3	BDL

[a] BDL: beyond detection limits, ca 15-35 ppb.

Modified Nitrile Procedures: The use of nitrile derivatives has been shown to be more effective than nitrilamine for improving the oxidative chemistry of peroxide.[13] To explore this avenue of research, we have examined the bleaching boosting effects of several nitrilamine derivatives including N-hydroxynitrilamine, 1,2-dicyanobenzene, and 1,3-dicyanobenzene, but todate we have been unable to identify an additive which substantially improves the performance of nitrilamine. Finally, preliminary studies have suggested that a delayed addition of nitrilamine (i.e., treat the pulp for 1 hour with peroxide followed by the addition of nitrilamine and an additional 1 hour of bleaching) may provide a means of reducing the charge of nitrilamine needed while still retaining the benefits of peroxide activation. These studies are ongoing and will be reported shortly.

Conclusion: The use of nitrilamine provides a valuable means of improving the delignification properties of hydrogen peroxide for southern softwood kraft pulps. Future studies will examine the implication of these studies with respect to chlorine dioxide bleaching sequences and low AOX generation.

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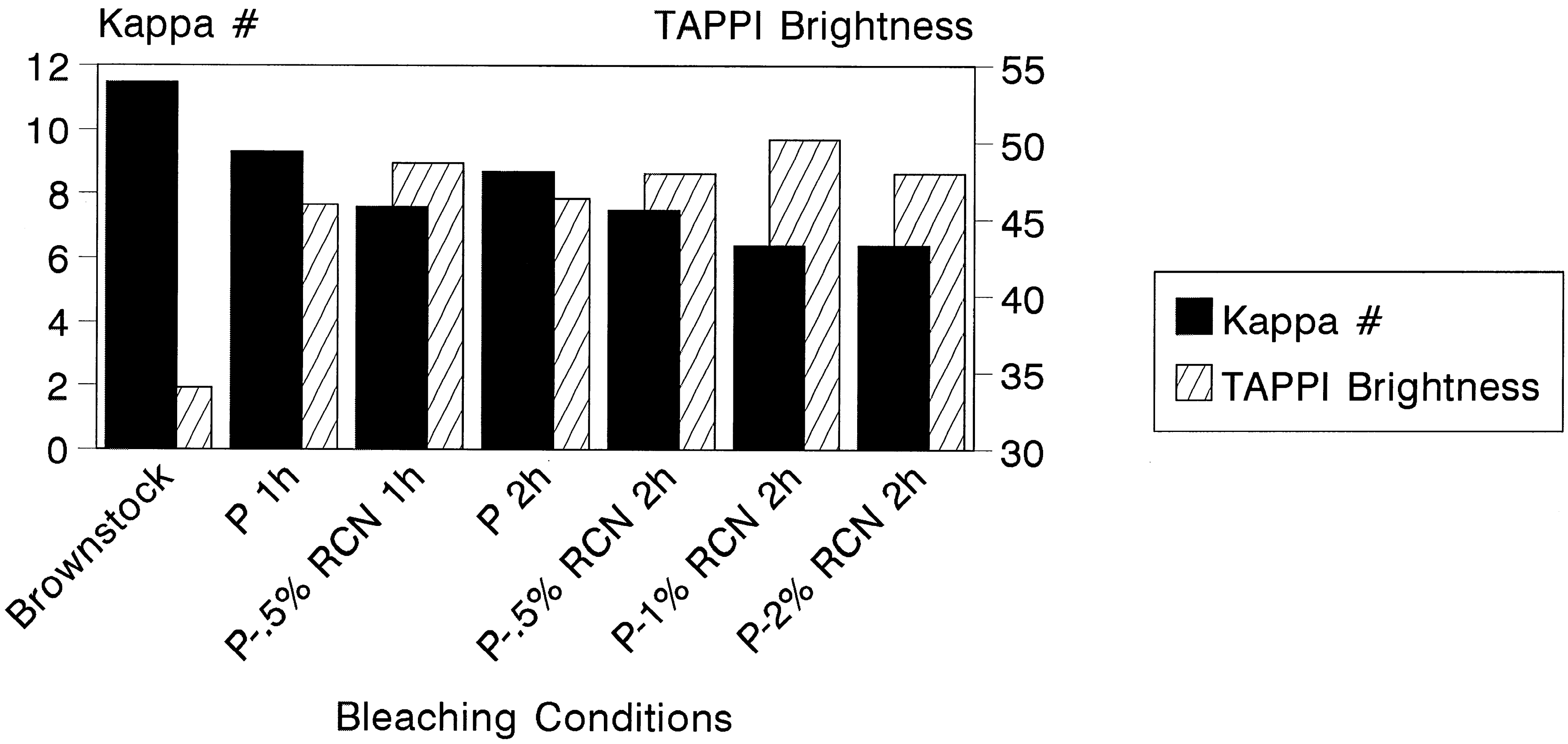
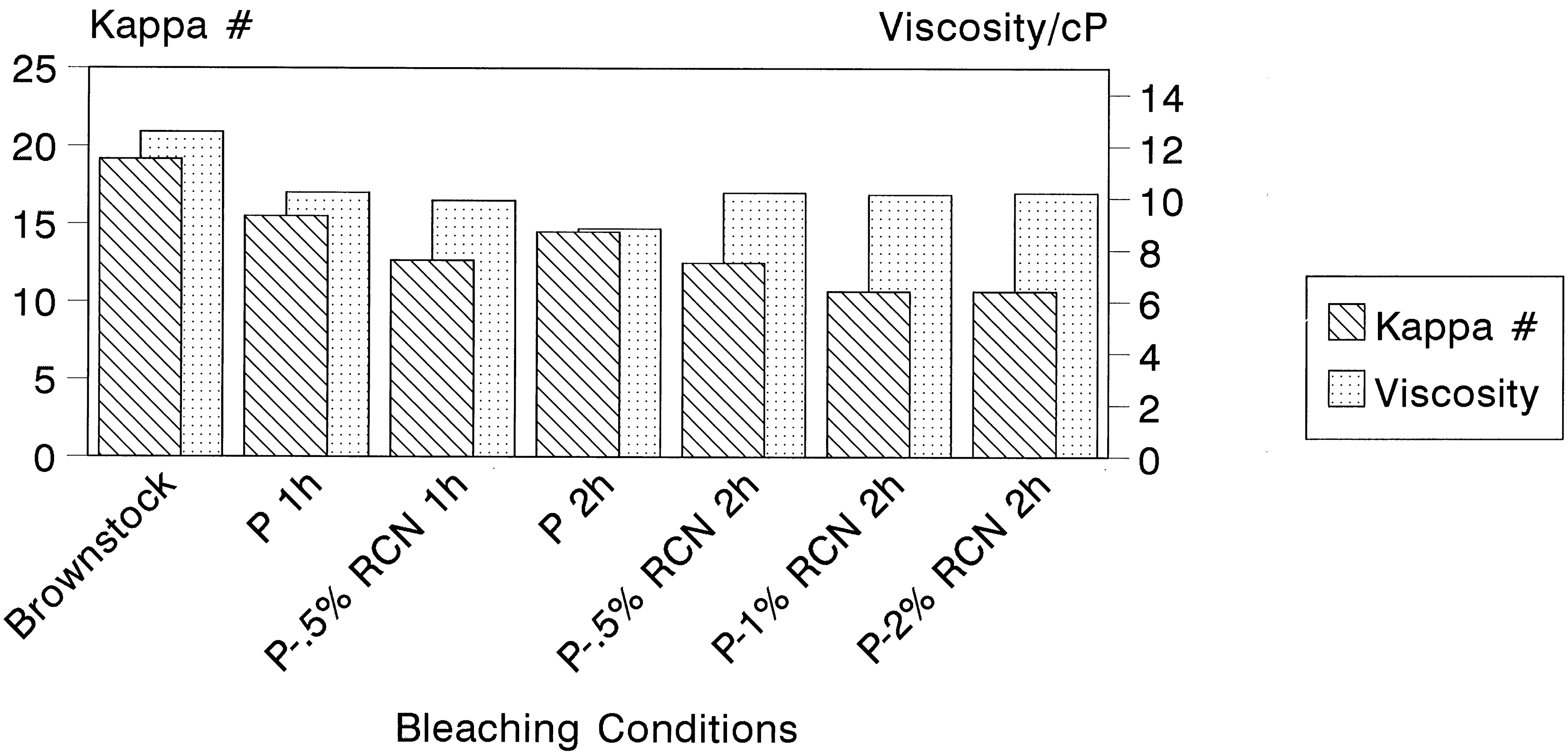
Figure 1: Peroxide bleaching[a] oxygen delignified southern softwood kraft pulp. Delignification/Brightness Trends



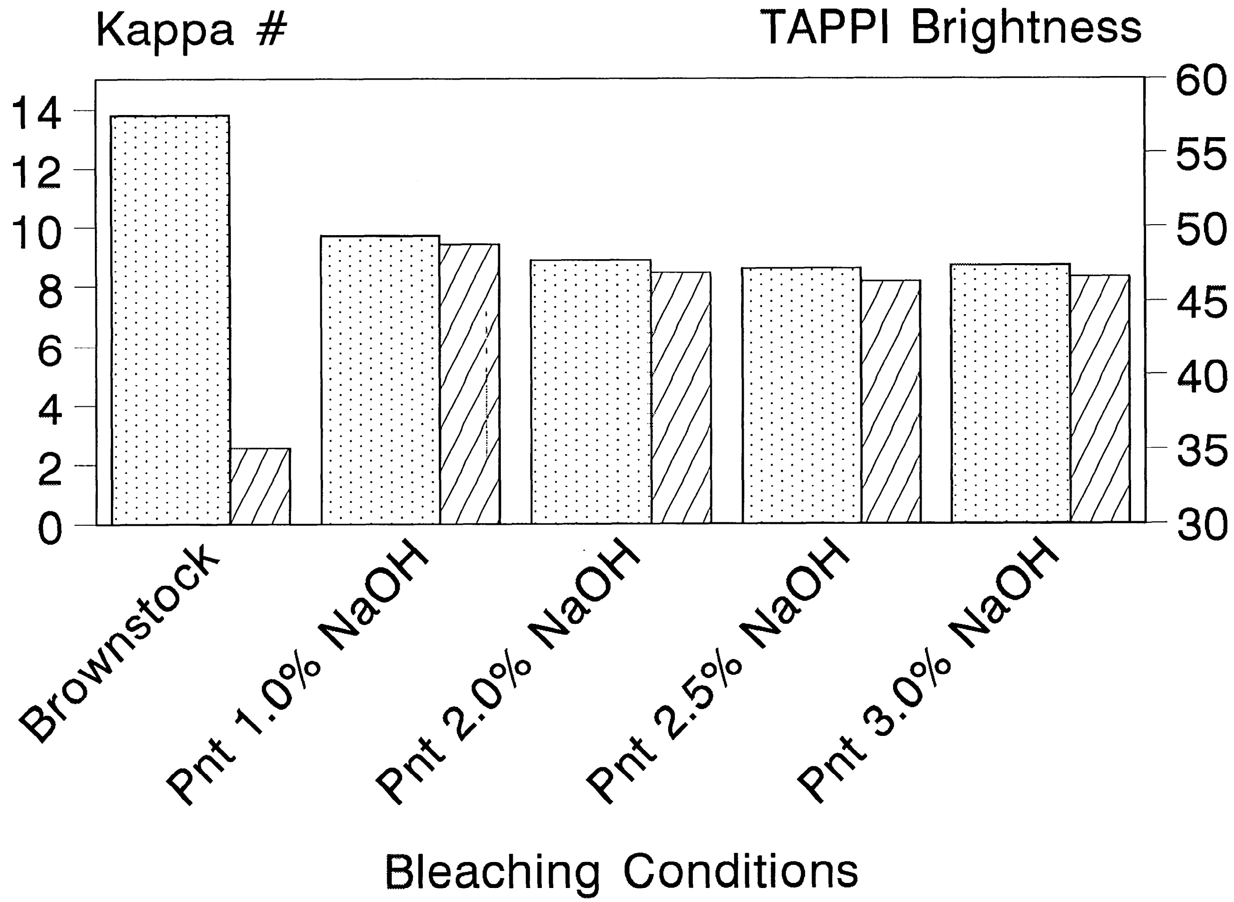
[a] 2.4% charge H_2O_2, 2.5% charge NaOH, 10% consistency, 70°C. RCN= NH_2CN.

Figure 2: Peroxide bleaching[a] oxygen delignified southern softwood kraft pulp. Viscosity/Delignification Trends



[a]2.4% charge H_2O_2, 2.5% charge NaOH, 10% consistency, 70°C.
RCN= NH_2CN.

Figure 3: Pn-bleaching[a] oxygen delignified southern sof
Effect of alkaline charge on delignification/



[a] 2.4% charge H_2O_2, 0.5% charge NH_2CN, 10% consistency, 70°C,

Figure 4a: 70°C Peroxide bleaching[a] of an oxygen delignified southern softwood kraft pulp. Effect of bleaching time on delignification/brightness

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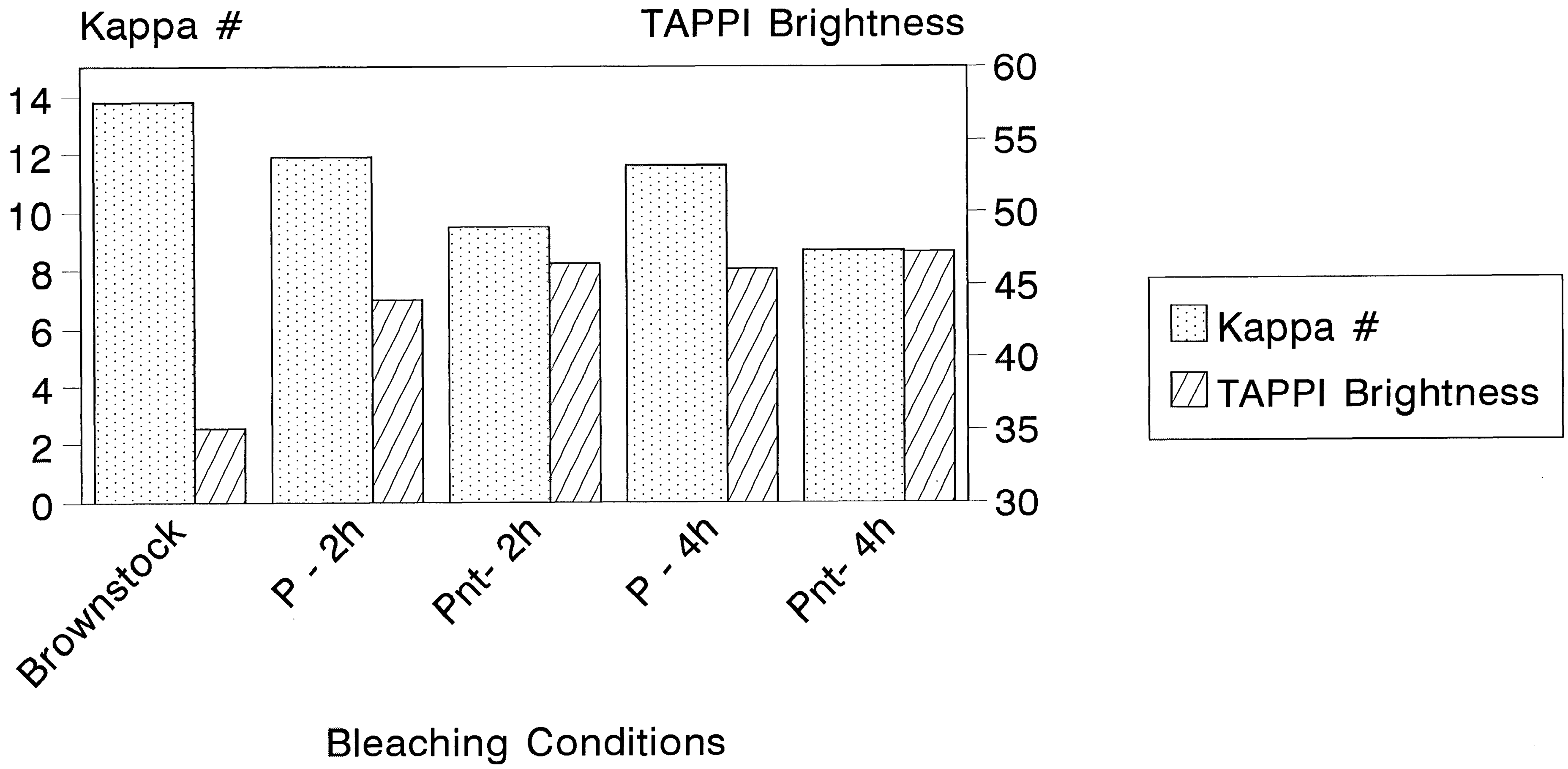

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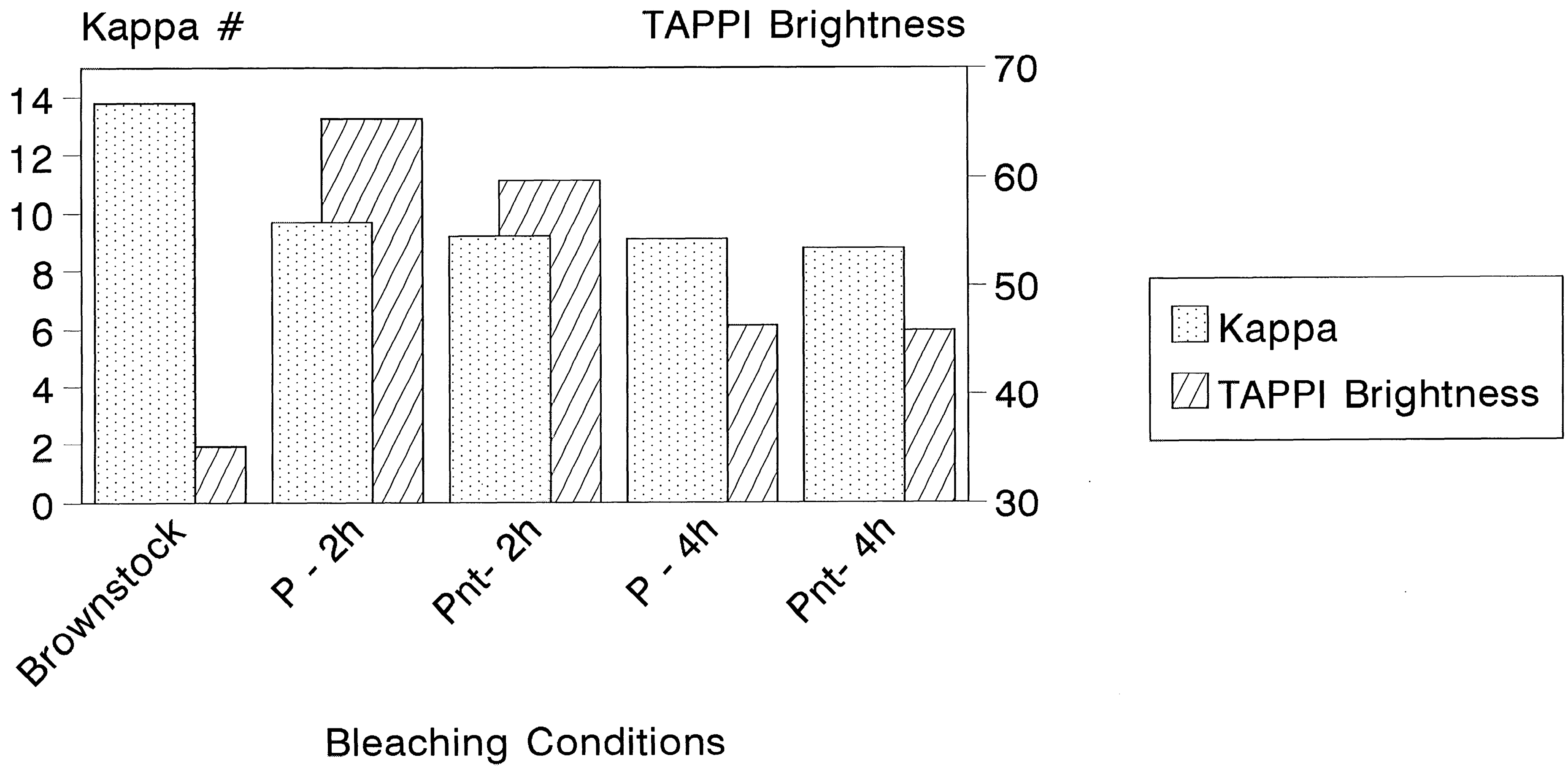
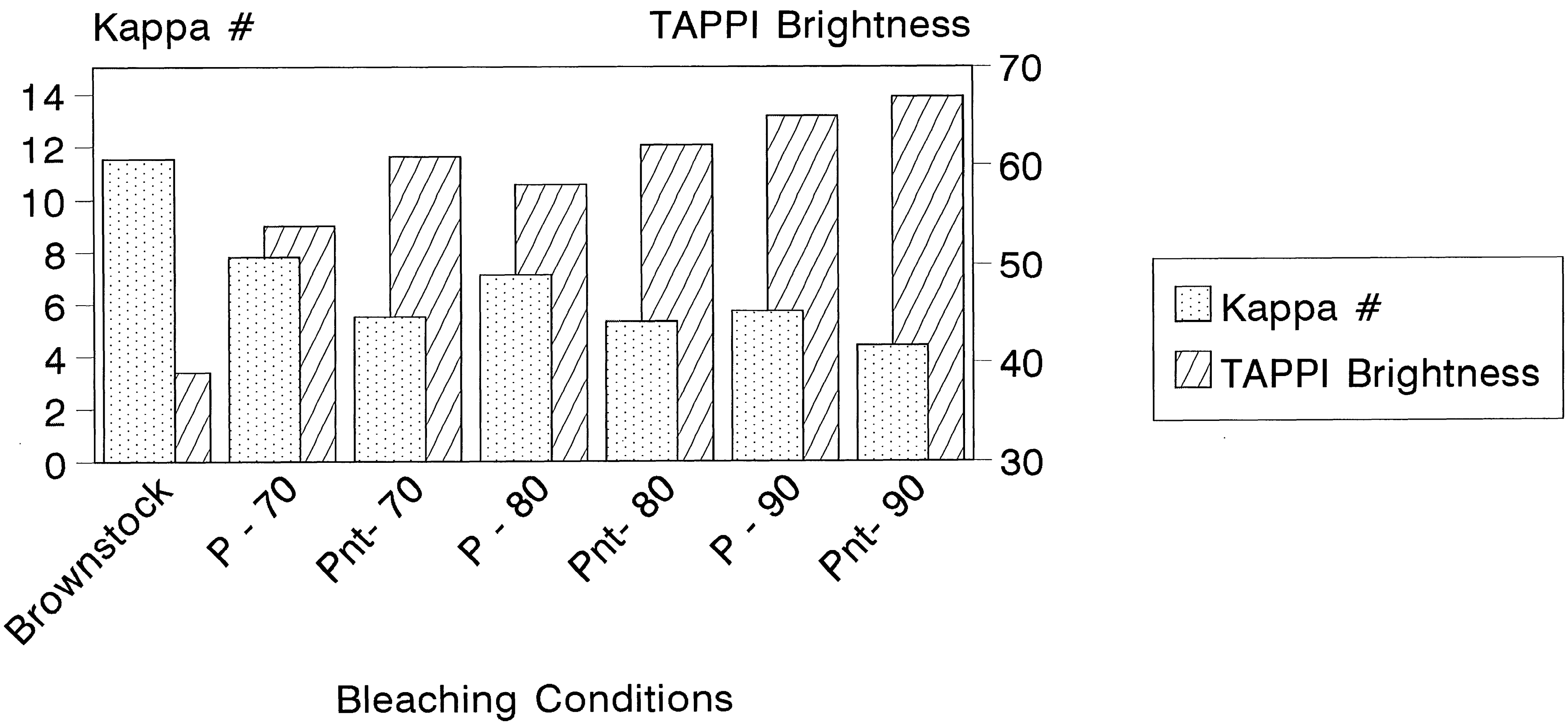
[a] 2.4% charge H_2O_2, 10% consistency, 70° C.
P-stages employed 0.5% $MgSO_4$, Pn-stages employed 0.5% NH_2CN.

Figure 4b: 90°C Peroxide bleaching[a] of an oxygen delignified southern softwood kraft pulp. Effect of bleaching time on delignification/brightness



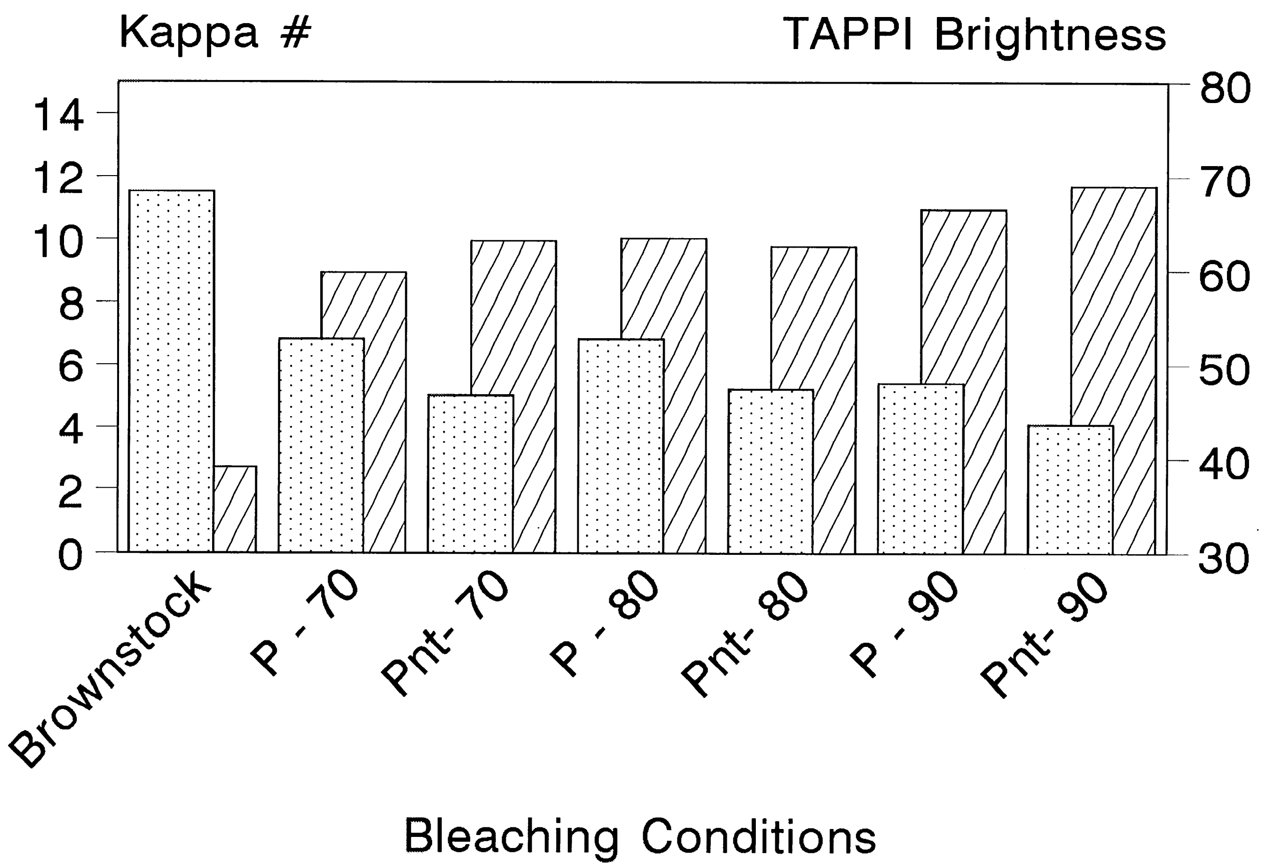
[a] 2.4% charge H_2O_2, 10% consistency, 90°C.
P-stages employed 0.5% $MgSO_4$, Pn-stages employed 0.5% NH_2CN.

Figure 5: Peroxide bleaching[a] chelated oxygen delignified southern softwood kraft pulp. Effect of bleaching temperature (70, 80, 90°C) on delignification/brightness Bleaching Time 2 h



[a] 2.4% charge H_2O_2, 10% consistency.
P-stages employed 0.5% $MgSO_4$, Pn-stages employed 0.5% NH_2CN.

Figure 6: Peroxide bleaching[a] chelated oxygen delignified southern
Effect of bleaching temperature (70, 80, 90°C) on delignific
Bleaching Time 4 h



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[a] 2.4% charge H_2O_2, 10% consistency.
P-stages employed 0.5% $MgSO_4$, Pn-stages employed 0.5% NH_2C

FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT F015

Subtask: OZONE FUNDAMENTALS

ANNUAL RESEARCH REVIEW

March 22, 1995

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TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE:	FUNDAMENTALS OF BLEACHING CHEMISTRY
PROJECT STAFF:	L.B. Sonnenberg, A.J. Ragauskas, D.R. Dimmel
BUDGET (FY 94-95):	$255,000
REPORTING PERIOD:	July 1994 - Feb.1995
DIVISION:	Chemical and Biological Sciences
PROJECT NUMBER:	F015

OBJECTIVE: Provide a fundamental understanding of the physical and chemical reactions that control lignin removal and residual lignin structure. Understand the reasons for selectivity of reactions that occur in selected bleaching sequences.

IPST GOAL: Improved bleaching processes

SUMMARY:

Interest in developing nonchlorine bleaching techniques continues to grow in response to changes in the marketplace and proposed changes in environmental regulations. The wood chemistry group at IPST is currently engaged in investigations into the fundamental chemistry and the effectiveness of nonchlorine bleaching.

Ozone Fundamentals

Properties of oxygen delignified, ozone bleached pulps

It is important to relate the chemistry of ozone bleaching to paper properties. The zero-span tensile strength was measured for the unbeaten kraft and oxygen bleached pulps to estimate the effects of oxygen and ozone on structural features that affect strength. There was little apparent relationship between strength and the drop in viscosity due to ozonation, possibly due to alkaline depolymerization of unstabilized ozonated pulps with the conventional viscosity test. Oxygen reduced strength more than ozone bleaching when ozone bleaching is carried out at low charges (<0.5%). Further work is needed in this area to ascertain the true effect of low oxygen and low ozone charges on strength.

Dissolved byproducts of oxygen and ozone bleaching

In order to fully understand the fundamental reactions taking place during delignification and carbohydrate degradation, it is important to characterize the dissolved products of bleaching as well as to characterize the bleached pulp. We compared the molecular weight distribution (MWD) of the dissolved byproducts from oxygen (55% delignification) and ozone bleaching (0.4% charge) of brownstock. Compared to the oxygen byproducts, the ozone byproducts had a more uniform distribution across the molecular weight ranges. Oxygen may depolymerize more effectively than ozone without introducing the same quantity of hydrophilic functional groups that ozone produces. The result is that smaller products are preferentially dissolved in the oxygen filtrate while the more oxidized components of all sizes are dissolved in the ozone filtrates.

Comparisons of ozone filtrates of oxygen delignified pulps showed that oxygen transforms the residual lignin so that the depolymerized (but still insoluble) residual lignin readily dissolves upon exposure to an effective oxidant such as ozone. Oxygen delignification probably promotes ozone efficiency by producing residual lignin that is smaller in size and enriched in carboxylic acid groups compared to brownstock residual lignin.

Fundamentals of improved bleachability of oxygen bleached pulps

The Wood Chemistry and the Pulping and Bleaching Groups have initiated a series of experiments to further examine the bleachability of oxygen delignified pulps. The goal of these studies is to find optimal conditions for efficient and selective bleaching using our knowledge of fundamental reactions that occur during various processes. The general approach is to oxygen delignify three different brownstock pulps to a range of kappa numbers, and then to ozone bleach these pulps at 0.4% ozone charge. Both fundamental and applied aspects of the processes are being monitored by measuring functional groups, dissolved products, and pulp properties. The oxygen bleaching has been completed by the Pulping and Bleaching Group, and the ozone bleaching is in progress by the Wood Chemistry Group.

GENERAL INTRODUCTION:

Interest in developing nonchlorine bleaching techniques continues to grow in response to changes in the marketplace and proposed changes in environmental regulations. The wood chemistry group at IPST is currently engaged in investigations into the fundamental chemistry and the effectiveness of ozone, dimethyl dioxirane, and xylanase as nonchlorine bleaching reagents. Previous work is reviewed and current work is reported in three sections pertaining to the three reagents, "Fundamentals of Pulp Ozonolysis", "Fundamental Studies of Dimethydioxirane", and "Effect of Xylanase Pretreatment Procedures".

Ozone Fundamentals

INTRODUCTION:

The paper industry is seriously considering ozone as an alternative to chlorine-containing bleaching reagents. Information about major byproducts from pulp ozonation and residual lignin structure can provide useful information about many aspects of this new bleaching technology, including mechanisms of delignification, optimal conditions for high efficiency and high selectivity, and optimal placement of ozone in a bleaching sequence. Previous work on ozonation byproducts and ozone delignification of oxygen bleached pulps is reviewed. Recent and current research further investigates the improved bleachability of oxygen delignified pulps from a fundamental standpoint.

Prior Results:

Previous ozone bleaching studies examined the byproducts formed from pulp ozonation and focused on the role of secondary reactions during bleaching. There was some evidence that the soluble constituents in ozone filtrates exert an ozone demand and are further fragmented; however, the relative importance in ozone consumption is likely to be minimal. The primary low molecular weight byproducts were identified as small fatty acids, short-chain and long-chain aliphatic acids and diacids.

The effect of oxygen bleaching on the selectivity and efficiency of ozone bleaching was evaluated last year (1). A softwood kraft pulp (kappa number = 22, viscosity = 23) was oxygen bleached to 30% and 50% delignification in the laboratory. Three pulps were ozonated, including the kraft pulp (K(22)), the oxygen delignified pulp at kappa number 16 (K-O(16)), and the oxygen bleached pulp at kappa number 12 (K-O(12)). Several ozone charges were applied ranging from 0.3% to 1.4% on o.d. pulp. The ozonations were conducted in a laboratory reactor, at high consistency, pH = 2, and at room temperature. The rinsed pulps were analyzed for kappa number, viscosity, methoxyl content, carboxyl content, and phenolic content. The pulp rinsates were fractionated by ultrafiltration into high molecular mass (MW > 1000 daltons) and low molecular mass fractions. The pH and the total organic carbon was measured in the whole rinsates and the ultrafiltration retentates.

The moderately oxygen delignified pulp exhibited superior selectivity during ozonation than the kraft pulp or the 50% delignified pulp. The carbohydrates in the K-O(16) pulp appeared to benefit from the protecting effect of the residual lignin, such that loss of viscosity was similar to that of the kraft pulp (K(22)). The 50% delignified pulp apparently had been delignified beyond the threshold of lignin levels that can provide protection to the carbohydrates. At low ozone charges, delignification efficiency was greater for the oxygen bleached pulps than for the kraft pulp. At higher charges, the kraft pulp appeared to be delignified more efficiently than the 50% oxygen delignified pulp; the latter result has been observed by other researchers. The K-O(16) pulp may have exhibited greater delignification due to the high concentrations of carboxyl groups in the lignin which would promote swelling, increasing ozone accessibility and byproduct diffusion.

From the data presented here, a picture of ozonation emerges in which oxidized, labile portions of both carbohydrates and lignin in unozonated pulp are readily removed at low ozone charges and produce soluble, acidic fragments. Concurrently, phenolic rings are cleaved and carboxylic acid groups are introduced onto the residual lignin. As ozone charge is increased, the ring fragments become solubilized, producing less acidic lignin fragments.

Recent Results:

Properties of oxygen delignified, ozone bleached pulps

It is important to relate the chemistry of ozone bleaching to paper properties. The zero-span tensile strength was measured for the unbeaten pulps described in the previous section to estimate the effects of oxygen and ozone on structural features that affect strength. In general, the strength of a pulp is indirectly related to the drop in viscosity. Decreases in viscosity serve as a measure of the modification of the features of carbohydrates that affect strength; reduction of the cellulose degree of polymerization itself is probably not great enough to greatly affect pulp strength even in these highly oxidized pulps. Interestingly, there was little apparent relationship between strength and the drop in viscosity due to ozonation (Figure 1). The physical and chemical characteristics of the fibers that affect strength is not tracked by viscosity of ozonated pulps. It is important to note that unstabilized ozonated pulps can undergo alkaline depolymerization during the viscosity test giving rise to atypical viscosity and DP results (1), which may contribute to the observed results. (For these reasons, future work

Figures

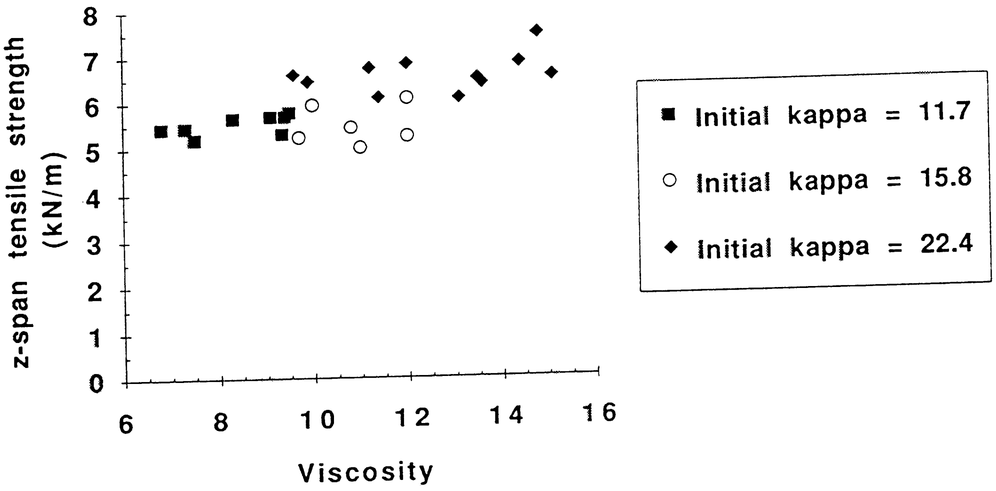

Figure 1. Relationship between viscosity and zero-span tensile strength of unbeaten pulps after ozonation of kraft and oxygen delignified pulps.

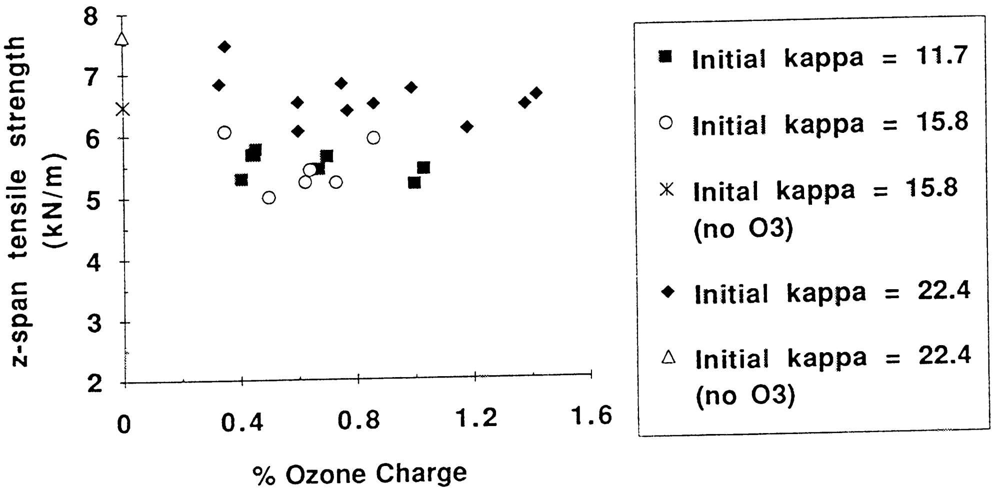

Figure 2. Relationship between ozone charge and zero-span tensile strength of unbeaten pulps after ozonation of kraft and oxygen delignified pulps.

will include viscosity measurements on sodium borohydride stabilized pulps). Functional group differences in the ozonated pulps (measured in earlier work) may manifest themselves more as strength differences in more refined pulps.

Examining the relationship between ozone charge and zero-span tensile strength for kraft and oxygen bleached pulp (Figure 2) indicates that oxygen tends to reduce strength more than ozone bleaching. The maximum impact of ozone on strength appears to be reached by about a 0.5 % charge; charges greater than 0.5% appeared to have little further impact on strength. While the advantage of keeping ozone charges below 0.5% revealed in earlier work is borne out by these results, the advantage of moderate oxygen delignification for carbohydrate protection is not as readily apparent in these data as in the viscosity data. Further work is needed in this area to ascertain the true effect of low oxygen and low ozone charges on strength.

Dissolved byproducts of oxygen and ozone bleaching

In order to fully understand the fundamental reactions taking place during delignification and carbohydrate degradation, it is important to characterize the dissolved products of bleaching as well as to characterize the bleached pulp. Molecular weight and acidity of bleaching liquor components are useful parameters to examine because delignification involves fragmentation and the introduction of hydrophilic groups. It has been recently suggested that oxygen and ozone are complementary bleaching agents because oxygen reduces the molecular weight of residual lignin, while ozone introduces large numbers of carboxylic acids without substantial depolymerization (2).

In preliminary studies, we compared the molecular weight distribution (MWD) of the dissolved byproducts from oxygen (55% delignification) and ozone bleaching (0.4% charge) of brownstock (Figure 3). Note that the two filtrates were diluted prior to analysis to obtain comparable ranges of concentration of total organic carbon (TOC). The two bleaching reagents produced dissolved byproducts of quite different molecular weights. Compared to the oxygen byproducts, the ozone byproducts had a more uniform distribution across the molecular weight ranges. Ozone also produced a fraction of very low molecular weight material, which was not observed in the oxygen filtrate, which substantiates the claim of Lachenal et al. that ozone will cleave and dissolve smaller fragments of lignin than oxygen (2). However, the results shown in Figure 3 indicate that in addition to compounds of very small molecular weight, ozone produces a substantial fraction of larger compounds. Oxygen may depolymerize more effectively than ozone without introducing the same quantity of hydrophilic functional groups that ozone produces. The result is that smaller products are preferentially dissolved in the oxygen filtrate while the more oxidized components of all sizes are dissolved in the ozone filtrates.

The impact of oxygen on residual lignin structure and consequently on the ozone bleachability of oxygen bleached pulps is further addressed by the data shown in Figure 4. The graph shows the MWD of the components of the ozone filtrates (0.4% ozone charge) of kraft brownstock and two oxygen-bleached pulps. Oxygen bleaching significantly affects the MWD of the ozone byproducts; oxygen delignification causes ozone to solubilize more of the low molecular weight compounds. Apparently, the oxygen transforms the residual lignin so that the depolymerized (but still insoluble) residual lignin readily dissolves upon exposure to an effective oxidant such as ozone. These results are consistent with our earlier finding that moderately oxygen delignified pulp is quite efficiently ozone bleached at low charges (3). Oxygen delignification probably promotes ozone efficiency by producing residual lignin that is smaller in size and enriched in carboxylic acid groups compared to brownstock residual lignin.

We have made some effort to quantify identified small reaction products from ozone bleaching. One important product found in earlier work (4) was formaldehyde which was of interest because of it's mechanistic implications as well as for industrial hygiene reasons. As part of a Master's student project (S.M. Nooney, 1994), the amount of formaldehyde found in solution during ozone bleaching was quantified. A softwood kraft pulp, an oxygen delignified softwood kraft pulp, and cotton linters were ozonated at high consistency. The formaldehyde concentrations in the filtrates were measured by derivatization with pentafluorobenzylhydroxylamine and analysis by GC/FID. Approximately 0.1 mg CH_2O/g pulp was found in the filtrates of a softwood kraft pulp ozonated at approximately 1% charge, increasing to 0.2 mg/g at charges up to 4% ozone. These numbers represent about 1% of the TOC that is generally found in unneutralized ozone filtrates. Interestingly, the quantities of formaldehyde in the ozone filtrates of the cotton linters suggested that most of the formaldehyde generated in pulp ozonation could arise from carbohydrate degradation reactions. Attempts were made to measure gas phase formaldehyde. None was detected; however, it is impossible to rule out method interferences.

Fundamentals of improved bleachability of oxygen bleached pulps

The Wood Chemistry and the Pulping and Bleaching Groups have initiated a series of experiments to further examine the bleachability of oxygen delignified pulps. The goal of these studies is to find optimal conditions for efficient and selective bleaching using our knowledge of fundamental reactions that occur during various processes. Based on our earlier, preliminary results, these studies are designed primarily to address the question of how oxygen transformations of residual lignin and carbohydrates affects the ozone chemistry at a later stage. The approach and initial results of the oxygen bleaching is reviewed for this work in progress.

The general approach is to oxygen delignify three different brownstock pulps to a range of kappa numbers, and then to ozone bleach these pulps at 0.4% ozone charge (Figure 5). The oxygen delignification ranges are achieved by adjusting time and alkali charge. The ozone charge was selected on the basis of our earlier results in which we found improved delignification efficiency of moderately oxygen delignified pulp at lower ozone charges. The industrial pulps were obtained from one mill. Several controls are run to determine the effect of alkali, heat, and pressure, and to compare ozone results to a more conventional bleaching reagent (i.e.,

ClO_2). Each type of pulp (brownstocks, oxygen bleached, and ozone bleached) is evaluated for general quality and functional groups. Furthermore, the oxygen and ozone filtrates are analyzed to better understand the modes of delignification. The oxygen bleaching has been completed by the Pulping and Bleaching Group, and the ozone bleaching is in progress by the Wood Chemistry Group.

Some of the results from the oxygen bleaches are presented in Figures 6-9. The brownstock values are included and controls are indicated. Nitrogen controls consist of a cook in which nitrogen is used in place of oxygen and alkali charges are comparable to those used to achieve 50% delignification in the presence of oxygen. Oxygen controls have no sodium hydroxide added.

The data in Figure 6 show selectivity curves for the oxygen bleaches for the two kraft pulps. The kappa number 22 pulp fell on the same curve as the kappa number 31 pulp, suggesting that the modified cook in the digestor effectively reduced lignin without degrading the carbohydrates any more than oxygen does. A second noteworthy aspect of the kappa number 22 pulp was the rather straight curve down to kappa numbers below 10; it did not exhibit the typical steep downward curve of viscosity values when delignified beyond 50%.

Functional group analyses are given in Figure 7. There is loss of methoxyl group with delignification as expected, but the scatter at low kappa numbers may reflect preferential removal of free phenols. The carboxylic acids remain constant with increasing oxygen delignification for the pulp, which is different from other pulps with which we have worked. The carboxylic acid content remains approximately 0.06 meq/g pulp, even at the lower kappa numbers, where oxidation of the carbohydrates would be expected to have occurred extensively and the decrease of lignin is not likely to contribute very much to changes in the overall carboxylic content.

The zero-span tensile strength is given as a function of viscosity in Figure 8. The ozonated pulps are stronger at comparable viscosities of the oxygen pulps, which agrees with the conventional wisdom that the viscosity strength relationship of ozone pulps is different from other pulps. The control data indicate that strength losses in the oxygen pulps are not brought about by the oxygen itself, but by the temperature and pressure of the cook itself. To further verify this conclusion, a second nitrogen control (data not shown) was conducted in which no alkali was added to the reactor; the result was a pulp with a strength comparable to the other controls. Brightness as a function of kappa number is given in Figure 8, where the brightening effect of ozone compared to oxygen is apparent. Further residual lignin and filtrate analyses may allow us to determine which chromophores are oxidized by ozone resulting in brightness increases.

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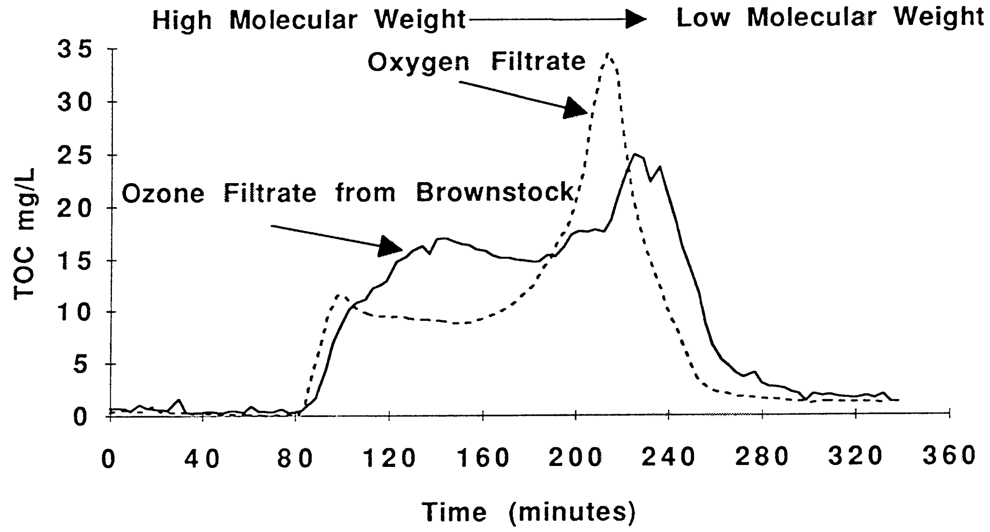

Figure 3. Molecular weight distributions of organic components of oxygen filtrates and ozone filtrates. Filtrates were diluted to provide comparable total organic carbon (TOC) concentration ranges.

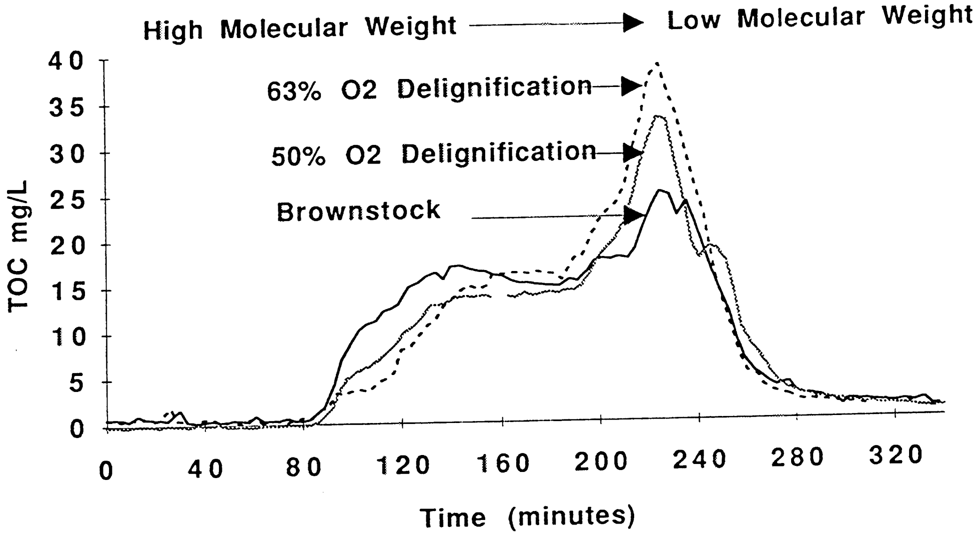

Figure 4. Molecular weight distributions of organic components of ozone filtrates obtained from ozonation of kraft and oxygen delignified pulps.

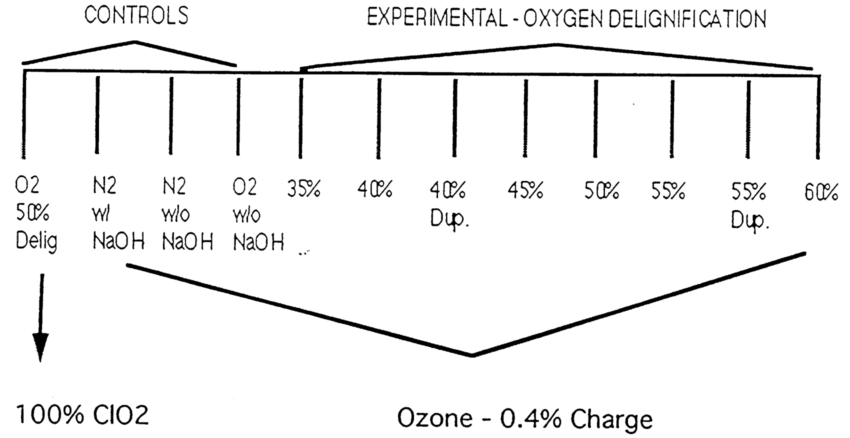

Figure 5. Experimental approach to current studies on the bleachability of oxygen delignified pulp.

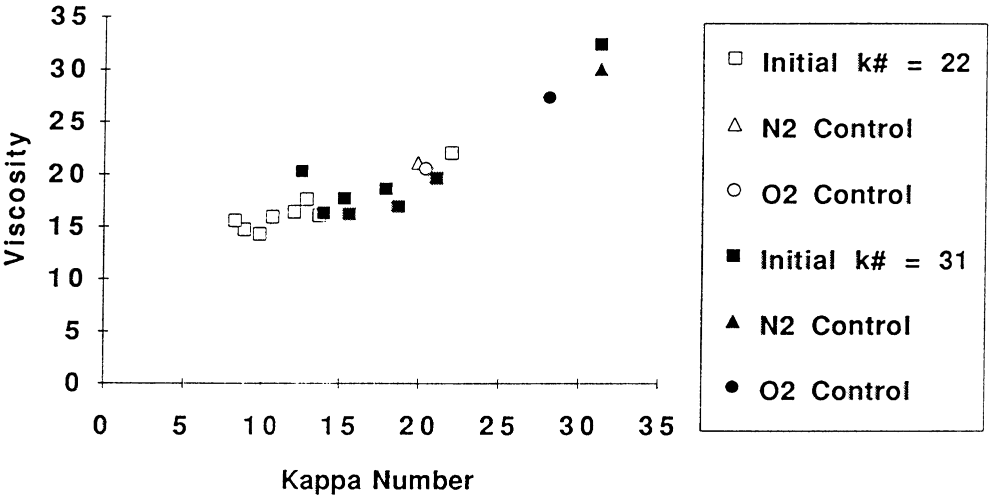

Figure 6. Kappa number and viscosity after oxygen bleaching two kraft pulps (initial kappa number 22 and initial kappa number =31).

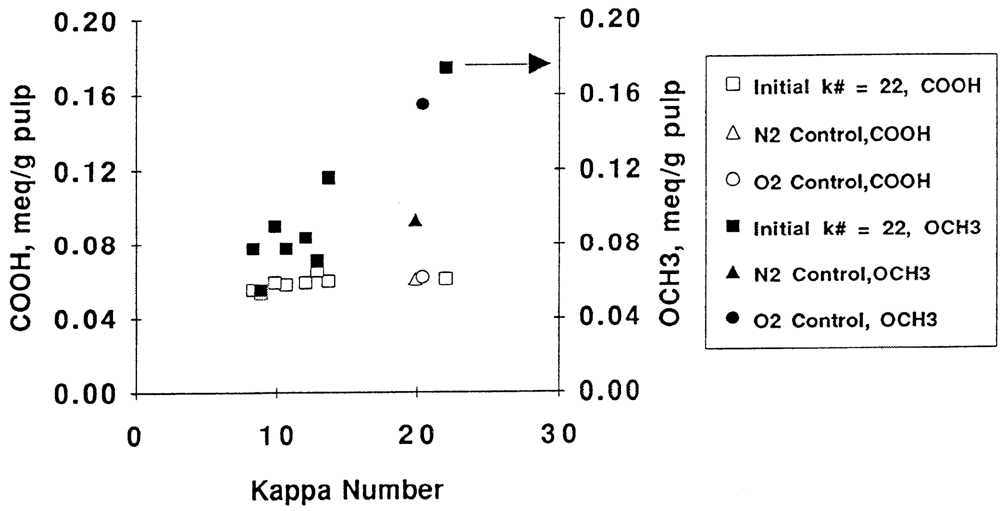

Figure 7. Carboxylic acid and methoxyl group content on pulp after oxygen bleaching a kraft pulp with an initial kappa number of 22.

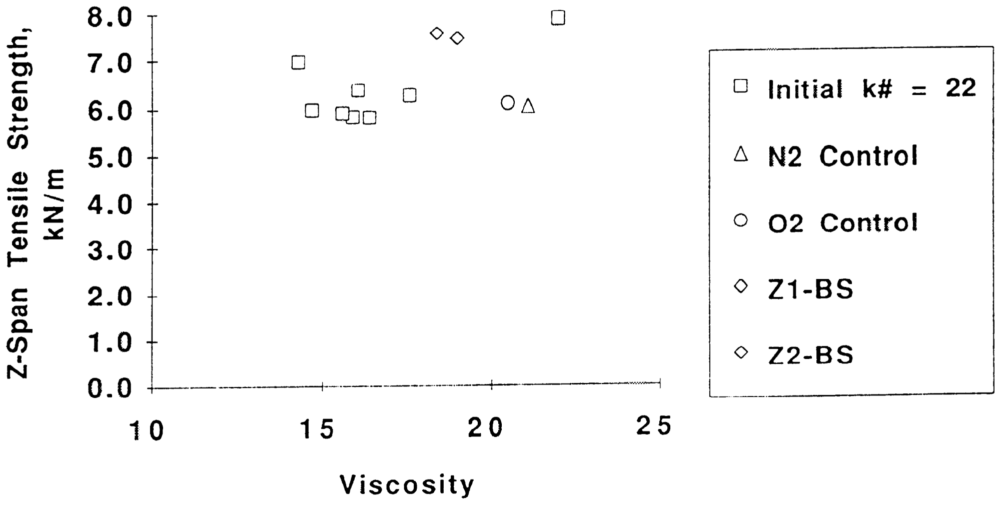

Figure 8. Zero-span tensile strength after oxygen bleaching a kraft pulp with an initial kappa number of 22.

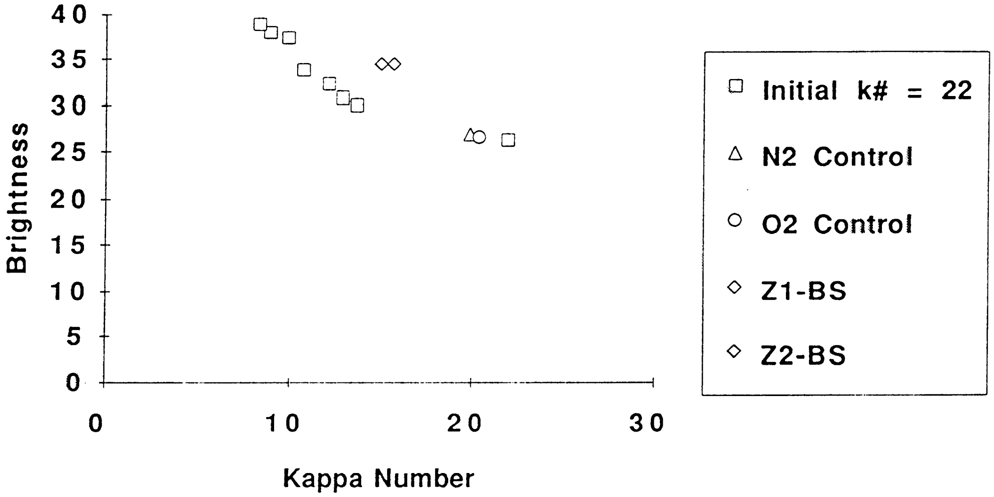

Figure 9. Brightness after oxygen bleaching a kraft pulp with an initial kappa number of 22.

Goals for FY 1994-1995

Completion of the extensive work in progress is a major goal for 1994-1995. When this series of studies is complete we will have generated a large database of information about the impact of different pulping and oxygen delignification processes on subsequent bleachability. This database will provide information about the chemistry of the processes coupled with data on pulp properties under controlled conditions. This approach will allow us to relate changes in chemical structures of pulp throughout pulping and bleaching processes to ultimate changes in bleached pulp properties.

SULFUR-FREE SELECTIVE PULPING PROCESS

PROJECT 3661

ANNUAL RESEARCH REVIEW

March 22, 1995

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Technical Program Review

DATE: February 27, 1995

PROJECT NUMBER, TITLE: 3661, SULFUR-FREE SELECTIVE PULPING PROCESS

PROJECT LEADER: Donald R. Dimmel

BUDGET (FY 94-95): $200,000

IPST GOAL: Improved pulping processes

OBJECTIVE: The objective of this project is to develop the synthesis of a low-cost catalyst which, when used in pulping systems, will increase pulping rates and product yields, while reducing the dependence on sulfur additives. The process under investigation is based on conversion of an inexpensive pulping by-product, lignin, to a useful quinone-type pulping catalyst.

SUMMARY OF RESULTS SINCE LAST REPORT:

Introduction:

A joint research effort between the Institute of Paper Science and Technology and the National Renewable Energy Laboratory (NREL) is being conducted on ways to produce cost-effective pulping catalysts from lignin. The funding for the research comes from the Department of Energy. Because of a discontinuity in funding, the research at NREL had a lapse of about 1 1/2 years (from October 1992 to February 1994). The disruption at IPST was less because we lagged behind NREL in receiving funds and, in anticipation of the lack of funding, we slowed the pace of the research to cover some of the dead period. Because of contract complications and a change in personnel at IPST, the actual amount of laboratory time spent on the project at IPST since the last major report (Feb. 1994) has been about 4-5 months.

The steps in producing pulping catalysts from lignin are shown in Figure 1. A lignin is treated with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones, which are converted into non-aromatic dimethylanthraquinone (DMAQ) precursors by treatment with a diene (Diels-Alder reaction). Final conversion of these precursors to DMAQ occurs by loss of methanol and hydrogen, either during reaction (Fig. 1) or in a separate step. The aromatization step may be unnecessary, since partially aromatic anthraquinone also functions as a pulping catalyst by *in situ* conversion to AQ.

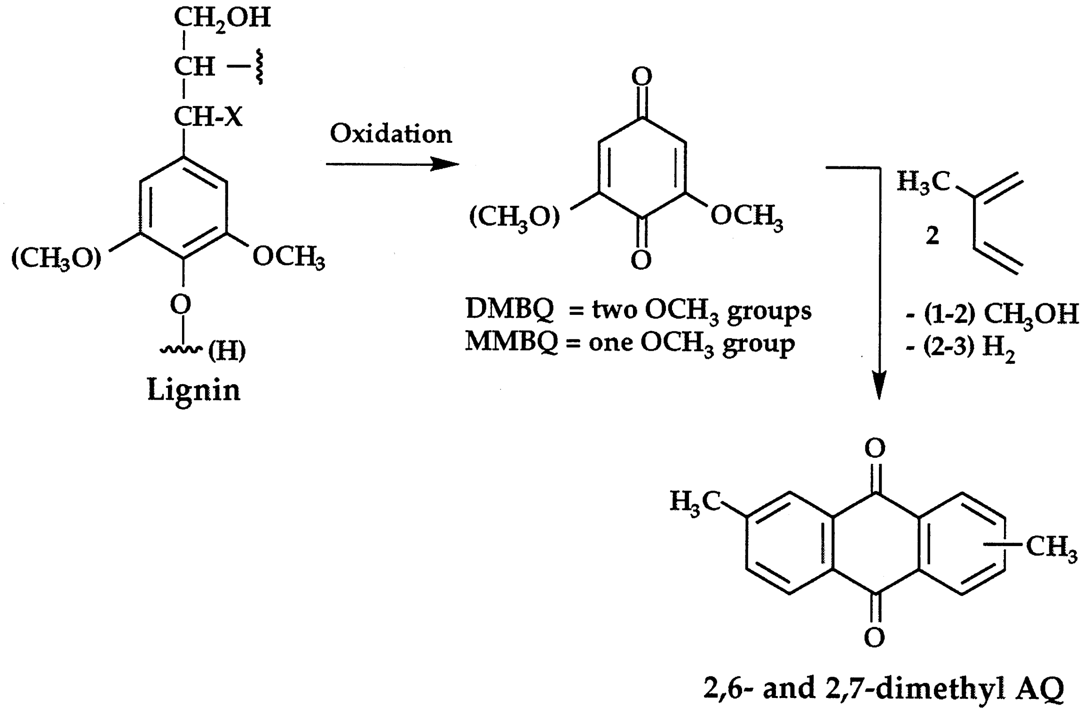

Figure 1. Chemical steps in the conversion of lignin to an AQ.

IPST Research Results since March 1994:

- We have conducted a larger scale (100x) NO_2 oxidation of syringaldehyde to dimethoxybenzoquinone (DMBQ); the yield was 84%.
- A Diels-Alder reaction with 1 g of DMBQ and excess isoprene gave 2 g of a mixture of 2,6- and 2,7-dimethylanthraquinone (DMAQ) and isoprene by-products.
- A crude chromatography removed most of the isoprene by-products. The resulting 1.3 g of product contained 40% DMAQ and 20% DMAQ-related components.
- The purified DMAQ mixture was tested for its ability to catalyze the alkaline pulping of pine and was shown to have the same activity as pure AQ.
- A pure sample of 2,6-/2,7-DMAQ was prepared and its catalytic pulping activity compared to the DMAQ mixture and to AQ. The pulping results indicated that (1) the DMAQ is twice as active as AQ, (2) the non-aromatic components of the mixcat may have little catalytic pulping activity, and (3) there was too much uncertainty in the data to develop a dose-response correlation.

- The DMAQ mixture was subjected to column chromatography in order to isolate the non-aromatic components from the mixture and determine their activity separately. However, during the chromatography, several of the non-aromatic components were converted to DMAQ. The components that aromatized by the silica gel will also likely be aromatized during pulping; separating and determining their activity will be difficult and possibly fruitless.
- NREL has conducted a larger scale DMBQ/isoprene reaction in an organic solvent in the presence of a Diels-Alder catalyst; their mixture of DMAQ-related products were also tested for catalytic pulping activity at IPST. The pulping results agree with what we have observed, namely that the activity is largely determined by the levels of DMAQ in the samples.
- We have conducted several aqueous Diels-Alder reactions in the presence of metal salts in an attempt to improve the yields of the aromatic component, DMAQ. Most of these trials were not successful, however, one metal experiment did improve DMAQ yields; additional studies will be done with this metal.
- If the yield of DMBQ from the oxidation of a low molecular weight lignin is 10% on a weight basis, then it appears that 100 g of lignin will provide 13 g of "AQ." This calculation is based on a limited set of experiments; therefore, care needs to be taken in making a firm set of conclusions.
- Several model NO_2 oxidations have been performed that have clarified the mechanism of DMBQ generation from phenolic substrates.
- NREL has also screened a number of oxidation technologies for preparing DMBQ from lignin. At this point, NO_2 appears to be the best with lignin.
- We have prepared a model which, when oxidized with NO_2 under select conditions, will allow us to assess methods to fragment lignins to monomers.
- The NREL/IPST team has prepared an annual report to DOE. We have also put together five papers for publication in the open literature on the results of NREL's organometallic oxidation studies and IPST's NO_2 oxidation reactions.

Planned Activities for FY 94-95:

- Continue to assess methods to fragment whole lignins to simple monomers, either prior to, during, or after NO_2 oxidation.
- Conduct further pulping studies with pure DMAQ and with the non-aromatic components in mixtures that contain DMAQ.

STATUS REPORT

Introduction

The research reported here outlines work done at IPST since the last Status Report. A substantial amount of research has been performed at NREL in the last year. As in other years, this will be described in our annual report to DOE, which will be submitted soon. The research at NREL compliments IPST research by examining alternative chemical synthesis methods, providing ways to get suitable lignin starting materials, and conducting technoeconomic evaluations. A very detailed description of the project and the research results to date is available in our past Status Reports, our publications,[1-11] and in the annual reports to DOE.[12-17]

A principal focus of the research has been to improve the overall yield of the synthesis; the yield is the most important factor in the cost of the catalysts. A large reduction in the cost of producing pulping catalysts from lignin has resulted from our research; significant improvements have been realized in the isolation, oxidation, and Diels-Alder steps. However, the yield of the first step is still low (15%).[11] The yield of benzoquinones from lignin needs to be approximately doubled to reach our targeted catalyst price of $1.00-1.50/lb. Research with lignin model compounds has indicated that only phenolic, syringyl lignin units are readily oxidized by NO_2.[8] This means that only *terminal* syringyl end units of a *hardwood* lignin polymer will be converted to benzoquinones by NO_2 oxidization.

Our research has shown that guaiacyl units (the dominant unit in softwood lignin) can be efficiently oxidized to benzoquinones if the guaiacyl units are first brominated to block the reactive 5-position.[9] However, such a step would probably be impractical in a low cost synthesis. We have also shown that the benzoquinone yields from certain hardwood lignins can be dramatically improved (from 3 to 15%) by treating the lignin with copper oxide before the NO_2 oxidation step.[11]

There appears to be four ways to improve yields of DMBQ from NO_2 oxidations of lignin: (1) lower the molecular weight of a whole lignin with treatments, such as copper oxide, before performing the NO_2 oxidation, (2) extract a lignin sample to obtain a low-molecular-weight fraction before NO_2 oxidation, (3) fragment the lignin during NO_2 oxidation, or (4) perform repetitive oxidation/fragmentation steps.

Scale-up of the NO_2 Oxidation Reaction

Large-scale NO_2 oxidation reactions have been done to examine the potential impact of scale up on the DMBQ yield. The substrate amount was 100 times larger than that used for routine small-scale runs. Reactions were performed in a 1 liter 3-necked round bottom flask at room temperature for 6 hours, using approximately 20 mL of methanol as solvent; no N-hydroxysuccimide was added. The results, which are summarized in Table 1, indicate that scaling up had little effect on the DMBQ yield.

Table 1. Yield data for the NO_2 reaction of syringaldehyde and lignin.

Starting material (g)	NO_2 (g)	DMBQ (g)	DMBQ %	Small-scale DMBQ %
Syringaldehyde (2.11)	2.5	1.6[a]	84[c]	81
Repap lignin #1109 (2.11)	2.9	0.14[b]	6.5[d]	6.4[d]

[a]obtained as solid; [b]estimated by GC; [c]mole % yield; [d]weight % yield.

Large-scale Diels-Alder Reaction

The following materials were placed in a 60 mL-capacity pressure vessel (bomb): 1 g of DMBQ, 6 mL of isoprene (10:1 mole ratio of isoprene:DMBQ), and 44 mL of water. The bomb was placed in an oil bath preheated to 167°C, tumbled in the bath at 167°C for 8 hours, and the tumbling continued overnight, with no external applied heat, as the temperature dropped slowly to 60°C. We wanted to run at 167°C for 24 hours but, for safety reasons, a heated oil bath could not be left unattended.

Approximately 2 g of crude product was recovered by chloroform extraction of the reaction mixture. Analysis by ^{1}H-NMR showed the presence of a large amount of aliphatic material, which was likely due to isoprene polymerization products. A crude chromatography was used to purify the product mixture. The crude product was placed on a column of silica gel and "washed" first with hexane (to remove the hydrocarbon isoprene components) and then with chloroform to give (after evaporation) 1.3 g of solid material. Both GC and ^{1}H-NMR analysis showed that the solid contained a much lower amount of aliphatic contaminants.

The yields of anthraquinone-related components (aromatic and nonaromatic) in the purified product mixture were estimated by GC after spiking the sample with a known amount of 2,3-dimethylanthraquinone; the latter is an isomer of the expected products and was assumed to have a GC response factor of 1.0 for the anthraquinone-related products. The principal product - a mixture of 2,6/2,7-dimethylanthraquinone (DMAQ) was present in 38% yield; the total AQ-like products yield was 57%. The purified product, called mix-cat, was then tested for its ability to catalyze the alkaline pulping of pine.

Alkaline Pulping Tests - First Experimental Set

Materials:	
Southern pine chips (on a dry basis)	60 g
AQ (commercial product)	30 & 60 mg
Mix-cat (synthesized)	30, 60 or 120 mg
Pulping conditions:	
NaOH (as Na_2O, % on wood)	18
Liquor-to-wood ratio (mL/g)	4
Time from 80°C to 100°C (min)	15
Time at 100°C (min)	15
Time from 100°C to 175°C (min)	90
Time at 175°C (min)	90

Pulping test results, which are summarized in Table 2, indicate that (1) the addition of AQ or mix-cat results in a substantial decrease of the pulp kappa number, meaning that delignification was promoted, and (2) the mix-cat and AQ have a comparable abilities as pulping catalysts.

Previous studies have shown that 2,6/2,7-dimethyl-AQ is twice as effective as AQ in promoting delignification.[3] If the activity of the mix-cat was <u>only</u> related to the DMAQ content (38%), the mix-cat should be ~75% as effective as AQ. If the nonaromatic components of the mixture were <u>as effective</u> as DMAQ in promoting pulping, the mix-cat should be ~14% more effective than AQ, since the total amount of AQ-like products in the mix-cat was 57%. Such differences (14-25%) are not easily determined by a single set of experiments; however, it appeared that the nonaromatic components of the mixture were contributing to the catalytic activity. To learn more about this aspect, we prepared some pure DMAQ for direct comparisons of its pulping activity to that of the mix-cat.

Table 2. Data of Soda AQ Pulping

Digester #	Additive	Addition % (on wood)	Pulp yield %	Pulp Kappa #
1	/	/	43.2	55.6
2	AQ	0.05	41.3	34.8
3	AQ	0.1	40.8	29.5
4	AQ	0.1	41.4	27.4
5	Mix-cat	0.05	41.7	35.1
6	Mix-cat	0.1	42.0	31.8
7	Mix-cat	0.1	40.6	29.1
8	Mix-cat	0.2	42.7	28.1

Isolation of 2,6/2,7-Dimethylanthraquinone

Since DMAQ is not commercially available, a sample of DMAQ was obtained by conducting a Diels-Alder reaction of DMBQ with isoprene, isolating the crude product mixture, and subjecting the mixture to a "filtration" through silica gel (to remove a large portion of the isoprene by-products), and then conducting a column chromatography separation. The chromatography was not, however, optimized to achieve the maximum separation of components; the column may have been somewhat over loaded, the elution was done rapidly, and solvent changes were performed frequently. The solvent system contained increasing amounts of toluene in hexane. The early fractions from the chromatography were composed of DMAQ, non-aromatic DMAQs, and naphthoquinones; however, later fractions contained relatively pure DMAQ. These fractions were combined and recrystallized from methanol; the resulting solid (a mixture of 2,6- and 2,7-DMAQ) was pure, based on GC analysis.

Alkaline Pulping Tests - Second Experimental Set

Additional pulping experiments were performed in order to compare the activity of pure DMAQ to that of our mix-cat and to that of pure AQ. The purpose of this study was to establish the catalytic activity of DMAQ relative to that of AQ and to determine if the non-aromatic DMAQs had pulping activity. Previous work in our laboratory[3] indicated that DMAQ was roughly twice as active as AQ and the first experimental set suggested that non-aromatic DMAQs may have some catalytic pulping activity.

The new pulping studies compared a 0.05% charge of DMAQ to 0.10% AQ and to varying charges of mix-cat. The charges selected for mix-cat were based on the following reasoning:

- If the non-aromatic DMAQs were as active as DMAQ then a charge of mix-cat of 0.08% should have the same activity as 0.05% DMAQ, since 0.08% x 60% (total DMAQ + non-aromatic DMAQs content) = 0.05%.
- If the non-aromatic DMAQs had no activity then a charge of mix-cat of 0.12% should have the same activity as 0.05% DMAQ, since 0.12% x 40% (DMAQ content) = 0.05%.
- If the non-aromatic DMAQs had some activity then a charge of mix-cat of 0.10% may have the same activity as 0.05% DMAQ.
- One additional higher charge of mix-cat was also examined in order see if a linear correlation exists for mix-cat charge to kappa number. [Actually, the correlation should be to the square root of the charge to the kappa number.]

The pulping studies were conducted with the same chips and presumably under the same conditions as used in the first experimental set; the results are presented in Table 3. The second run gave more lignin removal, suggesting that the temperature may have been higher than in the previously pulping run. Two duplicates were performed; the one with pure AQ showed a larger (1.1%) variability in kappa number than expected; the other, a duplicate of pure DMAQ, failed because of a bomb leak. The latest pulping results suggest that (1) the DMAQ is twice as active as AQ, (2) the non-aromatic components of the mix-cat may have little catalytic pulping activity, and (3) there was too much uncertainty in the data to develop a dose-response correlation.

Table 3. Comparison of the Effectiveness of Pulping Additives

Run	Additive	Level - % odw	Pulp Yield	Kappa Number
1	AQ	0.10	41.1	24.8
2	AQ	0.10	41.5	25.9
3	DMAQ	0.05	42.7	25.0
4	mix-cat	0.08	41.7	27.8
5	mix-cat	0.10	42.0	27.3
6	mix-cat	0.12	41.9	26.0
7	mix-cat	0.14	45.2	26.3

With a kappa number variability of ±1 unit, it will be difficult to determine the pulping activity of the (20%) non-aromatic components. The best approach to resolve this question is to isolate the non-aromatic components from the mixture and determine their activity separately. However, we have found that several non-aromatic components are converted to DMAQ during column chromatography. This presents a dilemma. The most important non-aromatic components cannot be tested for pulping activity because they cannot be readily isolated, while the least important non-aromatic components (the ones that can be isolated) will probably have low pulping activity. The reactive ones will probably aromatize during pulping and contribute to the activity of the mix-cat, as if they were DMAQ molecules; the least reactive ones will likely remain unaromatized and inactive.

Alkaline Pulping Tests - Third Experimental Set

Personnel at NREL have also conducted larger scale DMBQ/isoprene reactions; they are examining different catalysts that promote the Diels-Alder reaction in an organic solvent. Their mixture of DMAQ-related products were also tested at IPST for catalytic pulping activity; their samples contained relatively high amounts of naphthaquinone (NQ). The results are given in Table 4. The pulping results agree with what we have observed, namely that the activity is largely determined by the levels of DMAQ in the samples and that DMAQ is roughly twice as effective as AQ. The naphthaquinones do not have a large amount of pulping catalytic activity, confirming what we observed years ago.[3]

Table 4. Comparison of the effectiveness of NREL quinone mixtures

Run	Additive	Add. - % odw	Pulp Yield	Kappa #
1	AQ	0.05	45.8	37.5
2	AQ	0.10	45.8	33.2
3	~50% DMAQ/~50% NQ	0.10	45.7	35.3
4	~50% DMAQ/~50% NQ	0.10	45.7	34.2
5	~0% DMAQ/~100% NQ	0.10	47.4	53.2
6	~0% DMAQ/~100% NQ	0.20	46.1	52.0
7	~40% DMAQ/~60% NQ	0.10	46.6	41.9
8	~40% DMAQ/~60% NQ	0.10	46.1	42.0

Diels-Alder Modifications

We have conducted several aqueous Diels-Alder reactions in the presence of various iron salts and in the presence of NO_2 in attempts to improve the yields of DMAQ. The rational behind selecting these reagents is that the first step in the Diels-Alder reaction provides a non-aromatic adduct that probably rapidly aromatizes to a naphthahydroquinone by loss of methanol and enolization (Figure 2). The naphthahydroquinone is not a suitable reactant for another Diels-Alder reaction; it must be oxidized to a napthoquinone before further reaction can occur. How this oxidation occurs in our system is not known with certainty. However, if a reagent were present in the system that could promote the oxidation, without harming the other reactants, the reaction rate and final DMAQ yield would probably improve. Iron salts and NO_2 are know to oxidize hydroquinones to quinones.

Aqueous Diels-Alder reactions that were done with different levels of NO_2, iron sulfate, and iron nitrate led to poor yields of DMAQ (0-7%, compared to a control of 22%). However, an experiment with a more exotic metal did improve DMAQ yields; more will be reported about this metal after patent issues have been addressed. Additional studies will be done with this metal.

NO_2 Oxidation Studies

Additional experiments have been performed to clarify the mechanism of action of NO_2 as an oxidant that converts phenolic units to benzoquinones. These experiments have been incorporated into the papers that are attached to this report.

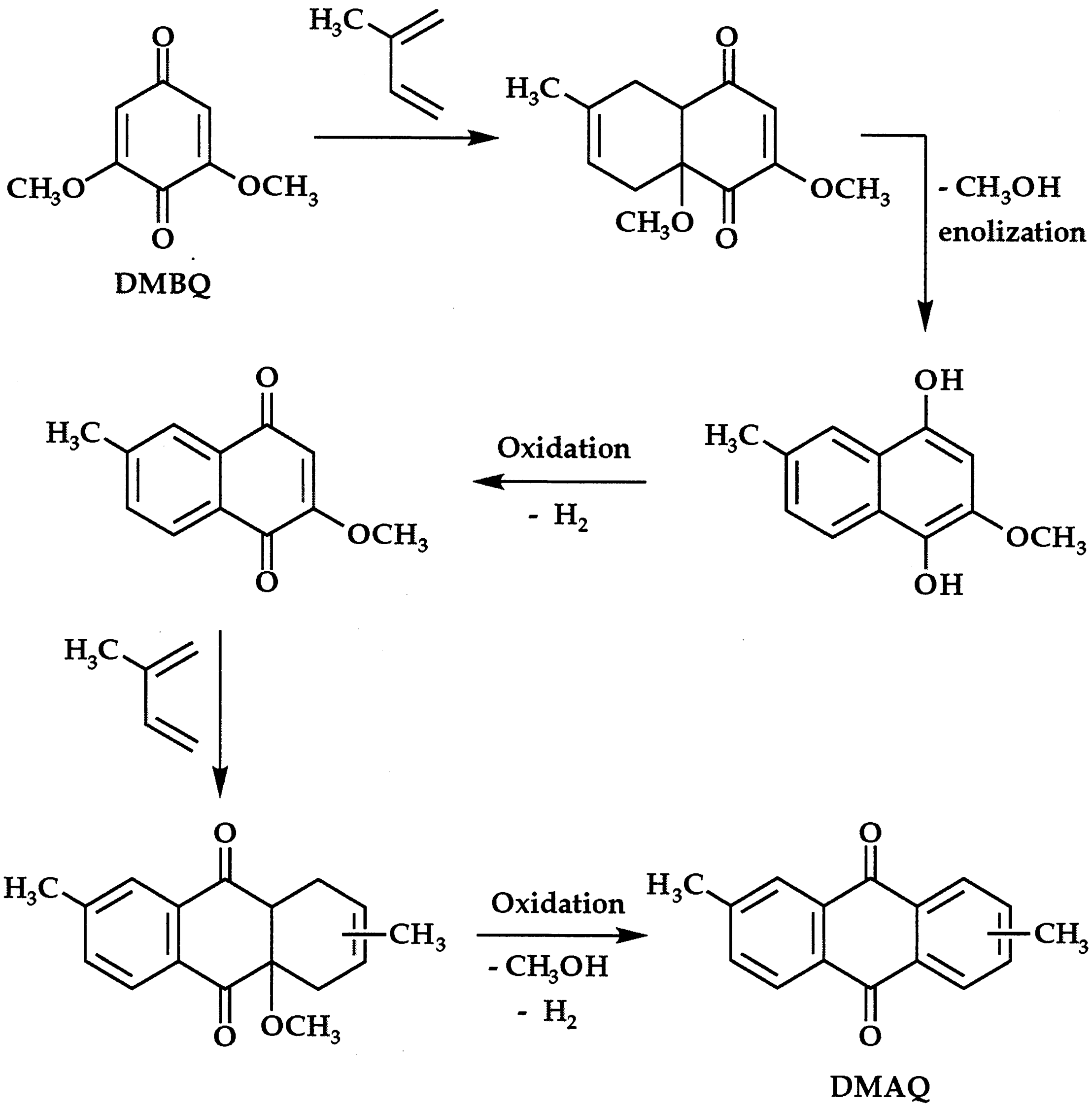

Figure 2. Steps in the conversion of DMBQ to DMAQ.

Summary

All indications continue to point to the fact that DMAQ is twice as active as AQ. We are uncertain as to the catalytic activity of the non-aromatic components in our Diels-Alder mixtures. One gram of DMBQ gave 1.3 g of mix-cat that has the same pulping activity of AQ. If we assume that the yield of DMBQ from the oxidation of a low molecular weight is 10% on a weight basis, then it appears that 100 g of lignin will provide 13 g of "AQ." Combining this observation with our previous cost analyses, we project that with our present synthesis yields would result in an effective "AQ" cost of about $2.50-3.00/lb.

We now have a good understanding of the chemistry of the NO_2 oxidation reactions. We are assessing methods to fragment lignins to monomers before, during, and after NO_2 oxidation.

Future Studies

Future research will focus on evaluating different starting materials, improving the yields of the synthetic steps, optimizing process steps, and evaluating the properties and performance of pulps which result when using the new catalysts, both in the absence of and in combination with sulfur additives.

The scale of the lignin-to-catalyst process will be progressively increased in size, thus, allowing more complete evaluation of the process steps and product characteristics. The size will be sufficient for updating technoeconomic assessments and for demonstrating the feasibility of each stage of the process prior to pilot plant operation and transfer of the technology to the industry.

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PULPING CATALYSTS FROM LIGNIN (5).

NOTROGEN DIOXIDE OXIDATION OF LIGNIN MODELS TO BENZOQUINONES

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PULPING CATALYSTS FROM LIGNIN (5). NITROGEN DIOXIDE OXIDATION OF LIGNIN MODELS TO BENZOQUINONES

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ABSTRACT

Several syringyl lignin models have been oxidized to 2,6-dimethoxy-*p*-benzoquinone (DMBQ) in high yields with nitrogen dioxide (NO_2) in methanol solvent. The yields of DMBQ were high for syringyl alcohol, syringaldehyde, and disyringyl methane and moderate for several other phenolic syringyl models. No benzoquinone was formed from non phenolic substrates. The yields were slightly improved by the presence of N-hydroxysuccimide. Guaiacyl lignin model compounds gave low benzoquinone yields; the major products were C-5 nitro substituted compounds. A radical mechanism is proposed to explain the observed results.

INTRODUCTION

We have been investigating ways to convert lignin to anthraquinone-type pulping catalysts.[2] The oxidation of certain lignin model compounds with Fremy's salt, $(KO_3S)_2N\text{-}O\bullet$, can provide high yields of methoxy-substituted benzoquinones in many cases;[2a] the benzoquinones can be treated with isoprene to give 2,6- and 2,7-dimethylanthraquinone (Fig. 1).[2b]

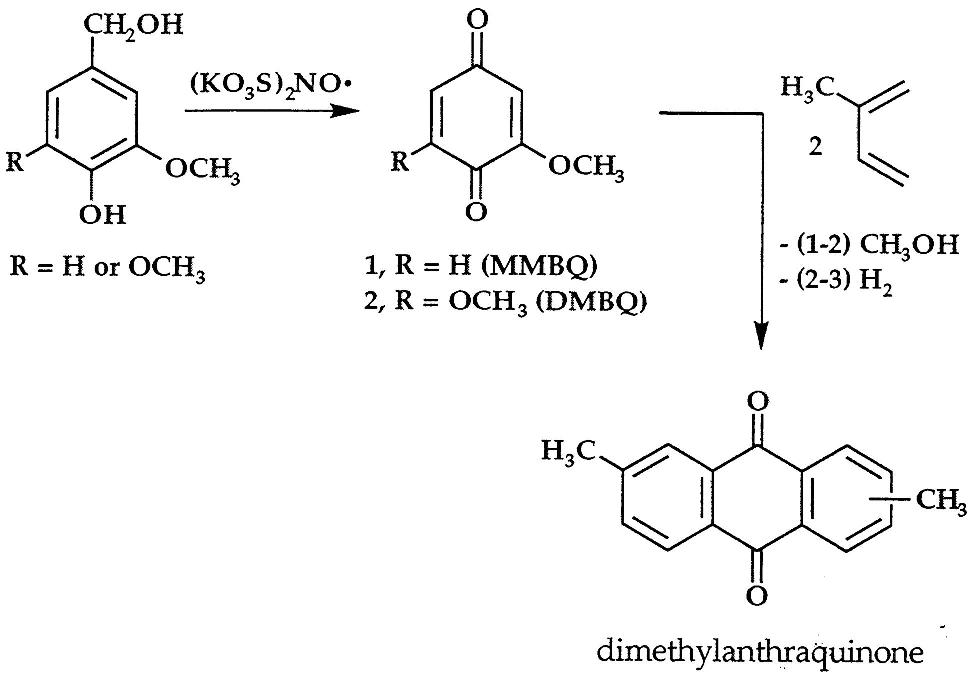
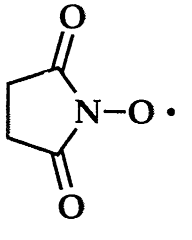


Figure 1. Steps in the conversion of a lignin model to an AQ-type catalyst.[2d]

Fremy's salt has been shown to be good oxidizing agent for converting certain lignin-like structures to benzoquinones;[2a] however, the reagent is expensive and its reactivity is unpredictable when used on large scale.[3] Therefore, we sought another oxidizing agent that was more suitable for commercial use. A reagent that might mimic the action of Fremy's salt is the radical of N-hydroxysuccimide (NHS), **3**. The parent compound, NHS (**4**), is commercially available and can be readily prepared from the amide **5**, a likely product of an NHS oxidation.



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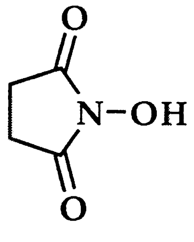

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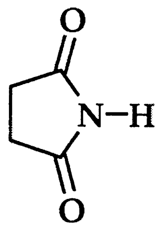

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A potential way to generate the NHS radical might be to treat NHS with nitrogen dioxide (NO_2), a natural radical. The latter is also capable of abstracting hydrogen atoms from phenols.[4] This led to the hypothesis that the combination of NO_2/NHS might oxidize appropriately substituted phenols to a benzoquinones by the chemistry shown in Figure 2. While the reactions of NHS• with lignins was our initial focus, we soon realized that NO_2 was an effective oxidizing agent in the absence of NHS. The investigation reported here examines the potential scope of NO_2 oxidations with lignin-related compounds.

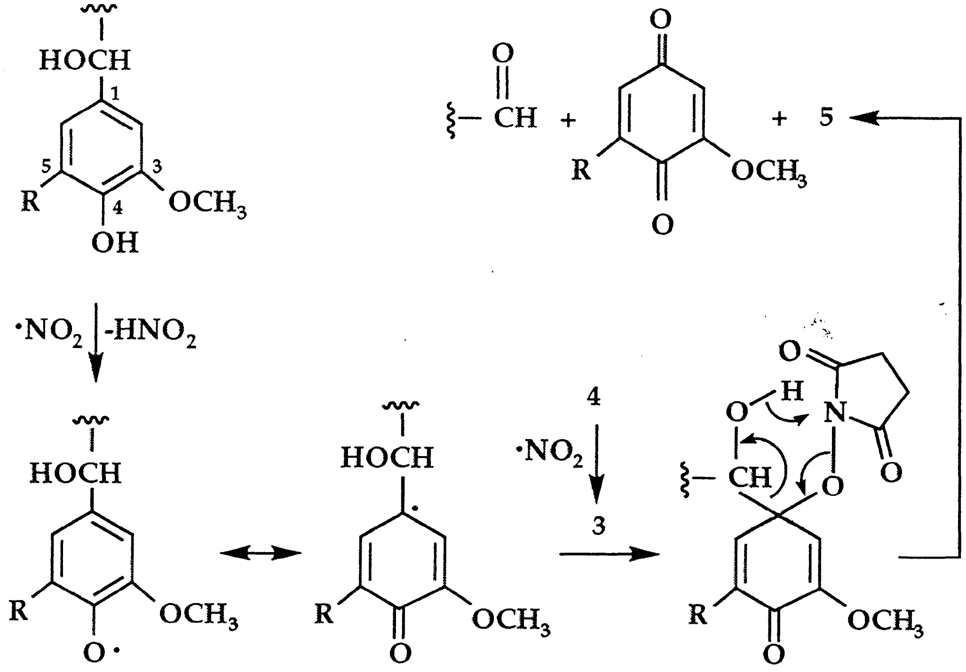
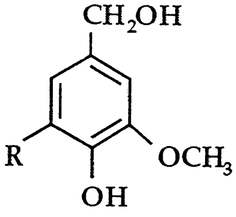


Figure 2. Projected phenol oxidation chemistry for NO_2/NHS.

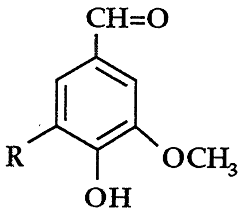
RESULTS AND DISCUSSION

Initial NO_2 Oxidations

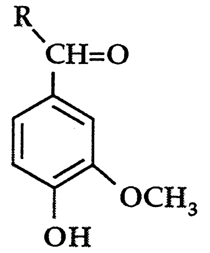
We began our studies by examining the reactions of vanillyl alcohol (6) and syringyl alcohol (7) with NHS/NO_2. These compounds are representative of the terminal guaiacyl and syringyl units found in softwood and hardwood lignin polymers.[5] While the compounds lack the typical 3-carbon side chain found in lignin units, they at least have a benzyl hydroxyl substituent that is common to many lignin units.



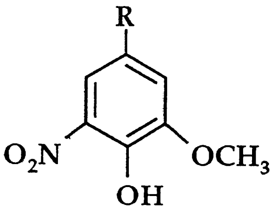
6, $R = H$
7, $R = OCH_3$



8, $R = H$
9, $R = OCH_3$



10, $R = CH_3$
11, $R = OH$



12, $R = CHO$
13, $R = NO_2$

We initially tried to react syringyl alcohol with NO_2/NHS in chloroform solvent; however, NHS is not very soluble in $CHCl_3$ and little happened. Ethylene glycol was then added to the NO_2/NHS/$CHCl_3$ mixture to dissolve the NHS and a noticeable reaction commenced. Subsequently, the reactions were carried out with ethylene glycol as the solvent. No noticeable reaction occurred when syringyl alcohol (7) was stirred for several hours with 2 equiv. of NHS in ethylene glycol. However, when 6 equiv. of NO_2 was added, the reaction mixture turned yellow and, after 10 minutes, gas chromatography (GC) analysis showed 2,6-dimethoxybenzoquinone (DMBQ, **2**) as the principal product.

Several lignin model compounds were then oxidized with NO_2/NHS in ethylene glycol. Compounds having a benzylic hydroxyl group, **6** and **7**, reacted rapidly; the starting materials were consumed after 10-15 minutes. Vanillyl alcohol (**6**) provided some monomethoxybenzoquinone (MMBQ, **1**); however, the major product was 5-nitrovanillin (**12**). Compounds containing an α-carbonyl group, such as vanillin (**8**) and syringaldehyde (**9**) and the ketone acetosyringone (**10**), reacted much more slowly than the benzyl alcohols; also, the benzoquinone yields were poor. Vanillic acid (**11**) gave no MMBQ under the standard conditions, but did produce some 4,6-dinitroguaiacol (**13**) in the presence of excess NO_2.

The relatively slow reaction and low yields of DMBQ observed for α-carbonyl compounds were attributed to the co-production of cyclic acetals under the reaction conditions. Nitrous acid (HNO_2), which is generated *in situ* by hydrogen atom extraction reactions of NO_2, could catalyze the reaction between the carbonyl compound and ethylene glycol to give a cyclic acetal (**14**) (Figure 3). [The acid catalyst could also be nitric acid (HNO_3), which is a disproportionation product of nitrous acid.[6]] The

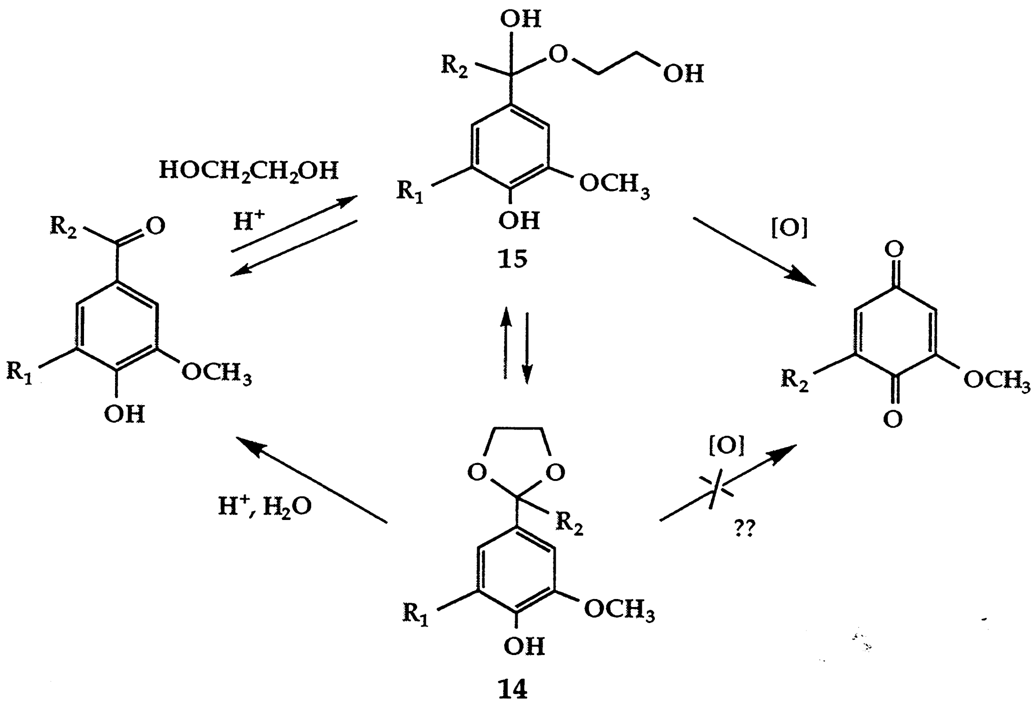


Figure 3. Proposed intermediates in the oxidation of aldehydes and ketones in ethylene glycol.

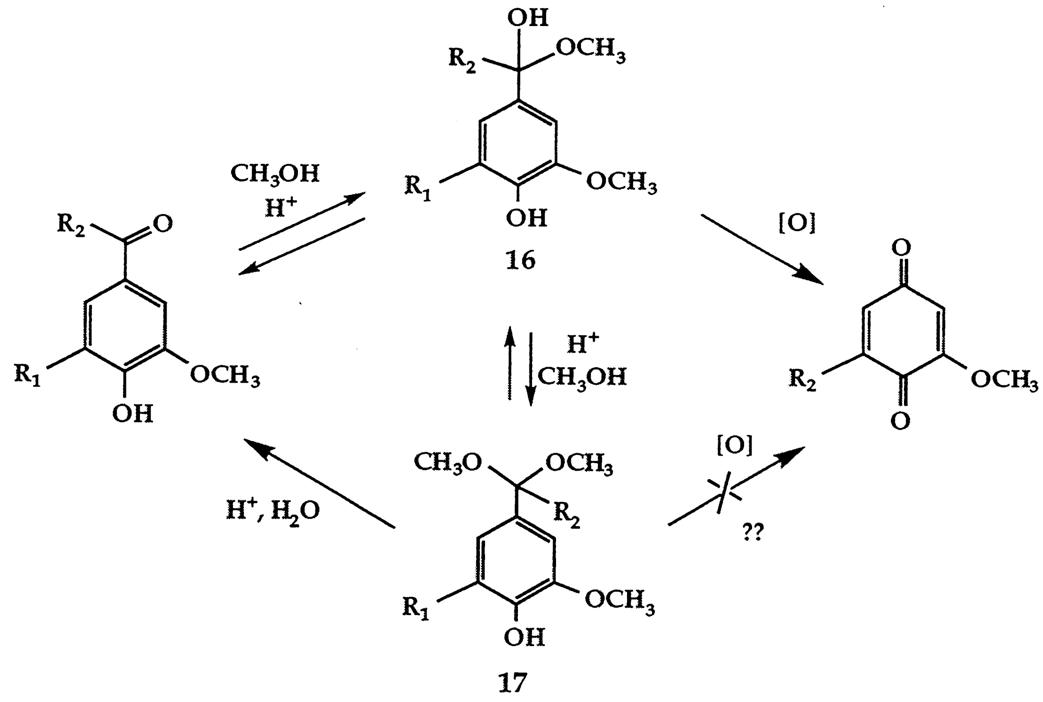


Figure 4. Proposed intermediates in the oxidation of aldehydes and ketones in methanol.

product mixture from the NO_2 oxidation of syringaldehyde contained a substantial amount of syringaldehyde cyclic acetal. The acetal was prepared by stirring a mixture of syringaldehyde and ethylene glycol in the presence of nitric acid. However, the acetal was difficult to isolate without decomposition. Oxidation of a 3/2 mixture of the cyclic acetal and syringaldehyde with NO_2 in ethylene glycol gave only a 7% DMBQ yield.

The NO_2/NHS oxidation of vanillin in ethylene glycol gave a 19% yield of MMBQ after 90 min, along with a substantial amount of another component. This other component disappeared when the reaction mixture was contacted with water and vanillin was formed. Obviously, an acid catalyzed reaction had occurred between vanillin and ethylene glycol that gave a cyclic acetal, which then reverted back to vanillin upon contact with water.

We suspect that cyclic acetals of aldehydes and ketones are not readily oxidized by NO_2/NHS and, thus, the benzoquinone yield is low in these cases. However, a hemiacetal is an alcohol and might be oxidized by NO_2/NHS. A cyclic acetal will be less prone to revert to an aldehyde, or an acyclic hemiacetal (**15**), than would a noncyclic acetal (**16**, Fig. 4).[7] Therefore, we decided to carry out NO_2 reactions in methanol, where the equilibrium concentration of aldehydes and hemiacetals may be greater. Aldehyde substrates were completely reacted after 4 hours; syringaldehyde provided a 90% yield of DMBQ.

Optimization of Reaction Conditions

The yield improvement observed with methanol prompted us to survey several other solvents (Table 1). Optimum reaction conditions for the conversion of syringyl alcohol (7) to DMBQ were 5-6 equiv. of NO_2 and 2-3 equiv. of NHS in MeOH for 30 minutes. The stability of DMBQ toward the reaction conditions was good for all solvents tested, with methanol giving reproducibly high DMBQ yields. Ethanol was a less effective solvent, as were water-alcohol mixtures and nonhydroxylic solvents.

The reasons for the superiority of methanol as a solvent for the NO_2 oxidations is probably a combination of factors: a reasonable level of hemiacetal may be available for reaction; DMBQ is not very soluble in MeOH

Table 1. DMBQ Yields from NO_2 oxidations of syringyl alcohol (7) in various solvents after 30 min reaction at room temperature.

Solvent	DMBQ (%)[a,b]	NHS[c]
Methanol (anhydrous)	87, 86, 89[d], 80[e]	+
	81, 80, 81	-
2% Aq. Methanol	76	+
4% Aq. Methanol	76	+
20% Aq. Methanol	60[e], 63[e,g]	+
20% Aq. Methanol	55[e,f]	-
40% Aq. Methanol	53[e]	+
Ethanol (anhydrous)	25[e], 22[e,f], 25[e,g]	+
20% Aq. Ethanol	24[e]	+
Ethylene Glycol	33[d], 14[e]	+
Water	25[h]	+
Ethyl Acetate	18[d]	-
DMSO	14	-
Diethyl ether	13	-
Chloroform	10[d]	+
1,4-Dioxane	2	-
3-Methylbutanone	5	-
Acetonitrile	0	+

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[a] Conditions (unless stated differently): 100^+ mL headspace; 5-6 eq. of NO_2; 2 mL of solvent. [b] Yield based on direct HPLC analysis of reaction mixture using an external standard. [c] 2-3 eq. when used (+). [d] GC yield for 4 mL of solvent, 2.5 eq. NO_2, 90 min, and anthraquinone as an external standard. [e] 2.5 mL headspace; 5-6 eq. of NO_2; 1 mL of solvent. [f] 15 min oxidation period. [g] 60 min oxidation period. [h] Isolated yield.

(precipitation would drive the reaction to completion and reduce secondary reactions); methanol is known[8] to react with NO_2 at room temperature to give MeONO and HNO_3 - possibly MeONO is a reactive oxidant.

Table 1 presents examples of oxidations in the absence of NHS. The yields of DMBQ from syringyl alcohol oxidation dropped by ~7% in the absence of NHS (88% -> 81% and 62% -> 55% for methanol and 20% aq. for methanol, respectively). Raising the ratio of NHS to syringyl alcohol from 2:1 to 4:1 in the presence of 4 equiv. of NO_2 dropped the yield of

DMBQ from 89% to 40%. Consequently, there is an optimium NHS concentration (~2 equiv.) that leads to the best yields of DMBQ. Similar trends have been seen in the case of oxidation of syringaldehyde.[9] The role of NO_2 in the NO_2 oxidations will become clearer in an subsequent publication.[10] The yields of DMBQ from model and lignin[9] oxidations are improved by the presence of moderate amounts of NHS in the system.

The oxidation of syringyl alcohol with varying amounts of NO_2 in the absence of NHS was examined (Table 2). The data given by entries 1-3 suggest that complete oxidation requires one equivalent of NO_2 with respect to the starting material. At higher concentrations the yields decreased somewhat. Substrate concentration has been found to have no significant effect on the yield of the desired product (Table 3). Optimum reaction times depend on the substrate: ~30 min for syringyl alcohol and ~3 hr for syringaldehyde. The probable reason for the slower reaction of the aldehyde is the competing formation of acetals, which are in equilibrium with reactive hemiacetal intermediates.

Table 2. Effect of NO_2 concentration on the oxidation of syringyl alcohol in methanol.

Entry	NO_2 (equiv.)	DMBQ (%)	9 (%)	% Unidentified
1	0.27	25	12	63
2	0.50	49	5	46
3	0.74	72	2	26
4	1.00	62	2	36
5	1.50	51	5	45
6	2.00	63	7	30

Table 3. Effect of syringyl alcohol (**7**) concentration in methanol with 4 equiv. of NO_2 in the absence of NHS.

Entry	7 (mM)	DMBQ (%)
1	125	69
2	63	62
3	42	68
4	31	64

We were curious to see what influence base would have on DMBQ yields. The autoxidation of phenols occurs more readily with phenolate ions than with neutral phenols.[11] The same may be true in NO_2 reactions. However, the NO_2 oxidation of syringyl alcohol in aqueous NaOH or $NaOCH_3/HOCH_3$ gave no more than a 10% yield of DMBQ, considerably below the typically 87-89% yield.

Concerning the reaction vessel size, there was 22% less DMBQ formed from 7 when the solvent volume was lowered from 2 to 1 mL and the headspace was simultaneously lowered from 100 to 2.5 mL. Additional headspace effects can be seen in the data given in Table 1. This yield reduction observation suggested that the amount of air in the reaction was a significant factor in NO_2 reactions. Consequently, a set of oxidations were run in the absence of air.

We examined two methods for air removal and two levels of NHS (one with NHS and one without); the results are given in Table 4. The small variation in the absolute yields have no obvious explanation; however, it is apparent that the oxidation proceeds to a high level in the absence of air. In the two cases studied, NHS did not help the yield.

Table 4. DMBQ yields as a function of air removal and the presence of NHS on the 2 hr NO_2 reaction of syringyl alcohol in methanol.

Air Removal Method	NO_2 Equiv.	NHS Equiv.	% DMBQ
Nitrogen purge[a]	9.5	--	85
Nitrogen purge[a]	8.6	2.9	81
Freeze-thaw/high vacuum[b]	5.5	--	76
Freeze-thaw/high vacuum [b]	5.3	3.2	62

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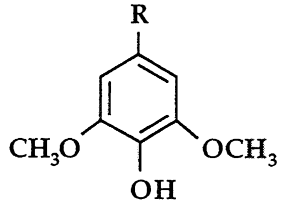
[a] Prior to NO_2 reaction, the solution was twice cooled to -78°C and subjected to high vacuum for 10 min. [b] Prior to NO_2 reaction, the solution was frozen using liquid nitrogen and then melted under high vacuum; the vacuum was replaced with argon.

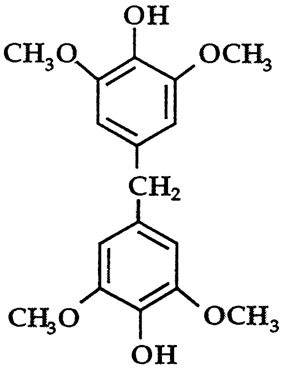
Finally, it should be noted that fresh NO_2 or material from a carefully sealed bottle should be used. We have observed poorer yields with certain batches of older NO_2.[9]

NO_2 Oxidations of Syringyl Lignin Models

Several additional model compounds have been subjected to the NO_2 oxidation conditions (Table 5). The data clearly indicate that a variety of side chains can be oxidatively cleaved when reacting syringol substrates with NO_2. The yields of DMBQ are high for benzyl alcohol (7), aldehyde (9), and benzyl (**24**) side chains, moderate for allyl (**21**), methyl (**20**), and methoxymethyl (**19**), and poor for a ketone (**18**), acid (**22**), and ester (**23**).



7, R = CH_2OH
9, R = CHO
18, R = $C(=O)CH_3$
19, R = CH_2OCH_3
20, R = CH_3
21, R = $CH_2CH=CH_2$
22, R = CO_2H
23, R = CO_2CH_3



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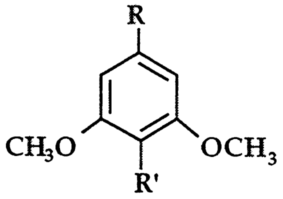

25, R = CH_2OH, R' = H
26, R = $\underset{\mathrm{OH}}{\mathrm{CHCH_3}}$, R' = OCH_3

Table 5. Yields of DMBQ from the NO_2 (5.5 equiv.) oxidations of selected syringyl models in methanol for 3 hr with 2 equiv. of NHS.

Entry	Substrate	% DMBQ
1	Syringyl alcohol (**7**)	88
2	Syringaldehyde (**9**)	90
3	4-Methoxymethyl syringol (**19**)	40
4	4-Methyl syringol (**20**)	38
5	4-Allyl syringol (**21**)	30
6	Disyringyl methane (**24**)	85[a]
7	Acetosyringone (**18**)	20
8	Syringic acid (**22**)	-
9	Syringic acid methyl ester (**23**)	-
10	3,5-Dimethoxybenzyl alcohol (**25**)	-
11	1-(3,4,5-Trimethoxyphenyl)ethanol (**26**)	-[b]

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[a] A 100% yield corresponds to the production of 2 equiv. of DMBQ in this case. [b] Discussed in greater depth in paper 7 in this series; the products were **26** - 60% and **9** + **19** - 40%.[12]

A phenolic hydroxyl group is essential for oxidation to a quinone; nonphenolic compounds **25** and **26** gave no quinones. Except for -CHO, carbonyl compounds generally provided poor yields of DMBQ. The oxidation of disyringyl methane, which has two syringyl units, provided nearly two equivalents of DMBQ (Table 5, entry 6). Obviously, disyringyl methane must have undergone side chain cleavage to give a highly reactive co-product, such as **7** or **9**, that was also oxidized to DMBQ.

Oxidation of a 3/2 mixture of cyclic acetal **14** (R_1=OCH_3, R_2=H) and syringaldehyde with NO_2 in methanol gave a 61% yield of DMBQ; the yield was only 7% in ethylene glycol. It appears that, over the 2-hour reaction period, about half of the cyclic acetal was converted (via acid catalyzed solvolysis) to a hemiacetal (**16**, R_1=OCH_3, R_2=H) that was oxidized.

Additional oxidation studies of acetosyringone (**18**) indicated a yield of 18% DMBQ after 2 hours; only 8% of the starting material remained. Other products were not detected by GC, which implies an oxidative degradation of unknown origin. A few drops of concentrated sulfuric acid were added in one experiment to promote the formation of a hemiacetal. The yield of DMBQ did not improve. Extending the reaction time to 24 hours only improved the yield to 25%. The ketone may be slow to react because, unlike aldehydes, acetal formation is rather slow.[13]

NO_2 Oxidations of Guaiacyl Lignin Models

The NO_2 oxidation of some guaiacyl models was studied in order to understand the low yields of MMBQ from vanillyl alcohol. The MMBQ yield varied with the amount of NO_2 used in the reaction. With 6 equiv. of NO_2 in MeOH, the MMBQ yield from vanillyl alcohol was only 5%; with 2.5 equiv., the yield was 11-18%. Vanillyl alcohol was completely consumed in these reactions. With excess NO_2, the major product was 4,6-dinitroguaiacol (**13**). The other products were 5-nitrovanillyl alcohol, 5-nitrovanillin (**12**), and 4-nitroguaiacol; their yields depended on the amount of NO_2 used. Oxidation of *p*-hydroxybenzyl alcohol, a non-methoxylated model, gave almost no *p*-benzoquinone.

Reaction temperature and pH were varied in the NO_2 oxidation of vanillyl alcohol to try to improve the yields of MMBQ. The results were not encouraging; increasing the reaction temperature increased the reaction rate but did not affect the product distribution. Under alkaline conditions, MMBQ was not detected by HPLC during the studied reaction time.

Vanillin (**8**) was also examined as a model substrate for NO_2 oxidation; it behaved similarly to vanillyl alcohol (Table 6). MMBQ was not produced, but vanillin was consumed at high NO_2 levels. In the presence of 4.6 equiv. of NO_2 (entry 3), starting material was completely consumed and 4,6-dinitroguaiacol (**13**) was the main product. The nitration appears to be a step process, proceeding through 5-nitrovanillin (**12**) to give 4,6-dinitroguaiacol as a final main product. The reaction of 5-nitrovanillin with 3.3 equiv. of NO_2 gives 4,6-dinitroguaiacol in 51% yield. Increasing the NO_2 level to 20 equivalents gives 4,6-dinitroguaiacol in 83% yield.

Table 6. Product composition (mol % yield) after reacting vanillin with NO_2 in the absence of NHS.

Entry	Equiv. of NO_2	MMBQ	starting material	5-nitro-vanillin	4,6-dinitro-guaiacol	4-nitro-guaiacol
1[a]	1.2	0	38	14	0	7
2[b]	1.3	0	33	53	0	0
3[a]	4.6	0	0	20	56	4

---

[a] In MeOH. [b] In benzene

An additional difficulty in obtaining good yields of MMBQ is the stability of MMBQ to prolonged exposure to NO_2 oxidation conditions. A mixture of MMBQ and NO_2 showed no significant loss of MMBQ after 90 minutes, 20% loss after 3 hours, and 77% loss after 20 hours of exposure.

Possible NO_2 Mechanism

Figure 5 presents a possible set of reactions for guaiacyl structures with NO_2 in the presence of air. The fact that the material balance was low when the NO_2 concentration was low (Table 2, entry 1) suggests that competing oxidation reactions may be occurring under these conditions; the product might be an unstable *o*-benzoquinone. At higher NO_2 concentrations, vanillin is nitrated in preference to oxidation. While the nitration is shown as a simple radical coupling reaction in Figure 5, there are several reports in the literature which indicate that NO_2 reacts ortho or para to the phenolic-OH and at the site of a substituent; the resulting dienone readily rearranges to a nitrophenol product.[14]

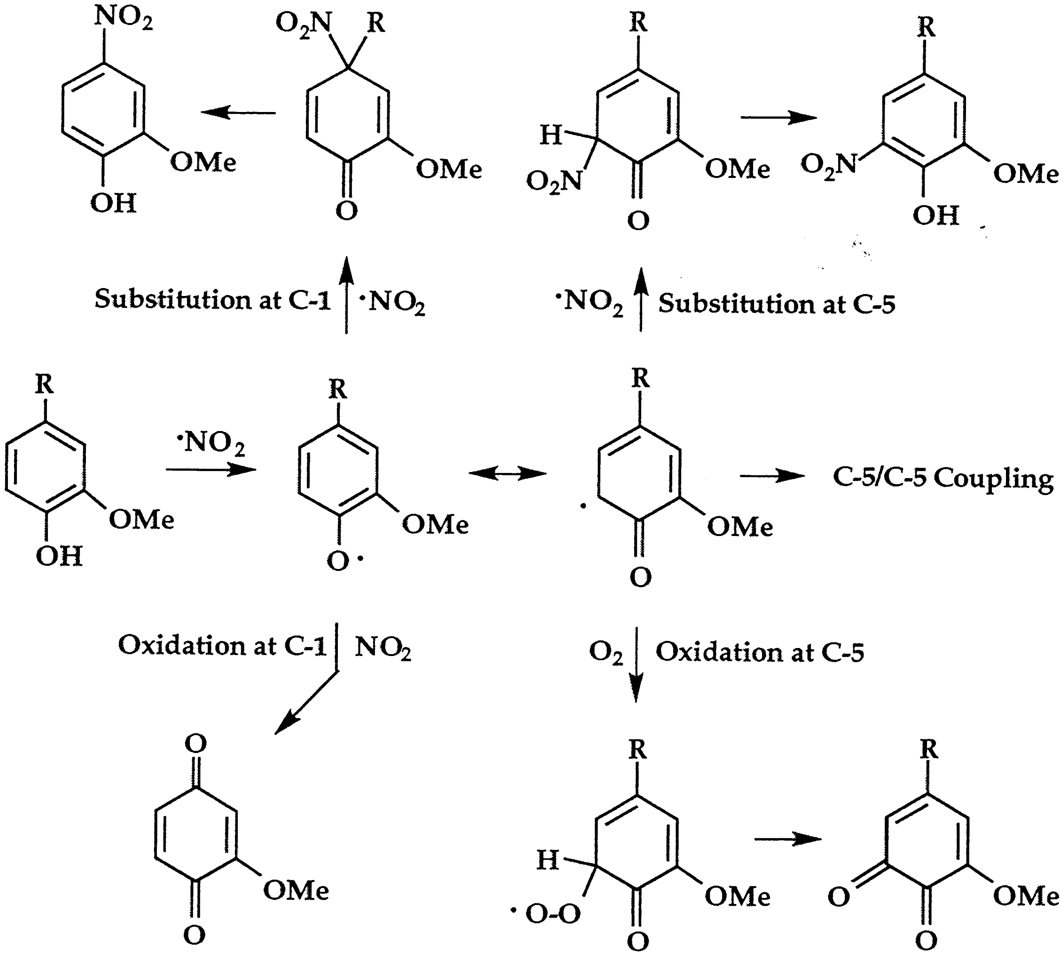

Figure 5. Reactions of NO_2 with guaiacyl structures.

The fact that the oxidation of syringyl compounds to DMBQ by NO_2 requires the presence of a phenolic OH group suggests that the first step in the reaction is hydrogen atom abstraction by NO_2. The production of high amounts of DMBQ in the absence of either air or NHS indicates that NO_2

is the principal oxidizing agent. A mechanism that fits our observations is presented in Figure 6. While path *a* might prevail in the absence of oxygen, we can not exclude that an oxygen pathway (*b*) is also involved.

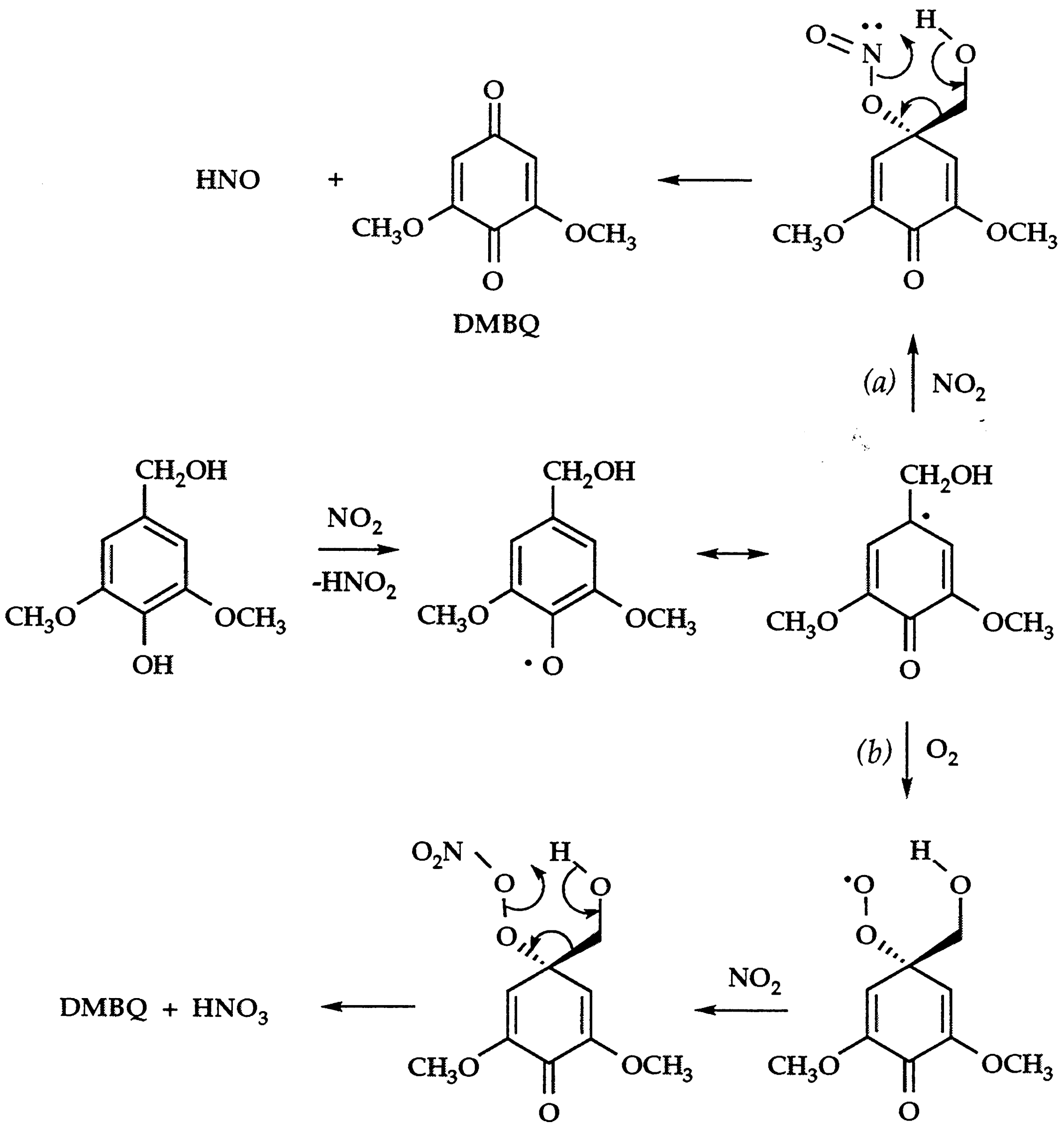

Figure 6. Proposed reaction pathways for NO_2 oxidation of a syringyl unit: (*a*) in the absence of oxygen, (*b*) in the presence of oxygen.

The stoichiometry indicated in the proposed mechanism suggests that two equivalents of NO_2 are needed for complete oxidation. Our studies (Table 2) in the case of syringyl alcohol imply that only one equivalent is necessary. However, byproducts, such as HNO_2 and NO (a radical, like

NO_2), might participate in the oxidation. Nitrous acid is known to quantitatively oxidize benzyl alcohols to aldehydes; yields near 500% (based on HNO_2) have been observed in air with excess substrate.[14]

The proposed mechanism could also explain the oxidation of aldehydes, assuming that they are in equilibrium with their hemiacetal structures (**16**). The simple mechanism cannot directly account for DMBQ production from compounds having methyl, allyl, benzyl, and methylether side chains (**20, 21, 24**, and **19**). However, several of these compounds have reactive benzyl hydrogens; possibly the side chain is first oxidized to give a reactive benzylic alcohol or aldehyde group. NO_2/NHS is capable of oxidizing benzyl alcohols to aldehydes.[12] HNO_2 can oxidize benzyl alcohol or benzyl methyl ether to benzaldehyde.[14] Using this reasoning, we believe that acetals, such as **14**, are not converted to benzoquinones because benzylic oxidation would give an unreactive acid derivative.

CONCLUSIONS

Nitrogen dioxide oxidation is an excellent way to generate benzoquinones from a variety of syringyl substructural units of the type that are present in hardwood lignins. Substrate reactivity appears to depend on having a phenolic hydroxyl group and substitution at both C-3 and C-5. Guaiacyl compound react with NO_2 to give NO_2 substitution at C-5, together with oxidation and/or replacement of side chains; the yields of MMBQ are generally low. Continued developmental work is needed to get better benzoquinone yields with guaiacyl units, since this is the predominant substructure in lignins.[5]

Oxidations performed in methanol provide the best yields. This is probably a consequence of the low solubility of DMBQ in methanol. The oxidation of syringaldehyde goes in high yield, but at a slower rate than syringyl alcohol. We believe that the aldehyde group must be in a hemiacetal form before oxidation to DMBQ can proceed. Conversion of the aldehyde to an acetal hampers reaction. Such is the case when reactions are done in ethylene glycol solvent. The oxidation is most likely radical in nature (Fig. 6). Addition of N-hydroxysuccimide generally provides small improvements in benzoquinone yields.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Gemini 300 spectrometer and reported by chemical shifts (relative to TMS), splitting patterns (singlet, doublet, triplet, quartet, pentet, multiplet), integration areas, and proton assignments. Gas chromatographic (GC) analyses on a Hewlett-Packard 5890 GC employed a HP-17 packed column, helium carrier gas flow rate of 22 mL/min., column temperature 150°C (1 min), 10°C/min to 275°C (hold), injector temperature 250°C, and detector temperature 275°C. Mass spectrometry (MS) analyses on a Hewlett-Packard 5890 GC-MS system employed a fused silica DB-5 capillary column (30 m x 0.25 mm x 0.25 μm), column temperature 150°C (1 min), 5°C/min to 280°C (hold), injector temperature 250°C, detector temperature 280°C, helium carrier gas at 30 mL/min, a jet separator at 275°C, a source temperature of 200°C, and an ionization voltage of 70 ev. Column chromatography purifications used Merck, 230-400 mesh, Grade 60, 60Å Silica Gel. Melting points are uncorrected.

Samples of monomethoxy-[15] and 2,6-dimethoxy-*p*-benzoquinone[16] (**1** and **2**, MMBQ and DMBQ), syringic acid methyl ester (**23**),[17] and 2,6-dimethoxy-4-(methoxymethyl)phenol (**19**)[18] were prepared by standard literature procedures and were identical to reported properties. Syringyl alcohol (**7**),[19] syringol (**20**),[19] disyringyl methane (**24**),[19] and 1-(3,4,5-trimethoxyphenyl)ethanol (**26**)[12] were available from other studies in our laboratory. Nitrogen dioxide, vanillyl alcohol (**6**), vanillin (**8**), syringaldehyde (**9**), 5-nitrovanillin (**12**), acetoguaicone (**10**), acetosyringone (**18**), vanillic acid (**11**), 4-allyl-2,6-dimethoxyphenol (**21**), syringic acid (**22**), 3,5-dimethoxy-benzyl alcohol (**25**), succimide (**5**), and N-hydroxysuccimide (**4**) were commercially available.

Standard NO_2 Oxidation Procedure (Syringyl Compounds). In a 100 mL two-necked round bottom flask was placed 20-30 mg of lignin model compound and 2-3 equiv. (~30 mg) of N-hydroxysuccimide (NHS) dissolved in 2 mL of anh. methanol. A weighed amount (generally 5-6 equivalents, 20-30 mg) of liquid NO_2 in a pressure-lock gas syringe was injected into the stirred reaction mixture. The headspace displayed a white vapor that disappeared quickly; the color of the solution turned to orange-yellow. As the reaction proceeded, an orange-yellow solid, DMBQ (**2**), precipitated. The reaction mixture was allowed to stir at ambient temperature for 2 hrs; following this, 2 mL of a chloroform solution, containing 1 mg/mL anthraquinone (GC internal standard), was added. The solid DMBQ dissolved. The solution was then analyzed by GC to determine DMBQ amounts and by GC-MS to identify other reaction products. The DMBQ (**2**) was identified by direct comparison of the GC retention time and mass spectrum to an authentic sample; an ^{1}H-NMR spectrum of the precipitate was identical to authentic DMBQ. The signal response factor for DMBQ vs internal standard was 1.0/2.2.

NO_2 Oxidation Vanillyl Alcohol (6). The procedure and work-up were the same as above; however, the products did not precipitate from the reaction mixture. Product analysis by GC and GC-MS, with comparisons to authentic samples where possible, indicated the presence of MMBQ, 4-nitroguaiacol, 5-nitrovanillin (**12**), 5-nitrovanillyl alcohol, and 4,6-dinitroguaiacol (**13**). With excess NO_2, **13** was the major product; at lower levels of NO_2, 5-nitrovanillyl alcohol was the major product. 5-Nitrovanillyl alcohol was prepared by $NaBH_4$ reduction of 5-nitrovanillin (**12**) and also isolated by silica gel column chromatography from a large scale NO_2 oxidation of vanillyl alcohol; both samples had the same spectral properties, including: ^{1}H-NMR ($CHCl_3$) δ 2.0 (s, 1, RO$\underline{H}$), 3.97 (s, 3, OC$\underline{H}_3$), 4.68 (s, 2, C$\underline{H}_2$), 7.20 (d, J = 1 Hz, 1, Ar$\underline{H}$), 7.68 (d, J = 1 Hz, 1, Ar$\underline{H}$), and 10.76 (s, 1, ArO$\underline{H}$). The yield data are given in the text. The mass spectral data for the other tentatively identified compounds were:

4,6-Dinitroguaiacol: *m/z* (%) 214 (M+, 100), 197 (85), 196 (26), 166 (28), 122 (26), 121 (39), 93 (20), 79 (26), 53 (29), and 50 (28).

4-Nitroguaiacol: *m/z* (%) 169 (M+, 100), 139 (21), 123 (22), 111 (14), 108 (25), 80 (14), 65 (16), and 52 (25).

NO_2 Oxidation Vanillin (8). The procedure and work-up were the same as above; however, the products did not precipitate from the reaction mixture. Product analysis was done by GC and GC-MS; comparisons were made to authentic samples and those from the previous experiment. The reaction produced varied amounts 5-nitrovanillin (**12**), 4,6-dinitroguaiacol (**13**), and small amounts of an acetal and hemiacetal of **12**. The yields of **12** and **13** varied with the amount of NO_2 used, as explained in the text. [The yield of **13** was based on the assumption that **12** and **13** have the same GC response factors.] Treatment of **12** with excess NO_2 in methanol gave **13**.

NO_2 Oxidation Syringaldehyde (9) in Ethylene Glycol. The procedure and workup were the same as above except that the solvent was ethylene glycol. The GC analysis displayed a long time retention signal at 13.9 min which was assigned to the cyclic acetal (**14**). The latter was identical in retention time and mass spectrum to a sample of **14** prepared by mixing syringaldehyde in ethylene glycol with a catalytic amount of *p*-toluenesulfonic acid. Compound **14** was very unstable and decomposed upon various attempted isolations. A mixture of 3 parts acetal and 2 parts syringaldehyde was the highest ratio of acetal that possible. The mass spectrum of cyclic acetal (**14**) was as follows: *m/z* (%) 226 (56, M^+), 225 (51), 181 (43), 167 (21), 154 (48), and 73 (100).

Nitrogen Dioxide Oxidation under Oxygen-Free Conditions. A solution of syringyl alcohol (20 mg, 0.11 mmol) in 5 mL of anhyd. methanol in a two-neck flask was frozen by immersion into a cooling bath containing liquid nitrogen. The solid mixture was then evacuated (0.03 mm Hg) and allowed to melt under vacuum. The vacuum was then replaced with argon. When the reaction flask had warmed to room temperature both necks were closed. To the stirred reaction mixture was added a weighed amount of nitrogen dioxide (5-6 equivalents) using a gas-tight syringe. Fumes were produced; however, these disappeared in a few minutes. The color of the solution turned orange and a pale yellow precipitate slowly formed. After stirring at room temperature for 2 hours, the reaction flask was evacuated using a water aspirator. Both necks were then open to the atmosphere and enough chloroform was added to dissolve all of the precipitate. Analysis of a sample for DMBQ was done by GC, using anthraquinone as an internal standard. The above experiment was also conducted with the addition of N-hydroxysuccinimide (44 mg, 0.308 mmol, 3.3 equivalents) before freezing. In addition, the oxygen-free conditions with syringyl alcohol were conducted by preparing a solution of syringyl alcohol in anhyd. methanol, and repetitively cooling to -78°C under high vacuum for 10 min, and then releasing nitrogen into the container. Nitrogen dioxide was added with a gas-tight syringe and reaction allowed to stir under a nitrogen atmosphere. A similar experiment was done in the presence of NHS. Yield data for each of these experiments are given in the text.

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PULPING CATALYSTS FROM LIGNIN (7).

NITROGEN OXIDE OF A LIGNIN MODEL DIMER

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PULPING CATALYSTS FROM LIGNIN (7). NITROGEN DIOXIDE OXIDATION OF A LIGNIN MODEL DIMER

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ABSTRACT

Oxidation of a lignin model disyringyl dimer with nitrogen dioxide (NO_2) in the presence of air and N-hydroxysuccimide (NHS) led to C_1-C_α cleavage with the formation of approximately equal amounts of 2,6-dimethoxy-*p*-benzoquinone (DMBQ) and glyceraldehyde-2-syringyl ether type structures. The result indicates that only the phenolic end syringyl units of a lignin polymer will be converted to DMBQ upon treatment with the current NO_2 reaction conditions. Internal (non-phenolic) lignin units, bonded by β-O-4 linkages, will resist oxidization.

INTRODUCTION

We have been investigating the feasibility of preparing low-cost anthraquinone (AQ) catalysts from lignin. The synthesis involves oxidation of lignin, or a lignin-related compound, to methoxy-substituted benzoquinones and then treatment of the latter with a diene (Diels-Alder reaction) to generate AQ-type structures (Figure 1).[1]

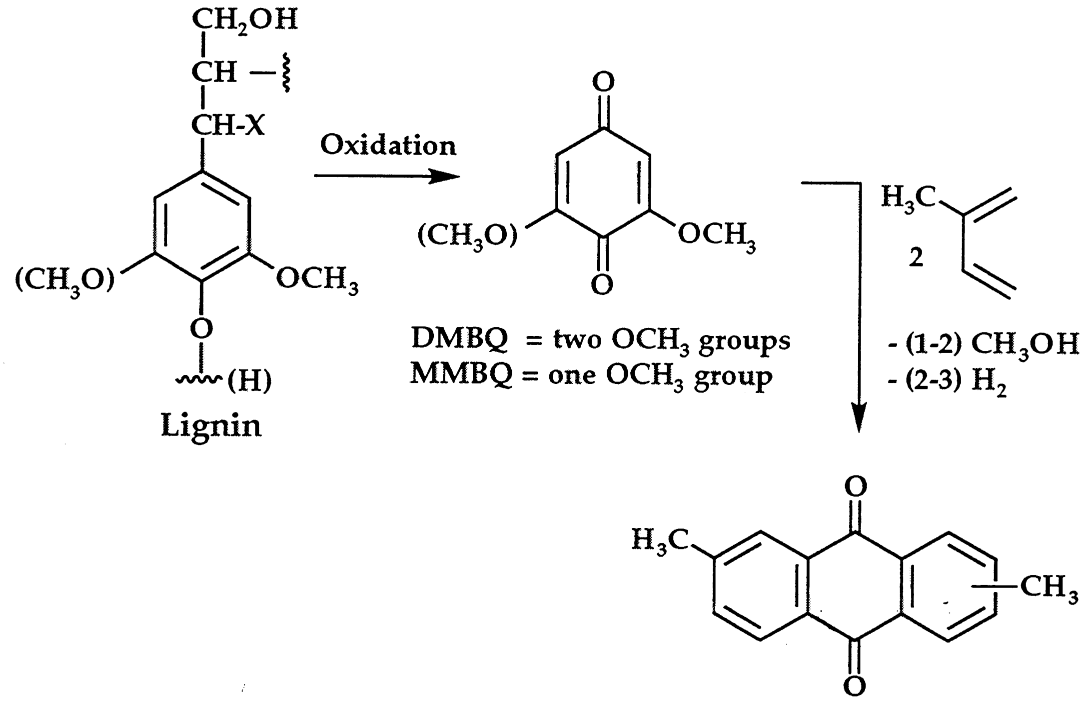


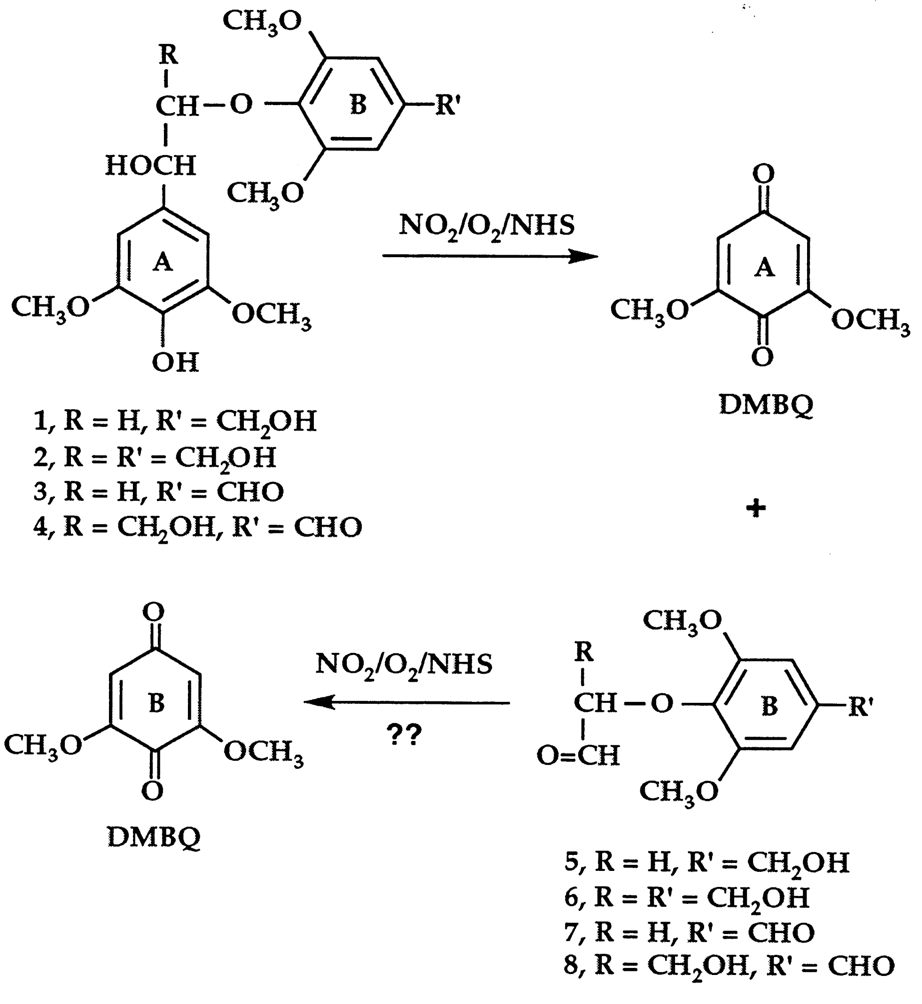
Figure 1. Chemical steps in the conversion of lignin to an AQ.[1]

Many syringyl lignin models (those having two CH_3O- groups per aromatic ring) have been oxidized to 2,6-dimethoxy-*p*-benzoquinone (DMBQ) in high (~90%) yields with nitrogen dioxide (NO_2) in the presence of air and N-hydroxysuccimide (NHS).[2] The yields of DMBQ from lignin oxidations are much lower, typically 4-15% for a low-molecular-weight hardwood lignin and <4% for a high-molecular-weight lignin.[3] This result suggests that few of the internal (non-phenolic) lignin units are being oxidized. The present study addresses the issue of internal lignin unit reactivity in NO_2 oxidations.

RESULTS AND DISCUSSION

Model Selection and Synthesis

In order to establish the reactivity of internal lignin units, we decided to examine the yields of DMBQ that result from oxidation of syringyl-syringyl dimers, such as **1-4**, Figure 2. The dimer was expected to give one equivalent of DMBQ from oxidation of the phenolic A-ring unit. We anticipated that the other oxidation product would be a non-phenolic structure (such as **5**-**8**) composed of the B-ring joined to the A-ring side chain. The question was whether this structure would also be oxidized under the reaction conditions to give another equivalent of DMBQ. If the dimer provided two equivalents of DMBQ upon treatment with NO_2/NHS, we rationalized that internal (non-phenolic) lignin units would also be susceptible to oxidation by NO_2. A syringyl-type dimer was selected for study because DMBQ yields are high from the NO_2 oxidations of syringyl compounds, while monomethoxybenzoquinone (MMBQ) yields are generally low for the corresponding oxidation of guaiacyl units.[2,4]



1, R = H, R' = CH_2OH
2, R = R' = CH_2OH
3, R = H, R' = CHO
4, R = CH_2OH, R' = CHO

5, R = H, R' = CH_2OH
6, R = R' = CH_2OH
7, R = H, R' = CHO
8, R = CH_2OH, R' = CHO

Figure 2. Potential NO_2 oxidation reactions of syringyl-syringyl dimers.

We first attempted a synthesis of the β-O-4 dimer **1**, using the synthetic route shown in Figure 3. β-Bromoacetosyringone (**9**) was coupled with sodium 4-formyl-2,6-dimethoxyphenoate (**10**) to get β-(4'-formyl-2',6'-dimethoxyphenoxy)acetosyringone (**11**) in 66% yield, and $NaBH_4$ reduction of **11** gave **1** in 72% yield. Various attempts to obtain a pure product were not successful. Analysis of the synthesized dimer by NMR indicated a purity of about 90%.

Syringyl-syringyl dimer **2** was prepared in 52% overall yield by the reactions shown in Figure 4. Compound **2** has been prepared by Miksche in 1973;[5] however, we selected a route analogous to that employed by Katayama et al. to prepare guaiacyl dimers.[6] The key step in the synthesis involved condensing 4-O-benzyl syringaldehyde (**12**) with ester acetal **13**. The acetal group in **13** prevents self-condensation in the presence of base; the benzyl group in **12** prevents ionization of the phenolic-OH in base and thereby facilitates a nucleophilic addition to the aldehyde group.

The ester acetal **13** and the resulting condensed acetal product were unstable; Katayama et al. observed similar instabilities in the guaiacyl analogs.[6] Each acetal was carried into the next step soon after preparation. Consequently, the dimer product from condensing **12** with acetal **13** was not characterized, but immediately hydrolyzed with acid to give a 7:1 mixture of stable erythro/threo aldehydes (**14e/14t**). Column chromatography resulted in partial separation of the two aldehydes. The minor threo isomer was easily crystallized; the major erythro isomer was about 95% pure; further purification attempts were not successful.

The synthesis of **2e** and **2t** was completed by reduction of the carbonyl groups in **14e** and **14t** with lithium aluminum hydride and removal of the benzyl protecting groups by hydrogenation. The threo isomer again crystallized; it had a sharp melting point (equal to a literature value). The erythro isomer, a solid with a broad melting point range, again resisted various recrystallization attempts. This isomer is reported to be difficult to purify.[7] NMR analysis, indicated that the compounds were ≥95% pure.

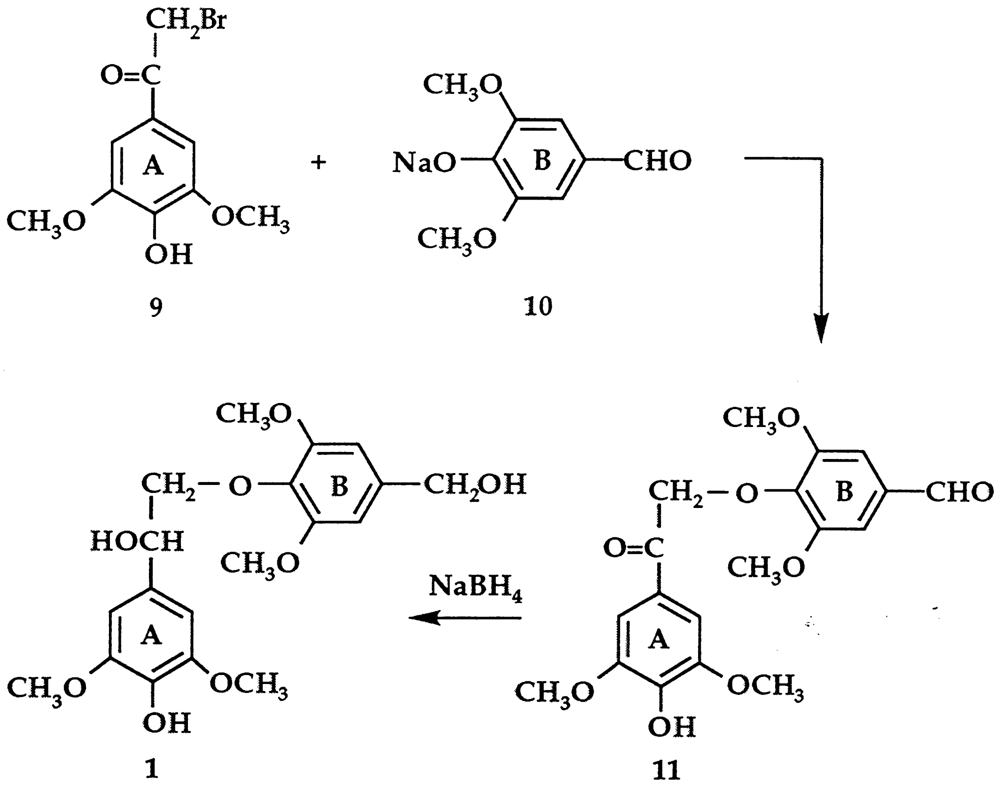


Figure 3. Synthesis of the β-O-4 dimer **1**.

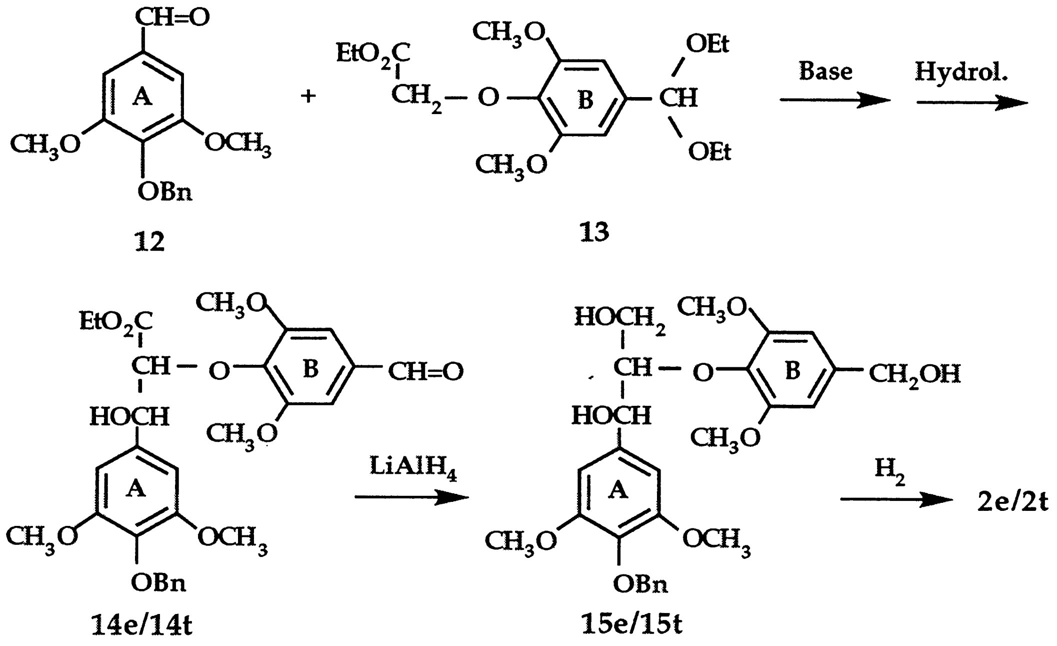


Figure 4. Synthesis of lignin model dimer **2**.

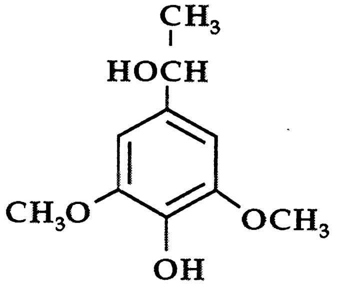
DMBQ Yields from NO_2 Oxidations

The syringyl dimers **1** and **2**, along with selected monomeric compounds (**16** and **17**), were oxidized with NO_2/NHS. The yields of DMBQ, as shown in Table 1, were similar for dimers **1** and **2** , namely ~40 mole % (~0.8 equiv. of DMBQ/dimer model). The yield difference between the two isomers of **2** was probably due more to a stereochemical difference than to a possible purity difference.

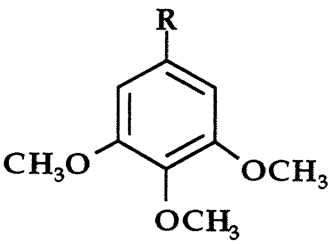
Table 1. Yields of DMBQ from the NO_2 Oxidations of Dimers **1** and **2**, and Selected Monomeric Models.[a]

Compound	DMBQ Yield (%)
Dimer **1**	~37[b]
Dimer **2e**	37, 38[c,d]
Dimer **2t**	44, 46[c,d]
α-Methylsyringyl Alcohol **16**	88
3,4,5-Trimethoxybenzyl Alcohol **17**	0

[a] In air with an excess of NO_2 and NHS in methanol at 22°C for 2 hours. [b] The reported yield was obtained by dividing the observed 33% yield by the purity (estimated by NMR to be ~90%). [c] Duplicate determinations. [d] If both syringyl units had been completely converted to DMBQ, the yield would be 100%; if one had been completely converted, then 50%.



16



17, R = CH_2OH
18, R = CHO
19, R = CH_2OCH_3

The DMBQ yields from oxidation of the dimers fit predictions based on the oxidation results of monomers **16** and **17**. The phenolic model, α-methylsyringyl alcohol (**16**), gave an 0.88 equiv. of DMBQ, while the non-phenolic model, 3,4,5-trimethoxybenzyl alcohol (**17**), provided no DMBQ. The former mimics the A-ring and side chain, while the latter mimics the non-phenolic B-ring of the dimer models. If we consider that the dimers are composed of a "combination" of **16** and **17**, the ceiling yield of DMBQ from the dimer should be ~45%.

Gas chromatography/mass spectroscopy (GC/MS) analysis of the NO_2 reaction solution from the non-phenolic model **17** showed starting material (60%) and a signal (40%) which contained two components: an oxidation product 3,4,5-trimethoxybenzaldehyde (**18**) and an (acid-catalyzed) solvent reaction product 3,4,5-trimethoxybenzyl methyl ether (**19**). The results indicate that a free phenolic hydroxyl group in the substrate is needed for DMBQ production and that the NO_2 conditions result in some benzyl alcohol oxidation to an aldehyde.

Other Dimer Oxidation Products

Apart from DMBQ, the product mixture from oxidation of dimer **2** contained two other principal components: non-phenolic compounds **6** and **8**, that are from the B-ring portion of the molecule. The structures of these components were established by GC/MS and by conversion of the components to a product (**21**) that was synthesized by a separate route, as shown in Figure 5. The product mixture containing **6** and **8** was treated with sodium borohydride to reduce the aldehyde groups in each component to alcohols, giving rise to the same product (**21**). The three component product mixture (DMBQ, **6** and **8**) became a two component mixture (reduced DMBQ and **21**). Compound **21** was identical to that prepared by coupling α-chloro diethyl malonate with syringaldehyde, followed by $LiAlH_4$ reduction.

The production of aldehydes **6** and **8** indicates that cleavage has occurred between C_1-C_α, without other alterations of the side chain. A possible cleavage mechanism is shown in Eq. 1. The dialdehyde com-

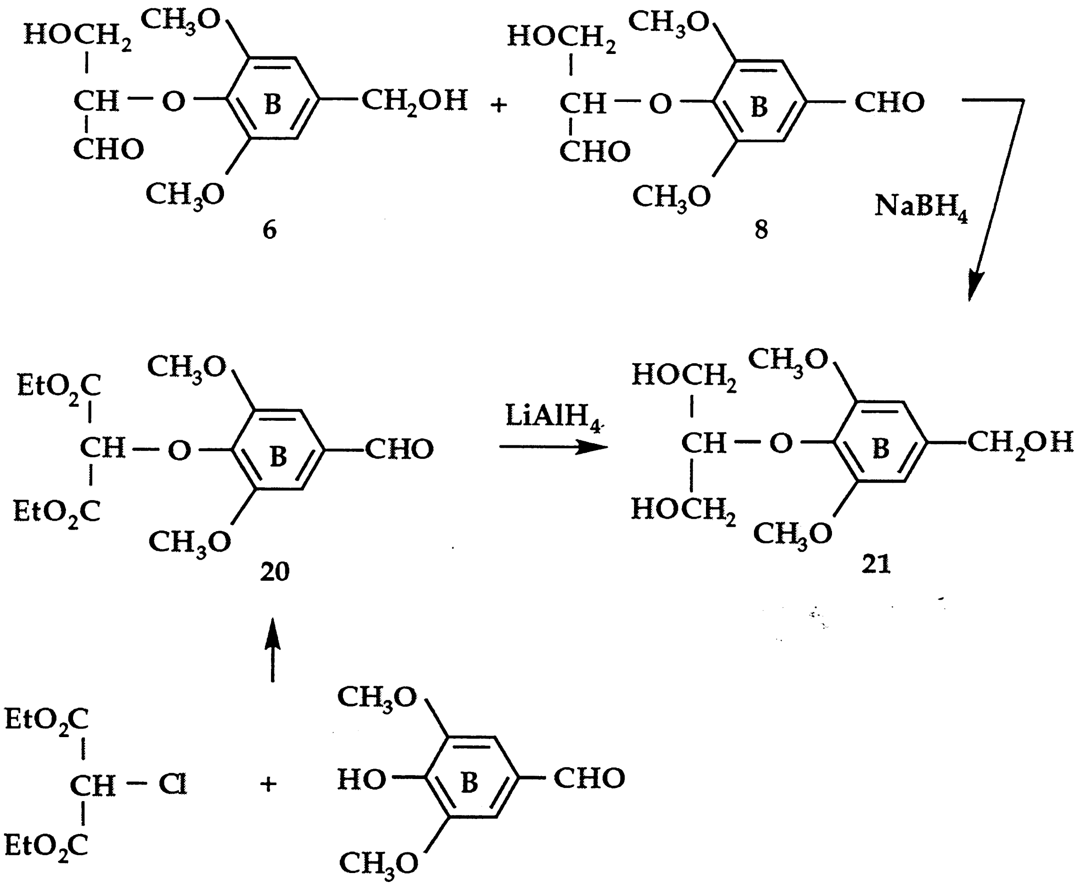
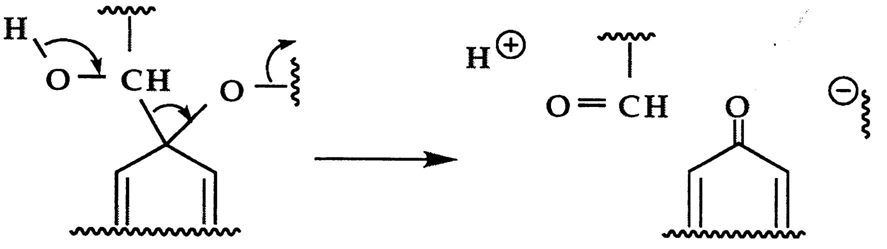


Figure 5. Structural confirmation of oxidation products **6** and **8**.

ponent **8** probably is a secondary oxidation product of **6** or an oxidation of the A-ring $-CH_2OH$ group before oxidative cleavage of dimer **2**. Its formation is analogous to the NO_2 oxidation of the $-CH_2OH$ group in the non-phenolic model **17** which gives rise to aldehyde **18**.



Eq. 1

CONCLUSIONS

The results obtained from this investigation indicate that the NO_2 oxidation of an α-syringyl-β-syringyl ether glycerol lignin model dimer (**2**) leads to formation of DMBQ and glyceraldehyde-β-syringyl ether structures via a C_1-C_α cleavage. It appears that the present NO_2 reaction conditions do not break down of β-O-4 linkages and are incapable of oxidative cleavage of non-phenolic units. These conclusions suggest that only phenolic (terminal) syringyl units in a lignin macromolecule will be converted to DMBQ upon NO_2 oxidation. To achieve good DMBQ yields from lignin by NO_2 oxidation, we apparently will have to degrade lignin into smaller pieces, either before or during the NO_2 oxidation. Such an approach is being taken.[3]

EXPERIMENTAL

The description of chromatography and NMR equipment and conditions were presented earlier.[2]

Synthesis of Lignin Model Compounds

Syringaldehyde, acetosyringone, 3,4,5-trimethoxybenzyl alcohol (**17**) and 3,4,5-trimethoxybenzaldehyde (**18**) are commercial products. α-Methylsyringyl alcohol (**16**)[8] was prepared by $NaBH_4$ reduction of acetosyringone in 80% yield; recrystallized from hexane/ethyl acetate gave mp 93-94°C (Lit.[9] mp 95-95.5°C). 4-O-Benzyl syringaldehyde (**12**) was prepared in 68% yield from syringaldehyde and benzyl bromide in the presence of potassium carbonate in ethanol and recrystallized from hexane/ethanol: mp 60-61°C (Lit.[9] mp 62.5°C); ^{1}H-NMR ($CDCl_3$) δ 3.90 (s, 6, 2 -$OC\underline{H}_3$), 5.13 (s, 2, $PhC\underline{H}_2$-), 7.12 (s, 2, $Ar\underline{H}$), 7.27 - 7.50 (m, 5, $\underline{Ph}CH_2$), and 9.87 (s, 1, -$C\underline{H}O$).

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(4'-formyl-2',6'-dimethoxyphenoxy)ethanone (11). Syringaldehyde sodium salt (**10**) was prepared by freeze-drying an aqueous solution of syringaldehyde (12 g, 66 mmol) and NaOH (2.7 g, 67 mmol). β-Bromoacetosyringone (**9**) was prepared in a manner analogous to the preparation of β-bromoacetoguaiacone;[10] 2.9 g (10 mmol) of **9** in 45 mL of DMF was added dropwise to a stirred solution of **10** (66 mmol) in 600 mL of DMF. The reaction conditions and work up were identical to that described for guaiacyl dimers prepared in a similar manner.[10] Column chromatography on silica gel provided 2.5 g (66% yield) of **11**: mp 152-5°C; ^{1}H-NMR ($CDCl_3$) δ 3.89 (s, 6, two $-OC\underline{H}_3$), 3.95 (s, 6, two $-OC\underline{H}_3$), 5.32 (s, 2, β-$C\underline{H}_2$), 7.15 (s, 2, Ar$\underline{H}$), 7.35 (s, 2, Ar$\underline{H}$), and 9.88 (s, 1, -$C\underline{H}O$).

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(4'-hydroxymethyl-2',6'-dimethoxyphenoxy)-1-ethanol (1). To a stirred solution of **11** (100 mg, 0.27 mmol) in 5 mL of ethanol was added an excess of $NaBH_4$ (130 mg, 3.4 mmol) in 5 mL of water. After 8 hr., another 100 mg (2.6 mmol) of $NaBH_4$ was added and stirring was continued overnight. The solution was neutralized by adding 6 N HCl to a pH of 2 and then extracted with chloroform. The extracts were combined and dried over Na_2SO_4, and evaporated to give 72 mg (72% yield) of an oily residue (**11**), that resisted crystallization from several solvent combinations: ^{1}H-NMR (acetone-d_6/D_2O) δ 3.68 (d of d, J = 9.3 and 10.6 Hz, 1, β-$C\underline{H}_AH_B$), 3.81 (s, 6, two $-OC\underline{H}_3$), 3.87 (s, 6, two $-OC\underline{H}_3$), 4.23 (d of d, J = 3.2 and 10.6 Hz, 1, β-$CH_A\underline{H}_B$), 4.59 (s, 2, $ArC\underline{H}_2OH$), 4.80 (d of d, J = 9.3 and 3.2 Hz, 1, α-$C\underline{H}OH$), 6.71 (s, 2, Ar$\underline{H}$), and 6.75 (s, 2, Ar$\underline{H}$).

Ethyl 4-diethylacetal-2,6-dimethoxyphenoxyacetate (13). A mixture of syringaldehyde (6.94g, 37 mmol), ethyl chloroacetate (5.86, 47 mmol), K_2CO_3 (6.49 g, 47 mmol), and KI (0.78 g, 4.7 mmol) in 100 mL of acetone was stirred at room temperature for 2 hr. The inorganics were filtered off and washed with ethyl acetate. The filtrates and washings were combined and concentrated. The residue was dissolved in ethyl acetate, washed with water, dried over Na_2SO_4, concentrated, and dissolved in 20 mL of anh. ethanol.

To this solution was added triethyl orthoformate (56 g, 370 mmol) and *p*-toluenesulfonic acid (110 mg). After stirring for 30 min, the mixture was neutralized by the addition of $NaHCO_3$. The excess $NaHCO_3$ was removed by filtration and washed with ethyl acetate. The filtrates and washings were combined and concentrated. The residue was dissolved in ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated with first a simple vacuum evaporation and then with high vacuum. Analysis by TLC showed one principal component, presumedly the acetal **13**, and only minor impurities. The acetal **13** was unstable, even towards crystallization from ethanol and, therefore, was used quickly after preparation without purification.

Ethyl 1 - (4'-formyl-2',6'-dimethoxyphenoxy) - 2 - (4-benzoxy-3,5-dimethoxyphenyl) - 2 - hydroxypropanoate (14). To a stirred solution of 1.34 g (13 mmole) of diisopropylamine (freshly distilled from sodium metal) in 20 mL of anh. THF (freshly distilled from $LiAlH_4$) was added dropwise 5.4 mL (13 mmole) of a solution of 2.5 M n-butyllithium in hexane at 0°C under nitrogen. After another 30 min at 0°C, the resulting lithium diisopropylamine solution was cooled to -78°C and stirred while 3.56 g (10 mmole) of **13** in 20 mL of anh. THF was added dropwise at -78°C. Thirty minutes later, a solution of benzyl syringaldehyde **12** (2.45 g, 9 mmole) in 20 mL of anh. THF was added dropwise to the stirred -78°C solution. After stirring for additional 90 min at -78°C, the reaction solution was neutralized by the addition of powdered dry ice and partitioned between ethyl acetate and water. The aqueous layer was extracted twice with ethyl acetate. The combined ethyl acetate extracts was stirred for 2 hr with 1 N HCl solution in order to hydrolyze the acetal dimers contained in the ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield 6.6 g of crude product.

Analysis of the product mixture by TLC showed one major component, without any significant amount of remaining starting materials. The major component was most likely an erythro/threo mixture of the desired product. Silica gel column chromatography, with solvent elution by methylene chloride/ethyl acetate (4:1), was used to give 2.3 g (70% yield) of **14e** and 0.3 g (10% yield) of **14t**. The latter was recrystallized from ethyl acetate/hexane: mp 126-8°C; ^1H-NMR ($CDCl_3$) δ 1.04 (t, 3, $-CH_2C\underline{H}_3$), 3.79 (s, 6, two $-OC\underline{H}_3$), 3.93 (s, 6, two $-OCH_3$), 3.98-4.06 (two q, 2, $-C\underline{H}_2CH_3$), 4.19 (d, 1, β-$C\underline{H}$), 4.97 (s + d, 3, α-$C\underline{H}$ and $PhC\underline{H}_2$-), 6.56 (s, 2, $Ar\underline{H}$), 7.16 (s, 2, $Ar\underline{H}$), 7.3-7.5 (m, 5, $\underline{Ph}CH_2$), and 9.90 (s, 1, $-C\underline{H}O$). The

14e spectra: ^{1}H-NMR ($CDCl_3$) δ 1.07 (t, 3, -$CH_2C\underline{H}_3$), 3.83 (s, 6, two -$OC\underline{H}_3$), 3.93 (s, 6, two -$OC\underline{H}_3$), 4.05-4.10 (two q, 2, -$C\underline{H}_2CH_3$), 4.82 (d, 1, β-C$\underline{H}$), 4.99 (s + d, 3, α-C$\underline{H}$ and PhC$\underline{H}_2$-), 6.68 (s, 2, Ar$\underline{H}$), 7.17 (s, 2, Ar$\underline{H}$), 7.3-7.5 (m, 5, $\underline{Ph}CH_2$), and 9.90 (s, 1, -C$\underline{H}$O).

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(4'-hydroxymethyl-2',6'-dimethoxyphenoxy)-1,3-propandiol (2). Compound **14**, erythro (1.2 g, 3.2 mmol) or threo (150 mg, 0.4 mmol), was dissolved in anh. THF and added to a stirred solution of $LiAlH_4$ (6 equiv.) in anh. THF at 50°C under nitrogen. After 1 hr, ethyl acetate was added to destroyed the excess $LiAlH_4$. The reaction mixture was neutralized with 1 N HCl and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated to give an oil (**15e** or **15t**) which was dissolved in methanol and stirred with 10% palladium/charcoal and hydrogen (1 atm) at room temperature until hydrogen consumption ceased. After 30 min, the catalyst was filtered off and washed with methanol. The filtrate and the washings were combined, concentrated, and chromatographed on a silica gel column with chloroform containing 5% methanol.

In the erythro isomer case, we obtained 630 mg (69% yield) of **2e**, a white solid that could not be successfully recrystallized: ^{1}H-NMR (acetone-d_6/D_2O) δ 3.40 (d of d, 1, γ-C$\underline{H}_AH_B$OH), 3.79 (s, 6, two -$OC\underline{H}_3$), 3.84 (s, 6, two -$OC\underline{H}_3$), 3.86 (shoulder on the large 3.84 signal, assumed to be d of d, 1, γ-C$H_A\underline{H}_B$OH), 4.12-4.16 (m, 1, β-C$\underline{H}$), 4.56 (s, 2, ArC$\underline{H}_2$OH), 4.96 (d, 1, α-C$\underline{H}$OH), 6.70 (s, 2, Ar$\underline{H}$), and 6.73 (s, 2, Ar$\underline{H}$). In the threo isomer case, we obtained 71 mg (62% yield) of **2t**: mp 153-4°C, from ethyl acetate/ hexane, (Lit.[5] mp 154-5°C); ^{1}H-NMR (acetone-d_6/D_2O) δ 3.27 (d of d, 1, γ-C$\underline{H}_AH_B$OH) and 3.65 (d of d, 1, γ-C$\underline{H}_AH_B$OH), 3.77 (s, 6, two -$OC\underline{H}_3$), 3.85 (s, 6, two -$OC\underline{H}_3$), 3.88-3.92 (m, 1, β-C$\underline{H}$), 4.54 (s, 2, ArC$\underline{H}_2$OH), 4.95 (d, 1, α-C$\underline{H}$OH), 6.72 (s, 2, Ar$\underline{H}$), and 6.74 (s, 2, Ar$\underline{H}$). Previous NMR spectra for **2e** and **2t** report only the tetraacetate derivatives.[4,11]

3,4,5-Trimethoxybenzyl methyl ether (19). A solution containing syringyl alcohol (7) (420 mg, 2 mmol), 4 mL of dioxane, 4 mL of 4 N NaOH, and 4 mL (40 mmol) of dimethyl sulfate was stirred at room temperature overnight. The pH of the mixture was maintained near 11 by adding 4 N NaOH. After acidification with HCl, the mixture was extracted with chloroform. The organic layers were dried over Na_2SO_4 and concentrated to yield a pale yellow oil material. Silica gel column chromatography with toluene/ethyl acetate gave 370 mg (87% yield) of a pale yellow oil, compound **19**: ^{1}H-NMR ($CDCl_3$) δ 3.42 (s, 3, ROC$\underline{H}_3$), 3.84 (s, 3, ArOC$\underline{H}_3$), 3.87 (s, 6, two ArOC$\underline{H}_3$), 4.39 (s, 2, -C$\underline{H}_2$OCH$_3$), and 6.57 (s, 2, Ar$\underline{H}$); MS *m/z* (%) 212 (M^+, 88), 197 (10), 181 (100), 169 (17), 151 (14), 138 (20), 123 (7), 111 (7), 95 (9), 77 (9), 66 (7), and 53 (9).

Diethyl 2-(4-formyl-2,6-dimethoxyphenoxy)malonate (20). The sodium salt of syringaldehyde was prepared by freeze-drying an aqueous solution containing 3.14 g (16 mmole) of syringaldehyde and 0.69 g (17 mmole) of NaOH. To a stirred solution of 4.05 g (21 mmole) of diethyl chloromalonate in 20 mL of DMF at 60°C was added dropwise 15 mL DMF containing the syringaldehyde sodium salt. The mixture was allowed to stir for another 1 hr at 60°C, then poured into 100 mL ice water, neutralized with 4 N HCl solution, and finally extracted with chloroform. The chloroform extract was washed with 1 N NaOH solution, dried over Na_2SO_4, and evaporated. The residue was chromatographed on a silica gel column using ethyl acetate/hexane as solvent to obtain 4.2 g (77% yield) of a pale yellow oil, which resisted crystallization. The ^{1}H-NMR showed a single product: ($CDCl_3$) δ 1.30 (t, 6, -CH$_2$C$\underline{H}_3$), 3.89 (s, 6, two -OC$\underline{H}_3$), 4.31 (two q or a finely split q, 4, -C$\underline{H}_2$CH$_3$), 5.28 (s, 1, -C$\underline{H}$-), 7.13 (s, 2, Ar$\underline{H}$), and 9.88 (s, 1, -C$\underline{H}$O).

2-(4-Hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propandiol (21). Compound **20** from above was reduced by $LiAlH_4$, following the same procedure used for compound **14**. The reduced product was purified by silica gel column chromatography with chloroform containing 10% methanol. ^{1}H-NMR (acetone-d_6/D_2O) δ 3.72-3.75 (m, 4, -C$\underline{H}_2$OH), 3.86 (s, 6, two -OC$\underline{H}_3$), 3.97 (p, 1, -C$\underline{H}$-), 4.58 (s, 2, ArC$\underline{H}_2$OH), and 6.75 (s, 2, Ar$\underline{H}$); MS *m/z* (%) 258 (M^+, 15), 184 (100), 167 (14), 155 (9), 123 (14), 109 (11), 95 (6), 81 (5), 65 (2), and 53 (3).

Nitrogen Dioxide Oxidations

NO_2 Oxidation of 3,4,5-trimethoxybenzyl alcohol (17). The standard NO_2/NHS oxidation conditions[2] with **17** provided a product mixture showing one principal GC signal (40%), besides that of the starting material (60%). The new GC signal was not symmetrical, suggesting that there were two components. Analysis by GC-MS indicated that the signal was a mixture of 3,4,5-trimethoxybenzaldehyde (**18**) and 3,4,5-trimethoxybenzyl methyl ether (**19**). A direct comparison of GC retention time and mass spectra with authentic samples of **18** and **19** confirmed the structural assignments. Compound **18** was available as a commercial product; compound **19** was synthesized, as described above.

NO_2 Oxidation of Dimer 2e and 2t. The standard NO_2/NHS oxidation conditions[2] with either dimer **2e** or **2t** provided a product mixture showing three principal GC signals: DMBQ at retention time 6.3 min, compound **8** at 9.5 min, and compound **6** at 11.3 min. The preliminary structural assignments for **6** and **8** were based on mass spectral data: **3-hydroxy-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)propanal** (**6**) *m/z* (%) 256 (M^+, 33), 226 (12), 197 (3), 183 (100), 168 (33), 155 (18), 127 (40), 109 (10), and 95 (18), and **3-hydroxy-2-(4-formyl-2,6-dimethoxyphenoxy)propanal** (**8**) *m/z* (%) 254 (M^+, 27), 224 (7), 195 (3), 181 (100), 166 (29), 153 (9), 125 (14), 107 (9), and 93 (9).

The crude product was dissolved in ethanol and stirred with an excess of $NaBH_4$ (100 mg) for 2 hr. The solution was neutralized by adding 1 N HCl and then extracted first with chloroform and then with ethyl acetate. The extracts were combined and dried over Na_2SO_4. An examination of the solution by GC showed that components **6** and **8** had been converted to a single component of retention time 12.4 min. A GC-MS indicated that this compound was 2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propandiol (**21**). This compound was identical in GC retention time and MS to a synthesized sample of **21**.

NO_2 Oxidation of Dimer 1 and Compound 16. The standard NO_2/NHS oxidation conditions[2] were employed with each of substrate; only the yields of DMBQ were examined.

ACKNOWLEDGMENTS

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FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT F014

ANNUAL RESEARCH REVIEW

March 22, 1995

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TECHNICAL PROGRAM REVIEW

Project Title:	FUNDAMENTALS OF BRIGHTNESS STABILITY
Project Code:	BRITE
Project Number:	F014
Division:	Chemical and Biological Sciences
Project Staff:	A. Ragauskas
FY 94-95 Budget:	$ 89,000

Program Objective:

Research activities are directed at investigating the fundamental chemical reactions which are initiated when high-yield pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases, methods to eliminate or significantly retard the yellowing process will be pursued.

IPST Goal:

Increase the usefulness of high-yield fibers.

Summary of Results Since Last Report:

Previous Results:

Research efforts in this project have become increasingly focused on screening, designing, and defining the mechanisms by which chemical additives can retard and/or halt brightness reversion. Our investigative studies have examined the use of novel UV-absorbers/quenchers, radical scavengers, and other photostabilization technologies for retarding brightness reversion. Past research efforts demonstrated that several UV absorbers, such as substituted hydroxylphenyl benzotriazole, benzophenones, and 1,3-diketones, could retard brightness reversion. To date, the % stabilization effects we have observed are not sufficiently effective as to justify commercial applications. Nonetheless, we are continuing to improve these technologies and believe that in the near future successful additive technologies will be developed to photostabilize mechanical pulps.

Previous studies have demonstrated that long term storage of photostabilization agents such as ascorbic acid or thiol derivatives may cause a deterioration in their photostabilization effects. Indeed, for ascorbic acid treated mechanical pulp testsheets, we demonstrated that this additive accelerated thermal reversion properties, despite its well-known photostabilization properties. The long-term photostabilization effects of thiol-derivatives were shown to be highly dependent upon the structure of the additive and compounds; for example ethylene glycol bisthioglycolate was shown to have excellent short-term and long-term photostabilization properties. Interestingly, we have also shown that many disulfide derivatives actually exhibit improved photostabilization properties after prolonged periods of storage in the absence of light.

The identification of several new and promising thiol-additives that substantially retard brightness reversion has lead to investigations directed at incorporating these additives into polymeric derivatives. The use of thiol-polymers to stabilize mechanical pulp was initiated on the assumption that these high-weight additives would not have any malodorous properties while retaining the photostabilization effects of the low molecular weight additives. To this end, we prepared a series of polymers which contained thiol derivatives incorporated into the back-bone of the polymer. These preliminary studies confirmed our hypothesis that the use of polymeric thiol-derivatives could remove the malodorous properties of low molecular weight compounds while retaining the photoreversion properties of the mercapto-group. Unfortunately, we have also discovered that a variety of secondary issues, such as physical compatibility with mechanical pulp and effective surface concentration of the additive on the pulp fiber, play an important role in influencing the photostabilization properties of these additives. The results of these studies will require further investigative studies to develop effective photostabilization techniques for mechanical pulps.

Current Results:

To date, no one additive has met all of the commercial requirements needed to photostabilize mechanical pulps. One of the most critical considerations in the design of photostabilization technologies for mechanical pulp is the requirement that the technology remain cost-competitive. Many photostabilization additives developed for mechanical pulps require high levels of additive application so as to achieve significant reductions in photoyellowing. The effectiveness of combinations of various additives as brightness stabilizers for hardwood and softwood BCTMP (bleached chemithermomechanical pulp) was examined during this years research program. Certain additive combinations exhibited synergistic interactions that provided a substantial level of brightness stability. Experimental results suggest that designing specific additive combinations is an effective approach to improving the brightness stability of mechanical pulps and to lowering the overall charge of additives.

Goals for FY 1995-1996:

Additives for Photostabilization (Ragauskas):

Future research studies will continue to examine the use of additive mixtures for the photostabilization of mechanical pulps. Specifically, we propose to study the use of benzotriazole derivatives in conjugation with a mixture of antioxidants applied onto mechanical pulps. Research plans will also determine if the application levels of well-known photostabilization polymer additives, such as polyethylene glycol, can be reduced when they are applied onto handsheets in the presence of several other additives.

Research efforts will also be directed toward determining the optimal type structural features needed for UV absorbers to effectively coat the surface of pulp fibers. Finally, the fundamental chemical properties influenced by the presence of additive mixtures during brightness reversion will be examined.

INTRODUCTION

Technological advances in mechanical pulping and bleaching have made it possible to manufacture mechanical pulps that have a Tappi brightness of above 80 %. The major obstacle to the use of mechanical pulps in high grade paper products is their tendency to photoyellow. This yellowing phenomenon, also known as brightness reversion, occurs primarily as a result of exposure to light and is attributable to photoxidation of lignin [1]. It is generally accepted that the basic mechanism of photoyellowing involves a variety of pathways including: direct absorption of near-UV light by conjugated phenolic groups to form phenoxy radicals; abstraction of phenolic hydroxyl hydrogen by aromatic carbonyl triplet excited state; cleavage of phenacyl-O-aryl ethers to phenacyl-phenoxy radical pairs; and breakdown of arylglycerol-β-O-aryl ethers to phenoxy radical and ketone [2].

Attempts to inhibit the photoyellowing of mechanical pulps are based upon our current understanding of the brightness reversion mechanism. One potential approach is to chemically modify the lignin in mechanical pulps so as to halt the initiation and subsequent radical-based reactions leading to the formation of chromophoric compounds. Although a variety of such preventative measures have been tried, including reduction with borohydride, methylation, acetylation, and hydrogenation, none have been fully effective [2].

On the other hand, the use of additives to inhibit the photoyellowing of mechanical pulps continues to provide encouraging results. A wide variety of potential brightness stabilizers has been studied to date. The application of UV-absorbers onto the surface of mechanical pulp has been shown by several researchers to be an effective method of retarding the overall rates of photoyellowing [3 - 6]. As stated above, all the proposed reaction pathways of photoyellowing involve a series of radical reactions leading to a phenoxy radical, which is a key intermediate to the formation of colored chromophores. Accordingly, radical scavenging antioxidants have been one of the most successful means of photostabilizing mechanical pulps via hydrogen donation to quench reactive intermediates, such as phenoxy radicals. Ascorbic acid is a well-known radical scavenger and reported to be capable of photostabilizing mechanical pulps to a certain extent [7, 8]. Sulphur-containing compounds have been shown to be effective in retarding light-induced yellowing [6, 7, 9 - 12]. Recently, diene-type compounds have also been investigated as antioxidants for photostabilizing hardwood mechanical pulps [13]. The photostabilizing activities of diene-type structures, such as 1,4-pentadien-3-ol and *trans,trans*-2,4-hexadien-1-ol, are believed to be due in part to radical trapping properties of these unsaturated structures [14]. In addition, conjugated diene structures, such as 2,4-hexadien-1-ol and 2,4-hexadienoic acid, have been shown to quench the excited state of lignin-like model compounds [15]. Ragauskas et al. have extended these studies onto mechanical pulp and suggested that one of the molecular pathways by which 2,4-hexadien-1-ol photostabilizes mechanical pulps is by quenching the excited state of lignin chromophores [16].

To date, no one additive has met all of the commercial requirements needed to photostabilize mechanical pulps. One of the most critical considerations in the design of photostabilization technologies for mechanical pulps is the requirement that the technology remain cost-competitive. Many photostabilization additives developed for mechanical pulps require high levels of additive application to achieve significant reductions in photoyellowing. To date, these difficulties have hindered the commercial development of a variety of photostabilization technologies. Furthermore, from a hypothetical view the development of a single additive which will substantially retard or halt photoyellowing of mechanical pulps is highly improbable since photoyellowing of mechanical pulps is a multi-facetted mechanism. Based on literature review [17] and our own research experiences, we believe that the necessary components required to photostabilize mechanical pulps include: UV-absorber, an excited state quencher, and a radical scavenger. By employing these three types of additives the amount of near-UV light which interacts with the fibers will be reduced, the presence of an excited state quencher will deactivate some of the lignin chromophores which absorb light, and the radical scavengers will retard the overall rates of lignin oxidation.

Until recently this field of research has been largely unexplored. Agnemo's ascorbic acid/sulphite patented photostabilization mixture (i.e., sulphite acts solely as a preservative for ascorbic acid) was one of the first successful additive blends for mechanical pulps [18]. Castellan and co-workers have also begun to be active in this field of research and recently patented a mixture of 2,4-dihydroxybenzophenone (i.e., UV absorber) and methylenebisthiopropionate (i.e., radical scavenger) as an effective photostabilization blend for mechanical pulps [19]. In this paper we wish to report our preliminary studies directed at evaluating the effectiveness of combinations of various additives including radical scavengers and UV absorber.

MATERIALS AND METHODS

All chemicals, ethylene glycol bisthioglycolate, 3,3'-dithiodipropionic acid ascorbic acid, 5-phenylpenta-2,4-dienoic acid, and 2,4-dihydroxybenzophenone, are commercial products and were employed as received. Commercial hardwood BCTMP and softwood BCTMP pulps, made from aspen and black spruce, respectively, using sodium sulphite for chemical pretreatment and hydrogen peroxide for bleaching, were used without modification.

Handsheets were prepared according to standard TAPPI procedure T-218. The handsheets were then air-dried at constant temperature (22.0 +/-2.0 °C) and relative humidity (50 +/-2.0 %). Weighed amounts of various additives were dissolved in approximately 10 ml of methanol and sprayed onto handsheets. The handsheets were again air-dried and re-equilibrated at ambient temperature and humidity. For thermal reversion study, the handsheets were stored in the dark at room temperature for five months.

The accelerated photoyellowing studies were conducted with an Oriel 1000W solar simulator which uses a xenon-arc lamp and is fitted with an air-mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. Although several light sources have been employed for accelerated brightness reversion studies, a recent report recommends the use of xenon-arc lamp systems [20]. The lamp and samples were located in a fumehood which provides sufficient air circulation to minimize heating of the samples. Untreated handsheets were used as controls and all experiments were carried out in triplicate. After irradiation, the handsheets were allowed to re-equilibrated at controlled temperature and humidity as described above prior to brightness measurements.

The brightness values of the handsheets were measured following standard TAPPI procedure T-452. Light absorption and scattering coefficients were measured according to TAPPI procedures T 220-om 88 and T 425 om 91.

RESULTS AND DISCUSSION

1. Additives

To explore the effects of additive combinations on the photoyellowing process we selected several representative agents. Three radical scavengers were studied: ethylene glycol bisthioglycolate (thiol), 3,3'-dithiodipropionic acid (disulphide), ascorbic acid, and two UV absorbers: 5-phenylpenta-2,4-dienoic acid (diene), and 2,4-dihydroxybenzophenone. Our recent research has demonstrated that ethylene glycol bisthioglycolate is an effective thiol additive that provides bleaching action and prevents thermal and light-induced brightness reversion [12]. Disulphide is an alternative mercaptan for photostabilizing mechanical pulps. The stabilization effect of 3,3'-dithiodipropionic acid, although moderate, can be retained upon long-term storage [12]. Both of the UV agents absorb in the near-UV and therefore when applied onto handsheets these additives can reduce the intensity of 300 - 400 nm light that pulp is exposed to.

Ascorbic acid is a well-known radical scavenger and reported to retard the photoyellowing of mechanical pulps [7, 8]. On the other hand, the ascorbic acid-impregnated mechanical pulp handsheets have a high tendency to yellow upon long-term storage at ambient temperature [21]. This phenomenon limits the application of ascorbic acid as brightness stabilizer. To explore potential methods of preventing ascorbic acid accelerated thermal reversion, we examined the application of thiol and disulphide as co-additives for ascorbic acid and these results are summarized in Table I.

It can be observed that ascorbic acid considerably reduces the rate of brightness reversion shortly after its application onto handsheets. The incorporation of ascorbic acid with thiol is shown to further photostabilize the pulp; but the addition of disulphide provides little improvement in brightness stabilization activity. However, after five month storage, there is a brightness loss of 44 percent points for the ascorbic acid-impregnated handsheets, whereas, only 3 points for the control. Interestingly, the presence of thiol successfully prevents yellowing caused by ascorbic acid; furthermore, the photostabilization activity of ascorbic acid can be retained. It was also shown that disulphide has no preventative effect on the thermal reversion of ascorbic acid. Our results demonstrate that a thiol/ascorbic acid mixture provides an effective alternative to Agnemo's ascorbic acid/sulphite patent. The thiol additive presumably acts as hydrogen donor (or radical scavenger) to quench reactive radical intermediates which contribute to an autoxidation of ascorbic acid to yellowed products.

2. Brightness stabilization

To assess the effects of various brightness stabilizers on mechanical pulps, we prepared a series of hardwood BCTMP handsheets impregnated by either one individual additive or a mixture of two different additives at varying charge levels, as summarized in Table II.

Generally, the addition of the reagents onto BCTMP handsheets resulted in brightness gains of one to two points, with the exception of 2,4-dihydroxybenzophenone. Presumably, for the radical scavenging agents, such as ascorbic acid, this brightening effect can be attributed to the donation of hydrogen to certain unsaturated structures in lignin, which are known to discolor mechanical pulps, and thereby reducing colored species in the pulp. The bleaching effect observed for the thiol has been suggested to be due to thiol Michael-type additions to α-β-unsaturated carbonyl and quinoid structures [10, 12]. The slight loss in brightness for the benzophenone treated handsheets is due to the well known UV/Vis absorption at λ_{max} 322 nm for 2,4-dihydroxybenzophenone which tails into the visible range. Studies summarized in Table II also demonstrate that 5-phenylpenta-2,4-dienoic acid is an efficient brightness stabilization agent comparable in activity to well known 2,4-dihydroxybenzophenone [5, 6].

To evaluate the efficiency of the additives in retarding photo-induced yellowing, brightness stabilization factors were calculated by the equation shown below and the results are reported in Table III.

$$\text{Brightness Stabilization Factor (BSF)} = \frac{100 \times (\text{Brightness loss of control} - \text{Brightness loss of sample})}{\text{Brightness loss of control}}$$

Individually, both the thiol and 2,4-dihydroxybenzophenone appear to be effective brightness stabilization reagents for the test pulp. The three other additives provide moderate photostabilization effects. Clearly the thiol is more efficient than 2,4-dihydroxybenzophenone for retarding the early phase of photoyellowing. However, the stabilizing activity of the thiol is substantially decreased by extended light exposure. This result suggests that the consumption of the additive is significant as a function of irradiation time. It is known that thiols are easily oxidized and can scavenge radicals by acting as hydrogen donors. There are at least two following ways in which the thiol is possibly being consumed while acting as brightness stabilizers: 1) reaction with carbonyl chromophores and quinones to provide both bleaching action and brightness stabilization effect, 2) scavenging free radicals to inhibit the formation of colored species. On the other hand, the 2,4-dihydroxybenzophenone absorber seems to have a good stability probably due to its mechanism involved in inhibition of photoyellowing. Therefore, this additive remains effective over a long period of time.

As can be seen from Table III, the brightness stabilization factors are not linearly proportional to the additive application levels employed in this study. These results suggest that the addition of high amounts of additives is an inefficient means of photostabilizing mechanical pulps. Interestingly, several of the multi-additive combinations were found to reduce relative rates of photoyellowing far more effectively than a treatment with a single additive. For example, the brightness stabilization factors (BSF) for thiol and 2,4-dihydroxy-benzophenone treated handsheets, at 0.5% application levels were shown to be 50.5% and 43.2% after 10 min. irradiation with the solar simulator. In comparison, a handsheet treated with 0.5% thiol and 0.5% 2,4-dihydroxy-benzophenone exhibited a BSF of 80.2% after a comparable 10 min. period of irradiation. To achieve similar levels of photostabilization with only one additive would have required in excess of 2% thiol or 2,4-dihydroxybenzophenone.

Several other additive mixtures, including thiol/2,4-dihydroxy-benzophenone, thiol/ascorbic acid, and thiol/5-phenylpentadienoic acid also exhibited substantially improved photostabilization properties over single additive applications. Although, to some extent, it was anticipated that the use of a UV-absorber in conjugation with a radical scavenging agent would provide improved photostabilization effects the photoaging properties observed for the thiol/ascorbic acid treatment were unexpected. Since both of these latter reagents are antioxidants, it was anticipated that the use of this mixture would not exhibit substantially improved photoaging performance when applied as a mixture. Inspection of the reversion data in Tables II and III indicates that the use of 0.5% ascorbic acid and 0.5% thiol application on hardwood BCTMP retards the photoyellowing process to such an extent that comparable photostabilization effects by a single additive would require greater than 2% application levels. These results suggest that the photostabilization mechanisms of ascorbic acid and thiol operate, at least in part, on different components of the overall brightness reversion process.

Our results also indicate that not all additive mixtures result in a beneficial cooperative photostabilization effect for BCTMP testsheets. For example, the use of disulphide/ascorbic acid or ascorbic acid/diene provide no net benefit from applying the additives as a mixture onto mechanical pulp handsheets. Indeed, the mixture of ascorbic acid and 5-phenylpentadienoic acid appeared to contribute to the reversion phenomena.

Among the brightness stabilizers investigated in this study the thiol/2,4-dihydroxybenzophenone absorber is the best additive combination for the hardwood BCTMP. Figure 1 shows that the brightness stabilization effects by these additives are shown to be of the following order, namely, (0.5 % thiol + 0.5 % ascorbic acid + 0.5 % 2,4-dihydroxybenzophenone) > (0.5 % thiol + 0.5 % 2,4-dihydroxybenzophenone) > 2 % 2,4-dihydroxybenzophenone > 2 % thiol. The implication of this observation is significant. In order to achieve a given brightness stabilization level, designing specific additive combinations will be more beneficial than using a single additive and could provide an effective approach to photostabilizing mechanical pulps.

To further examine the effectiveness of the additives in photostabilizing mechanical pulps, we prepared a series of softwood BCTMP test sheets. Here, only the thiol and 2,4-dihydroxybenzophenone absorber were elected for investigation, since they were shown to have the greatest brightness stabilizing activity for the hardwood BCTMP, as discussed above. The brightness data and BSF are reported, respectively, in Table IV and Figure 2.

Generally, the overall trend of brightness change appears similar to the case of hardwood BCTMP. However, the thiol additive was found to be more effective than 2,4-dihydroxybenzophenone in preventing brightness reversion for softwood BCTMP. It was also observed that the softwood BCTMP pulps exhibit a greater sensitivity to the additive applications levels. Compared to hardwood

BCTMP, softwood BCTMP can be photostabilized more efficiently by employing higher additive charges. These differences in sensitivity to additive application levels are presumably due to differences in lignin content and the nature of lignin found in softwood and hardwood BCTMP.

3. Absorption and Scattering Coefficients

In addition to the regular brightness measurements, we have measured absorption and scattering coefficients for hardwood BCTMP handsheets impregnated with the thiol and 2,4-dihydroxybenzophenone to obtain more information about color formation during brightness reversion. Table V shows that for the BCTMP handsheets studied nearly all testsheets exhibited identical scattering coefficients which are not altered by both the addition of reagents and irradiation. It is also seen that both the thiol and 2,4-dihydroxybenzophenone absorber can reduce the absorption coefficient upon irradiation indicating that the formation of color can be retarded. The thiol seems to be more efficient than the 2,4-dihydroxybenzophenone absorber in preventing the early phase of yellowing, which is in agreement with the brightness changes observed beforehand.

CONCLUSIONS

The results presented here indicate that certain additive combinations provide cooperative interactions, which can substantially retard the rate of brightness reversion for mechanical pulps. In general, it is more beneficial to design specific additive combinations than to employ one single agent for maximizing brightness stabilization.

Hardwood and softwood BCTMP pulps respond differently to the stabilizing action of the various additives. For the hardwood BCTMP, there is a lower additive requirement. To obtain a high degree of brightness stabilization, combining two additives is more efficient than using one single additive at higher application levels. However, the addition of relatively high amounts of additives can more efficiently photostabilize softwood BCTMP.

In summary, the combination of thiol/ascorbic acid/2,4-dihydroxybenzophenone is an effective brightness stabilizer mixture. The thiol/ascorbic acid is a representative example of the cooperative effect of two additives for photostabilizing mechanical pulps. The interaction of thiol and ascorbic acid, although both acting as radical scavenging antioxidant, not only prevents the thermal reversion caused by ascorbic acid but also retains the brightness stabilization activity of ascorbic acid upon a long-term storage.

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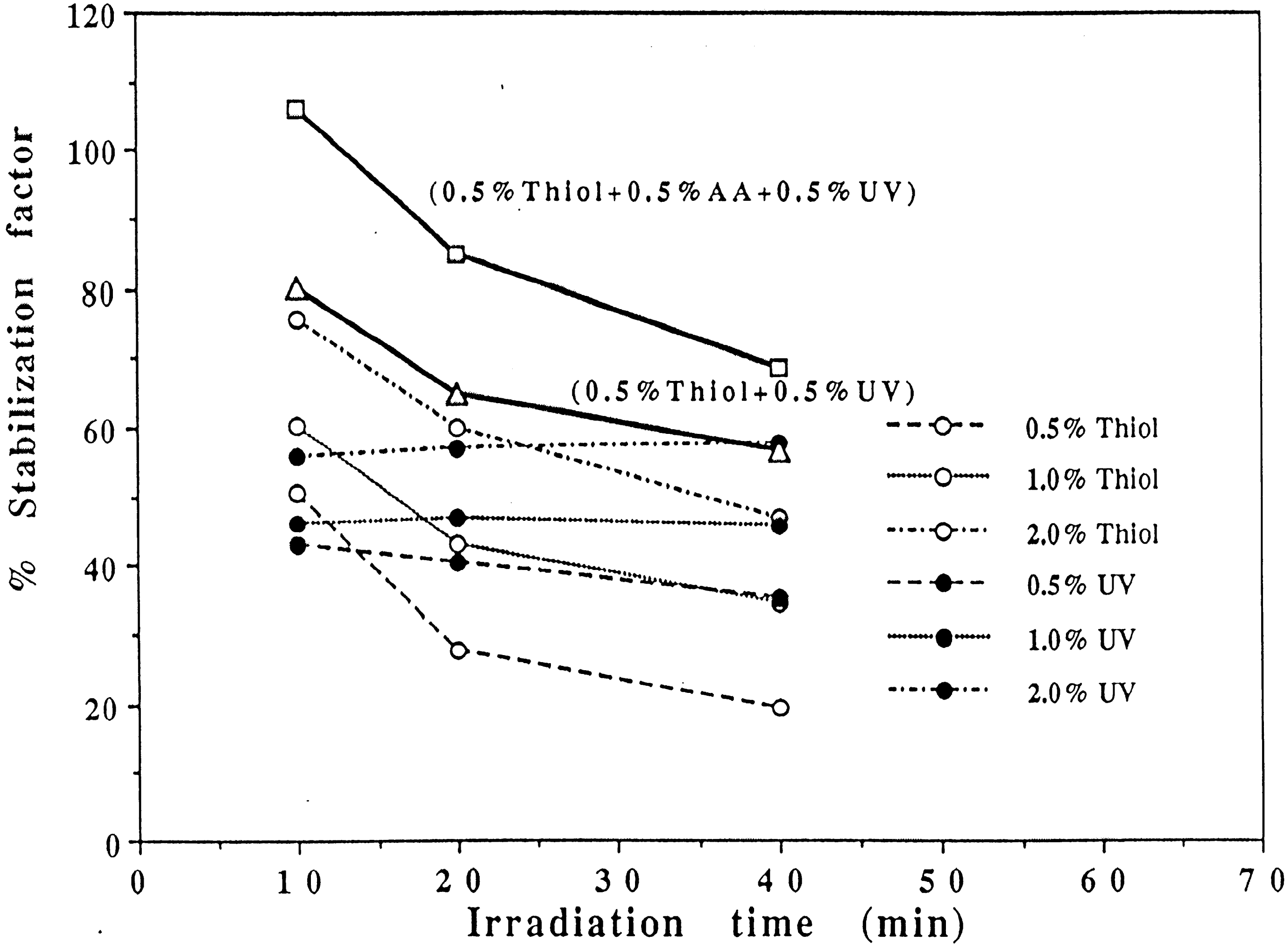

Figure 1. Brightness stabilization factors of combinations of varying application levels for hardwood BCTMP as a function of irradiation time; AA: ascorbic acid; UV: 2,4-dihydroxybenzophenone.

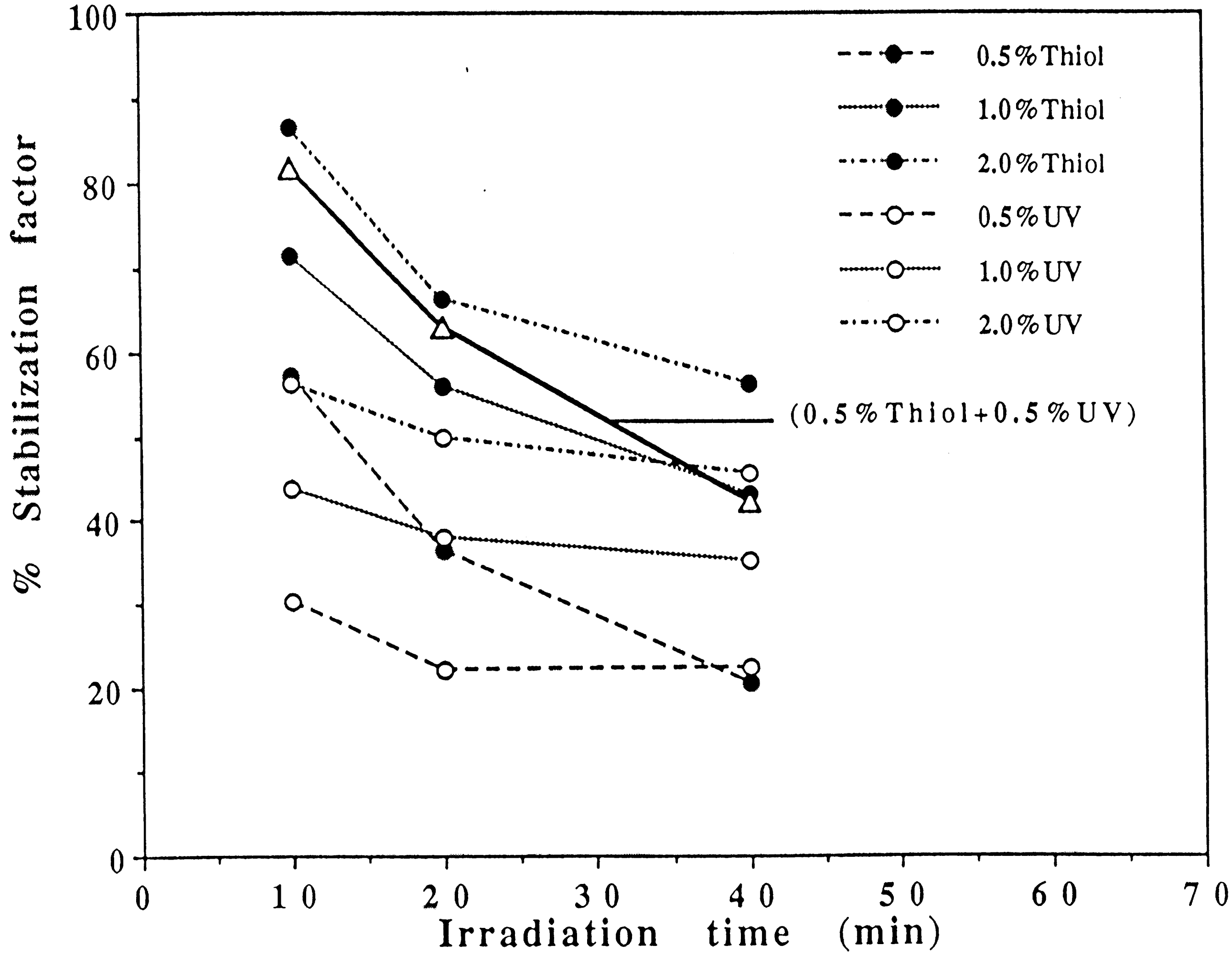

Figure 2. Brightness stabilization factors of combinations of varying application levels for softwood BCTMP as a function of irradiation time; UV: 2,4-dihydroxybenzophenone.

Table I: TAPPI brightness values of hardwood BCTMP handsheets before and after addition of additives and after storage and solar simulator irradiation.

Additive[a]	TAPPI Brightness					
	Initial	Post Addition	Post Storage	Irradiation/min		
				15	30	60
Control	84.7	-	-	67.9	61.9	55.5
Ascorbic Acid	84.4	83.7	-	75.1	71.1	63.3
Thiol/Ascorbic Acid	84.8	86.3	-	83.3	80.4	78.5
Disulphide/Ascorbic Acid	84.2	85.6	-	78.0	73.8	62.9
		Five Months Dark Storage				
Control	86.8	-	83.6	50.3	64.5	58.9
Ascorbic Acid	86.2	84.1	41.9	-	-	-
Thiol/Ascorbic Acid	86.4	87.7	87.7	85.2	83.8	81.0
Disulphide/Ascorbic Acid	83.8	85.3	42.7	-	-	-

[a]5% (wt of additive/wt of od paper %) per additive application levels were incorporated onto each testsheet.

Table II: TAPPI brightness values of hardwood BCTMP handsheets before and after addition of additives and after solar simulator irradiation.

Additive	TAPPI Brightness					
	Application level[a]	Initial	Post Addition	Irradiation/min		
				10	20	40
Control	-	80.2	-	68.8	64.1	59.4
Thiol	0.5	82.7	84.7	76.1	69.7	64.9
	1.0	81.6	83.4	77.2	72.2	67.9
	2.0	81.5	84.2	78.9	75.0	70.5
Disulphide	0.5	79.9	81.9	71.7	67.1	62.4
	1.0	79.5	81.8	72.9	68.1	63.3
	2.0	79.8	81.2	73.3	68.5	64.1
Ascorbic Acid	0.5	81.1	83.1	74.3	68.9	63.5
	1.0	80.7	81.4	73.8	68.5	63.3
	2.1	81.0	82.4	75.9	70.2	65.0
Diene	0.5	80.5	82.1	73.3	68.5	63.6
	1.0	79.6	81.5	73.4	68.8	63.9
	2.0	80.7	82.0	74.4	70.5	65.1
Benzophenone[b]	0.5	81.6	81.9	75.3	71.8	68.1
	1.0	80.4	80.3	75.6	72.8	70.3
	2.0	80.5	80.2	76.7	74.5	72.8

(Note: Table 2 continued next page)

Table II continued:

Additive	Application level[a]	Initial	TAPPI Brightness Post Addition	Irradiation/min 10	20	40
Thiol/Disulphide	0.5/0.5	80.4	84.6	77.6	71.8	66.2
Thiol/Ascorbic acid	0.5/0.5	80.9	86.0	78.9	73.8	67.9
Thiol/Diene	0.5/0.5	80.2	84.2	78.1	73.0	66.8
Thiol/Benzophenone	0.5/0.5	81.6	83.2	79.5	75.8	72.5
Disulphide/Diene	0.5/0.5	82.4	83.8	75.3	70.9	65.4
Disulphide/ Benzophenone	0.5/0.5	79.5	81.2	75.8	73.1	69.6
Ascorbic acid/Diene	0.5/0.5	82.6	77.4	70.4	65.2	61.0
Ascorbic acid/ Benzophenone	0.5/0.5	80.7	81.8	77.1	73.6	69.9
Diene/Benzophenone	0.5/0.5	79.2	81.3	74.8	71.8	67.7
Thiol/Ascorbic acid /Benzophenone	0.5/0.5/0.5	80.4	84.1	81.1	78.0	73.9

[a] wt of additive/wt of od paper; [b]Benzophenone referres to 2,4-dihydroxybenzophenone.

Table III. Brightness Stabilization Factors of Various Additives Applied to Hardwood BCTMP Handsheets.

Additive type	Addition[a] %	Irradiation (min) 10	20	40
	0.5	50.5	27.9	19.6
Thiol	1.0	60.4	43.0	34.4
	2.0	75.7	60.0	46.9
	0.5	38.5	20.0	16.7
Disulphide	1.0	43.6	28.7	22.9
	2.0	44.5	29.4	25.2
	0.5	41.9	23.7	16.2
Ascorbic acid	1.0	41.0	23.7	17.1
	2.0	56.4	32.5	23.8
	0.5	38.5	25.0	19.5
Diene	1.0	47.0	32.5	25.2
	2.0	46.2	36.2	25.7
	0.5	43.2	40.6	35.4
Benzophenone[b]	1.0	46.0	46.7	45.9
	2.0	55.9	57.0	57.9
Thiol/Disulphide	0.5/0.5	75.4	46.6	31.4
Thiol/Ascorbic acid	0.5/0.5	82.5	55.9	37.2
Thiol/Diene	0.5/0.5	81.6	55.3	35.3
Thiol/Benzophenone	0.5/0.5	80.2	64.8	56.5
Disulphide/Diene	0.5/0.5	39.3	28.1	19.0
Disulphide/Benzophenone	0.5/0.5	68.4	60.0	52.9
Ascorbic acid/Diene	0.5/0.5	-4.3	-8.8	-2.9
Ascorbic acid/Benzophenone	0.5/0.5	67.5	55.6	48.6
Diene/Benzophenone	0.5/0.5	62.4	53.7	45.2
Thiol/Ascorbic acid /Benzophenone	0.5/0.5/0.5	106.0	85.1	68.6

[a]wt of additive/wt of od paper; [b]Benzophenone referres to 2,4 dihydroxy-benzophenone.

Table IV: TAPPI brightness values of softwood BCTMP handsheets before and after addition of additives and solar simulator irradiation.

Additive	TAPPI Brightness					
	Application level[a]	Initial	Post Addition	Irradiation/min 10	20	40
Control	-	77.5	-	67.0	63.0	57.6
Thiol	0.5	77.6	80.7	73.1	68.4	61.8
	1.0	77.7	80.7	74.7	71.3	66.4
	2.0	77.1	80.4	75.7	72.2	68.4
Benzophenone[b]	0.5	77.5	78.0	70.2	66.2	62.1
	1.0	77.1	77.4	71.2	68.1	64.2
	2.0	77.7	78.2	73.1	70.4	66.9
Thiol/Benzophenone	0.5/0.5	77.5	80.2	75.6	72.1	66.0

[a] wt of additive/wt of od paper; [b]Benzophenone referres to 2,4-dihydroxybenzophenone.

Table V: Absorption and scattering coefficients of hardwood BCTMP handsheets treated with thiol and 2,4-dihydroxybenzophenone before and after irradiation with the solar simulator.

Additive	Application level[a]	Absorption coefficient[b]			Scattering coefficient		
		I_0	I_{10}	I_{40}	I_0	I_{10}	I_{40}
Control	-	0.2	0.45	0.86	34	33	33
Thiol	0.5	0.19	0.31	0.77	34	35	34
	1.0	0.16	0.25	0.59	35	35	34
	2.0	0.17	0.22	0.46	34	34	33
Benzophenone[c]	0.5	0.21	0.36	0.69	34	34	33
	1.0	0.22	0.36	0.57	35	35	33
	2.0	0.22	0.32	0.53	35	35	33
Thiol/Benzophenone	0.5/0.5	0.16	0.24	0.62	34	35	34

[a]wt of additive/wt of od paper; [b]I_0:before irradiation;I_{10}:10 min irradiation;I_{40}:40 min irradiation; [c]Benzophenone referres to 2,4-dihydroxybenzophenone.