Institute of Paper Science
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STATUS REPORTS

To The

CHEMICAL PULPING AND BLEACHING PROJECT ADVISORY COMMITTEE

March 23, 1994

IPST
Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

1994 ANNUAL SPRING RESEARCH REVIEW

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ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

PROJECT 3474

T.J. McDonough
M. Carden
C.E. Courchene
T. Kubicar
H. Ham
T. Ard
T. Schwantes
C. Walker
C. Woitkovich

March 23, 1994

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, GA 30318

TECHNICAL PROGRAM REVIEW
FY 93-94

Project Title:	**ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP**
Project Code:	BLECH
Project Number:	3474
Division:	Chemical and Biological Sciences
Project Staff:	T.J. McDonough, M. Carden, C.E. Courchene, T. Kubicar, H. Ham, T. Ard, T. Schwantes, C. Walker, C. Woitkovich
FY 93-94 Budget:	$634,000

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 law governing the kinetics of delignification and cellulose degradation by ozone.

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. Establish experimental techniques for measuring selectivity of catalyzed hydrogen peroxide delignification in a model system and compare effects of catalytic metal ion complexes on selectivity (Ph.D. Thesis Research - C. Walker).

5. Evaluate novel chlorine-free bleaching agents.

6. Compare toxicity of ozone bleaching effluents to that of effluents from bleaching with chlorine dioxide and chlorine (Ph.D. Thesis Research - T. Ard).

7. Evaluate sulfite-anthraquinone-nonchlorine routes to high- brightness, kraftlike pulps.

B. Environmentally Compatible Bleaching with Chlorine Compounds

1. Quantify the effect of bleaching conditions on AOX and chlorophenols formation over a wide range of kappa factors in CE, (CD)E and DE partial bleach sequences.

2. 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).

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

SUMMARY:

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

Totally Chlorine-Free Bleaching:

Ozone Bleaching Kinetics

Emphasis was shifted from cotton linters to kraft pulps. Data from runs designed to yield rate laws for both delignification and cellulose depolymerization are being analyzed over the entire duration of the flow reactor experiments, in contrast to the method used earlier, which emphasized initial rates. The newer method of analysis reveals features of the reaction that were obscured by the initial rate approach. The reaction with oxygen delignified kraft pulp displays a brief induction period before accelerating to a rate that is only weakly dependent on ozone concentration and temperature. Dependence on the residual lignin remaining in the fiber is stronger. Reactions with cotton linters display much longer induction periods, to the point of being autocatalytic.

Totally Chlorine Free Bleaching with Dimethyldioxirane

Totally chlorine free (TCF) sequences based on dimethyldioxirane (DMD) were studied. One objective was to evaluate the use of DMD in a short sequence with oxygen and peroxide stages. A second was to compare its effectiveness as a delignifying agent, at a position early in the sequence, with its brightening ability when used later in the sequence. The sequences evaluated were OIQP, in which the I stage is primarily a delignifying stage, and OQPI, in which DMD assumes a brightening role. Chemical charges and bleaching conditions were identical for both sequences.

The degree of delignification achieved indicated the existence of a synergistic effect between DMD and peroxide, allowing very low kappa numbers to be achieved in a final peroxide stage. Both viscosity retention and response of the final brightness to increased DMD charge were much better when the I stage appeared early in the sequence. A final I stage had either no effect or a slightly detrimental effect on brightness. It was concluded that DMD is both effective and selective as a delignifying agent but is neither as a brightening agent.

As a TCF bleaching sequence, OIQP appears to hold considerable promise. A brightness in the mid-80's was reached with modest viscosity loss and no evidence of strength loss.

Catalysis of Peroxide Delignification

Experiments were done in Fe, Fe-EDTA and hemoglobin catalyzed peroxide systems to determine selectivities, as ratios of rate constants, for the respective degradations of lignin and polysaccharide. This was complicated by the observation that the two rate laws are of different order, making the ratio of their rate constants meaningless. To circumvent this, competition experiments were performed in the presence of both lignin and polysaccharide. This led to the discovery of fast condensation reactions between the two, forming a lignin-polysaccharide complex. Since the existence of such condensation reactions is probably a key reason why real peroxide delignification systems are not more effective, this was a significant finding. Subsequent work has been directed at gaining a better understanding of the condensation process and making selectivity comparisons at fixed peroxide concentration.

Characterization of Effluents from Chlorine Dioxide Delignification

Effluents from OC(EO), OD(EO) and D(EO) sequences were characterized. Replacement of chlorine with chlorine dioxide after oxygen bleaching sharply reduced AOX, TOC and chlorine:carbon ratio, expressed as Cl/C_{100}. Larger AOX and TOC reductions were seen in the ether soluble fractions, as well as in the phenolic and acidic subfractions of the ether soluble material. Since both Cl/C_{100} and the size of the ether soluble fractions may be expected to correlate with the potential of an effluent for negative environmental effects, these observations show that replacement of chlorine by chlorine dioxide may be more beneficial than the resulting reductions in whole effluent AOX would suggest.

Oxygen delignification prior to a 100% chlorine dioxide stage reduced whole effluent AOX and TOC in rough proportion to the amount of lignin removed in the oxygen stage, but did not affect the overall Cl/C_{100}. The reductions in AOX and TOC in the environmentally significant ether soluble neutral and phenolic fractions were slightly larger. There was also a significant reduction in Cl/C_{100} in these fractions. Oxygen delignification, like chlorine dioxide substitution, may therefore be more beneficial than the overall AOX reduction would suggest.

The effect of D stage pH on effluents from the OD(EO) partial sequence was also studied. Lower pulp kappa number, higher effluent TOC and lower effluent Cl/C_{100} were obtained at pH 4. The Cl/C_{100} ratios in the ether soluble fraction and its phenolic subfraction were lower at pH 4 but the size of these fractions was greater, with the result that their AOX contents were unaffected by pH. These results suggest that an existing pH 2 stage can be improved by reducing the kappa factor and increasing the pH to 4 to maintain the same delignification extent with reduced environmental effect.

The effect of D stage reaction time has also been investigated with interesting and potentially commercially applicable results. A reaction time of only three seconds gave 67% of the delignification achieved in 30 minutes, while generating only 26% of the AOX. In addition, the AOX produced was more likely to be innocuous, having a chlorine to carbon (Cl/C) ratio only 34% as high as that of the AOX produced in 30 minutes. A one-minute D-stage achieved 84% of the delignification of the 30-minute stage, while generating only 42% of the AOX with a Cl/C only 51% as high. These results show that it is possible to have a major impact on the environmental characteristics of the effluent from a chlorine dioxide based bleach plant by controlling the extent of delignification in a given stage.

A method of aqueous gel permeation chromatography was developed to provide additional information on the characteristics of chlorine dioxide effluents generated under all of the conditions described above. It employs serial columns for improved resolution, a neutral eluent for improved analyte stability and continual analysis of the eluate for total organic carbon as a universal detection method that is free of the bias inherent in the more conventional ultraviolet method. The molecular weight distributions of conventional bleaching effluents determined by this method were much lower than those determined previously by ultrafiltration. The entire (C+D) effluent and over 70% of the E effluent were eluted at retention volumes corresponding to molecular weights of less than 1000.

Comparative Toxicities of Oxygen, Ozone, Chlorine Dioxide and Chlorine Bleaching Filtrates

A brief laboratory study of the toxicity of effluents from chlorine-based and nonchlorine bleaching processes was conducted. Oxygen delignified softwood kraft pulp and its associated filtrate were obtained from an operating mill and further delignified in the laboratory with ozone (Z), chlorine dioxide (D) or chlorine (C), prior to a standard oxygen reinforced caustic extraction (EO) stage. All Z, D, C and (EO) effluents were subjected to triplicate determinations of Microtox toxicity after being stored for either 24 hours or two weeks, with or without neutralization, at either 4°C or 20°C in a complete factorial experimental design. The resulting data were expressed as toxicity units (TU=100/EC50) and subjected to analysis of variance.

Several conclusions were reached, as follows:

1. There is a background level of toxicity which originates in the oxygen stage, process steps prior to bleaching, or in the wood raw material. It is decreased by neutralization and storage, but residual toxicity may still be detected after two weeks. More complete removal may be achievable in biological secondary treatment systems, which were not investigated in this study.

2. The toxicities of fresh, untreated effluents may be ranked as follows, assuming additivity of first and second stage filtrate toxicities: Control (Background) > D(EO) > Z(EO) > C(EO). However, these toxicities are of no importance in regard to environmental effects because of their ephemeral nature and the likelihood of their being reduced or eliminated prior to effluent discharge. Evidence for this statement is the ease with which all except the C(EO) were detoxified by neutralization and storage. It appears likely that even more complete detoxification would be achieved in biological treatment systems.

3. After neutralization and storage for two weeks at room temperature the ranking of toxicities becomes (assuming additivity of first and second stage filtrate toxicities): C(EO) > D(EO) > Z(EO) > Background. The last three are similar in magnitude.

4. The toxicities of filtrates from the D(EO) and (Z(EO) sequences are insensitive to oxidant charge.

Sulfite-Anthraquinone Pulping

A study of the effect of dissolved lignin on pulping rate was completed. The dissolved lignin inhibited pulping at high temperature (150 deg. C) but catalyzed it at low temperature (120 deg. C). The latter observation may have application in the design of an improved process.

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 rise occurs when the rate of disappearance of ozone due to reaction with the pulp becomes sufficiently small in comparison to the rate at which ozone is being continuously fed to the reactor. These phenomena are illustrated by Figure 1, which shows the results of a run in which an oxygen treated softwood kraft pulp was added in an amount sufficient to give a consistency of 0.4% in the reactor. The shallowness of the minimum and the low slope of the curve during the recovery period following the minimum are due to the fact that the ozone demand of the pulp is high in relation to the ozone feed rate. In the case of this particular run, numerical integration of the concentration-time curve showed that the pulp sample (initial kappa no. 10.8) had consumed 0.25% ozone (o.d. pulp basis) during a 24-minute reaction period. In runs under different conditions, this pulp consumed as much as 0.78% ozone during the same time period.

The mass balance around this type of semibatch reactor is

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

This equation shows that at the beginning of the reaction, just after the sample is added, the rate of reaction is equal to the slope of the concentration-time curve. In the preliminary data analysis reported earlier, these initial slopes were used as rate estimates. This approach, however, has two shortcomings. One is that inaccuracies may be introduced in the initial slope measurement by axial dispersion of ozone in the reactor outlet tubing between the reactor and the ultraviolet absorbance measurement point. The second is that data obtained during the remainder of the run is sacrificed.

More recently, we have analyzed the data from the entire concentration time curve 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. If the latter is assumed to be of the form

$$r=k[O_3]^a[Lignin]^b$$

then, for a given lignin concentration,

$$\log(rate)=\log k'+a\cdot\log[O_3]$$

and a plot of log(rate) vs log(ozone concentration) should be a straight line having a slope equal to a. Since the reaction rate, r, is defined in terms of rate of formation of a species, the rate of disappearance of ozone is -r and the appropriate variable to plot is log(-r).

Figure 2 shows this plot for the data of Figure 1. Since it is obviously very different from a straight line, at least one of the above assumptions is not valid. Nevertheless, these assumptions provide a framework for interpreting it. Since ozone concentration initially decreases with time, the rightmost point on the curve represents the start of the reaction. The rate apparently undergoes an initial sharp increase, followed by a levelling off to a nearly constant value prior to the point at which the minimum concentration is reached. The initial increase in rate may be an artifact due to dispersion in the line leading from the reactor, or it may represent an induction period. In either case, it is inconsequential, since comparison to Figure 1 shows that its duration is very short, only a few seconds and a few ten-thousandths of a percent ozone consumption. The largest part of the period prior to occurrence of the concentration minimum is characterized by a nearly constant rate, in spite of the very large change in ozone concentration that occurs during the same period. It may be concluded from this that the rate of reaction is relatively insensitive to ozone concentration, i.e. the reaction is of low order in ozone.

The period following the occurrence of the minimum concentration is protracted (Figure 1) although it spans only a limited ozone concentration range and therefore appears short on Figure 2. The decrease in rate that is seen during this period is attributable to depletion of lignin in the pulp. Given the low order in ozone and the nearly constant ozone concentration, the data obtained during this period will allow determination of the order in lignin. This has not been possible to date because of a lack of information on the stoichiometry of the reaction. 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. This was not possible in the runs described here due to the small size of the pulp sample and the need to obtain viscosity data.

Figure 3 shows the results of two sets of near-duplicate runs at two different temperatures, 25 and 35°C. A number of interesting features are apparent. At either temperature, the difference between the starting and minimum concentrations, the maximum rate and the slope of the post-minimum lines are closely reproducible. Another interesting feature is the fact that the rates are similar at both temperatures, the lower rate at 35° being attributable to the necessarily lower ozone concentration at the higher temperature. It may be concluded that the activation energy of ozone delignification is very low.

The results of a series of runs done with different pulp sample sizes (and therefore different consistencies) are shown in Figure 4. The regular progression in the shapes and positions of these curves again speaks to the reproducibility of the data. The maximum rate increases with consistency, as expected. It is not proportional to consistency, however, presumably because of the inverse relationship between consistency and ozone concentration. The effect of consistency on maximum rate is shown in Figure 5, which also shows the reproducibility of duplicate runs at a given consistency.

It is apparent in Figure 4 that there is a regular progression in the parts of the curves that correspond to the part of the reaction that occurs after the minimum concentration has been reached. The lower the consistency, the higher the ozone concentration during this period, due to reduced depletion, and the greater the decrease in rate per unit increase in ozone concentration, because of the greater relative decrease in the lignin concentration.

All of the results of the above experiments, including ozone consumption and final pulp viscosity, are laid out in Table 1. Ozone consumption, on a dry pulp basis, varied with consistency and ozone concentration in the expected ways, and was quite reproducible between runs. Viscosity decreased with increasing ozone consumption in the expected manner.

Figure 6 shows data from a cotton linters ozonation. Because cellulose reacts with ozone more slowly than lignin, the reaction did not proceed to the minimum concentration in the 30-minute time period allowed. Interestingly, the rate increased steadily throughout, suggesting that the reaction is autocatalytic, i.e. that oxidized cellulose is more susceptible to oxidation than the unoxidized starting material.

TOTALLY CHLORINE FREE BLEACHING WITH DIMETHYLDIOXIRANE:

Dimethyldioxirane (DMD), which can be generated on site or in situ from acetone and peroxymonosulphuric acid, has been shown to be capable of extensively and selectively delignifying kraft pulp. This observation suggests the possibility of totally chlorine free (TCF) sequences based on it. The purpose of the present study was to assess DMD's potential as part of a TCF bleaching strategy by evaluating it in a short sequence with oxygen and peroxide stages. A second objective was to compare its effectiveness as a delignifying agent, at a position early in the sequence, with its brightening ability when used later in the sequence.

An oxygen delignified softwood kraft pulp was obtained from an operating mill and bleached in the laboratory by either of two sequences, each consisting of DMD (I), ethylenediaminetetraacetic acid, EDTA (Q) and hydrogen peroxide (P) stages. The sequences evaluated were OIQP, in which the I stage is primarily a delignifying stage, and OQPI, in which DMD assumes a brightening role. Chemical charges and bleaching conditions were identical for both sequences.

The degree of delignification achieved in the chelant-peroxide partial sequence was enhanced by a preceding DMD stage. A similar enhancement of the DMD stage was observed when it was preceded by the peroxide stage. The OQPI arrangement gave a lower kappa number at low DMD charges, but the lowest final kappa number was obtained with 4% DMD in the OIQP sequence. Viscosity retention was far superior when the I stage was located early in the sequence. Similarly, the response of the final brightness to increased DMD charge was much better when the I stage appeared early in the sequence. In fact, a final I stage had either no effect or a slightly detrimental effect on brightness. In summary, the OIQP sequence was clearly superior to the OQPI sequence. It may be concluded that DMD is both effective and selective as a delignifying agent but is neither as a brightening agent.

As a TCF bleaching sequence, OIQP appears to hold considerable promise. A brightness in the mid-80's was reached with modest viscosity loss. The slight viscosity losses incurred are not manifested in decreased pulp strength.

A full report on this topic is appended as Attachment 1.

CATALYSIS OF ACIDIC PEROXIDE DELIGNIFICATION:

A unique experimental system has been developed to study the effect of three iron-based catalysts on the hydrogen peroxide oxidation of polymeric models of lignin and cellulose. Iron chelated by sequestering agents or bound in porphyrin structures , in the presence of hydrogen peroxide or other oxidants, mimics the delignifying action of lignin peroxidase. The selectivity of these so-called biomimetic compounds for lignin is the subject of this study.

Lignosulfonate (LS) and hydroxyethyl cellulose (HEC) have been chosen as the polymeric models for lignin and carbohydrate. Their molecular weights were measured by size exclusion chromatography and viscometry, respectively. Reactions with hydrogen peroxide were performed at pH 3.0, the optimum for lignin peroxidase activity. The three catalysts evaluated were $FeSO_4$, Fe-EDTA and hemoglobin.

Rates of LS and HEC degradation were separately determined in the presence of each catalyst. The two were then compared to determine the selectivity of each catalytic system. In experiments with both LS and HEC present, the formation of a condensation product was observed. This product is presumably the result of a condensation or coupling reaction between the lignin and cellulose models. Its formation is significant inasmuch as it models a counterproductive process that may be responsible for limitations on the effectiveness of enzymatic delignification systems.

A full report is of the separate degradations of LS and HEC is appended as Attachment 2. Also appended, as Attachment 3, is a briefer account of studies of the formation of the condensation product.

CHARACTERIZATION OF EFFLUENTS FROM CHLORINE DIOXIDE DELIGNIFICATION:

Effluents from OC(EO), OD(EO) and D(EO) sequences were characterized. Replacement of chlorine with chlorine dioxide after oxygen bleaching sharply reduced AOX, TOC and chlorine:carbon ratio, expressed as Cl/C_{100}. Larger AOX and TOC reductions were seen in the ether soluble fractions, as well as in the phenolic and acidic subfractions of the ether soluble material. Since both Cl/C_{100} and the size of the ether soluble fractions may be expected to correlate with the potential of an effluent for negative environmental effects, these observations show that replacement of chlorine by chlorine dioxide may be more beneficial than the resulting reductions in whole effluent AOX would suggest.

Oxygen delignification prior to a 100% chlorine dioxide stage reduced whole effluent AOX and TOC in rough proportion to the amount of lignin removed in the oxygen stage, but did not affect the overall Cl/C_{100}. The reductions in AOX and TOC in the environmentally significant ether soluble neutral and phenolic fractions were slightly larger. There was also a significant reduction in Cl/C_{100} in these fractions. Oxygen delignification, like chlorine dioxide substitution, may therefore be more beneficial than the overall AOX reduction would suggest.

A full report on the characterization of effluents from OC(EO), OD(EO) and D(EO) sequences is appended as Attachment 4.

The effect of D stage pH on effluents from the OD(EO) partial sequence was also studied. Lower pulp kappa number, higher effluent TOC and lower effluent Cl/C_{100} were obtained at pH 4. The Cl/C_{100} ratios in the ether soluble fraction and its phenolic subfraction were lower at pH 4 but the size of these fractions was greater, with the result that their AOX contents were unaffected by pH. These results suggest that an existing pH 2 stage can be improved by reducing the kappa factor and increasing the pH to 4 to maintain the same delignification extent with reduced environmental effect. A full report is appended as attachment 5.

The effect of D stage reaction time has also been investigated with interesting and potentially commercially applicable results. A reaction time of only three seconds gave 67% of the delignification achieved in 30 minutes, while generating only 26% of the AOX. In addition, the AOX produced was more likely to be innocuous, having a chlorine to carbon (Cl/C) ratio only 34% as high as that of the AOX produced in 30 minutes. A one-minute D-stage achieved 84% of the delignification of the 30-minute stage, while generating only 42% of the AOX with a Cl/C only 51% as high. These results show that it is possible to have a major impact on the environmental characteristics of the effluent from a chlorine dioxide based bleach plant by controlling the extent of delignification in a given stage. A full report is appended as Attachment 6.

A method of aqueous gel permeation chromatography was developed to provide additional information on the characteristics of chlorine dioxide effluents generated under all of the conditions described above. It employs serial columns for improved resolution, a neutral eluent for improved analyte stability and continual analysis of the eluate for total organic carbon as a universal detection method that is free of the bias inherent in the more conventional ultraviolet method. The molecular weight distributions of conventional bleaching effluents determined by this method were much lower than those determined previously by ultrafiltration. The entire (C+D) effluent and over 70% of the E effluent were eluted at retention volumes corresponding to molecular weights of less than 1000. A full report is appended as Attachment 7.

COMPARATIVE TOXICITIES OF OXYGEN, OZONE, CHLORINE DIOXIDE AND CHLORINE BLEACHING FILTRATES:

A brief laboratory study of the toxicity of effluents from chlorine-based and nonchlorine bleaching processes was conducted, as summarized at the beginning of this report. A more detailed summary is appended as Attachment 8.

GOALS FOR 1994-95:

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, phenolic 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 novel chlorine-free bleaching agents, including dimethyldioxirane, by studying their response to process variables and their interactions with other bleaching agents.

5. Evaluate the toxicities of ozone, chlorine dioxide and chlorine bleaching effluents in comparison with one another.

B. Environmentally Compatible Bleaching with Chlorine Compounds

1. Quantify the effect of mixing on AOX and chlorophenols formation over a wide range of kappa factors in CE, (CD)E and DE partial bleach sequences.

2. 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.

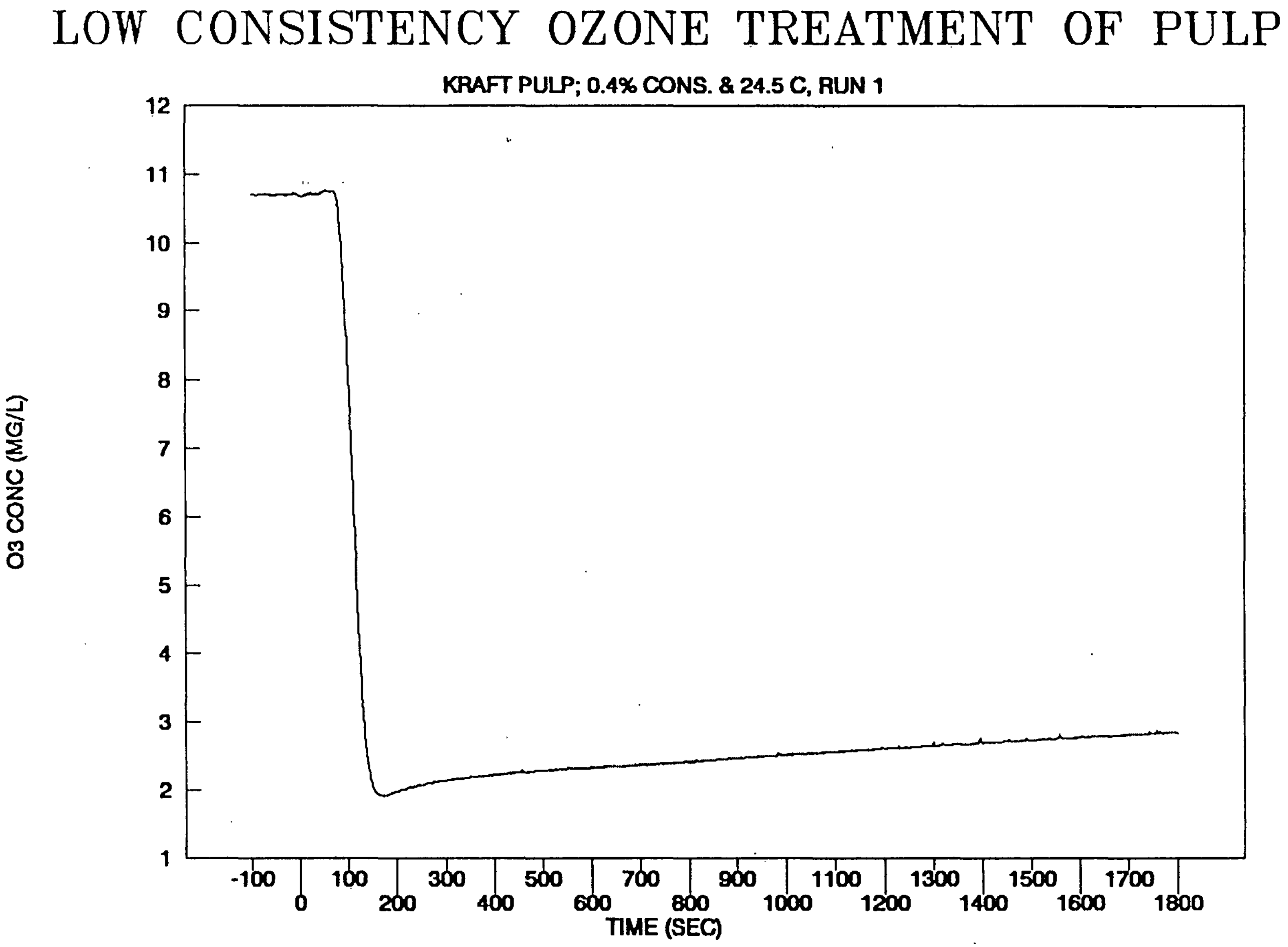


Figure 1. Typical Concentration - Time Curve

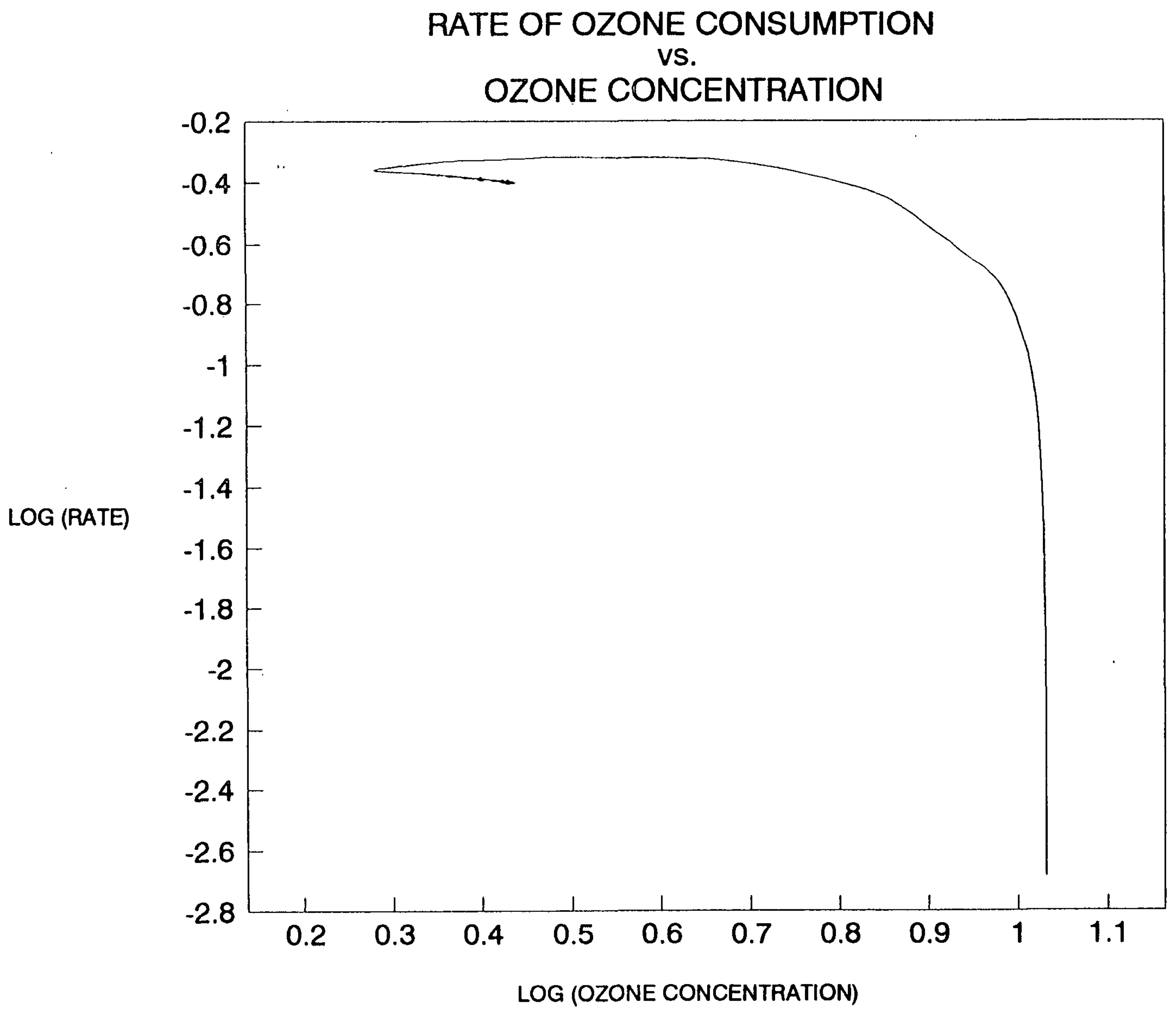


Figure 2. Typical log (rate) vs Log (O_3 concentration) curve

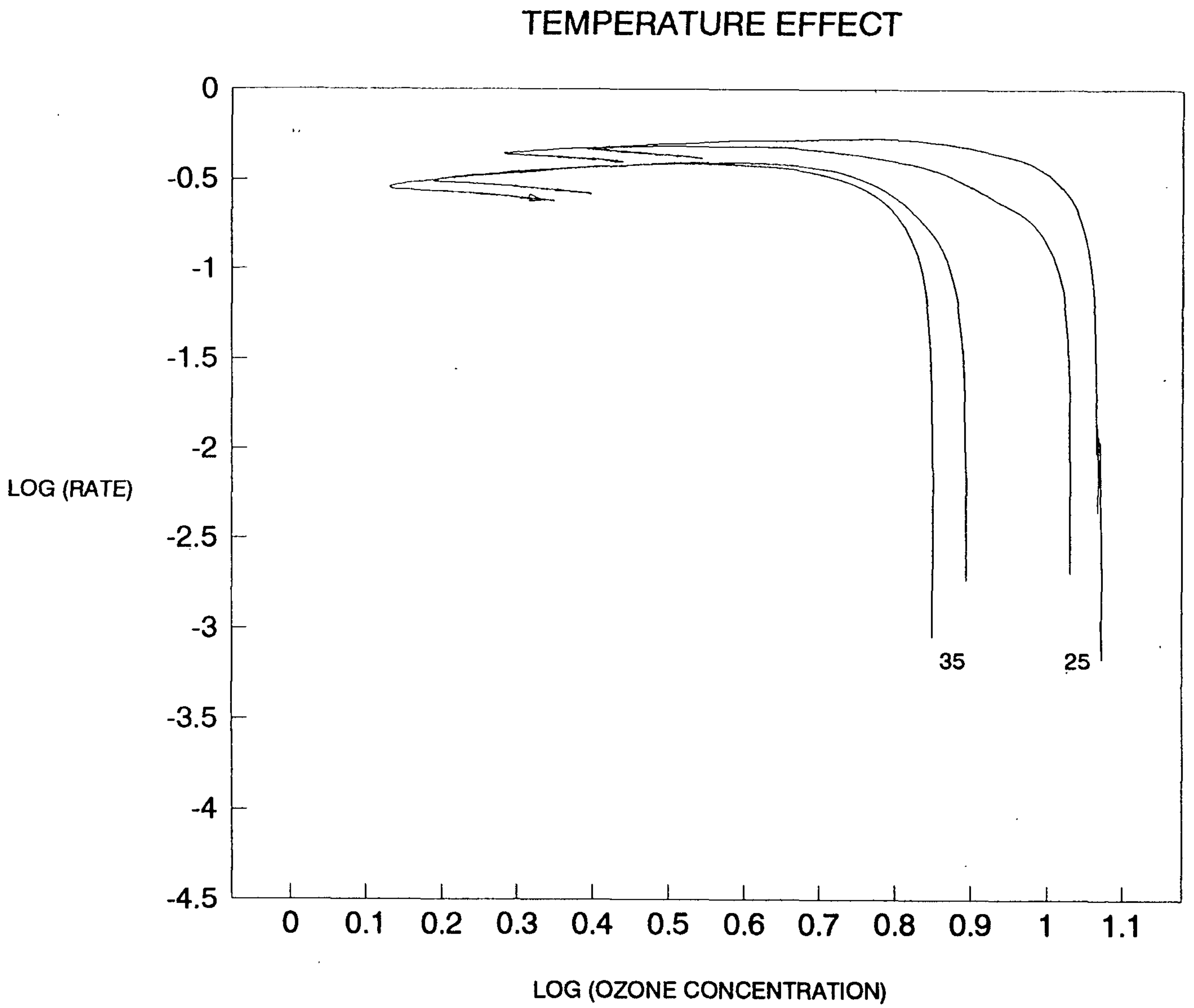


Figure 3. Effect of temperature

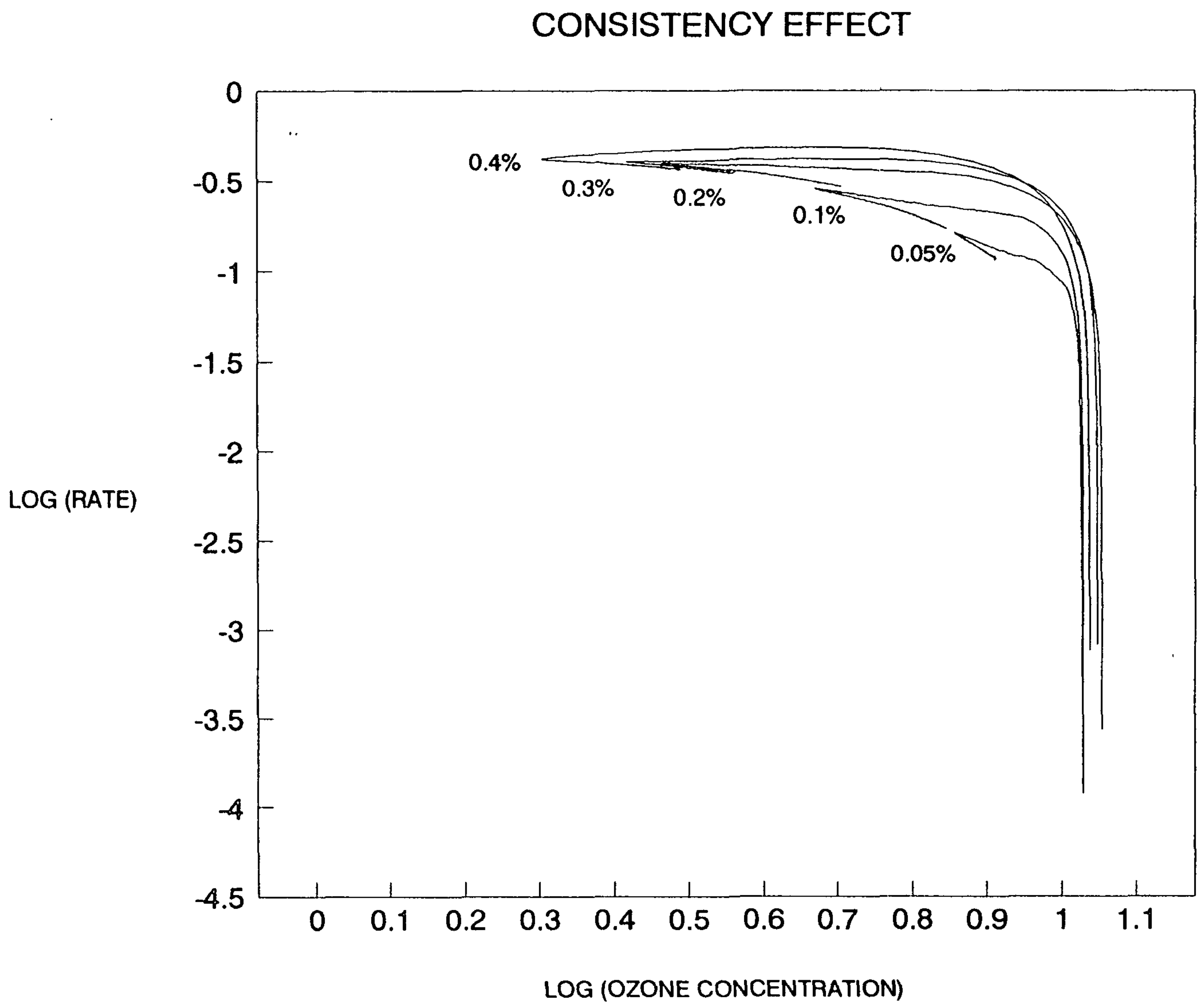


Figure 4. Effect of consistency

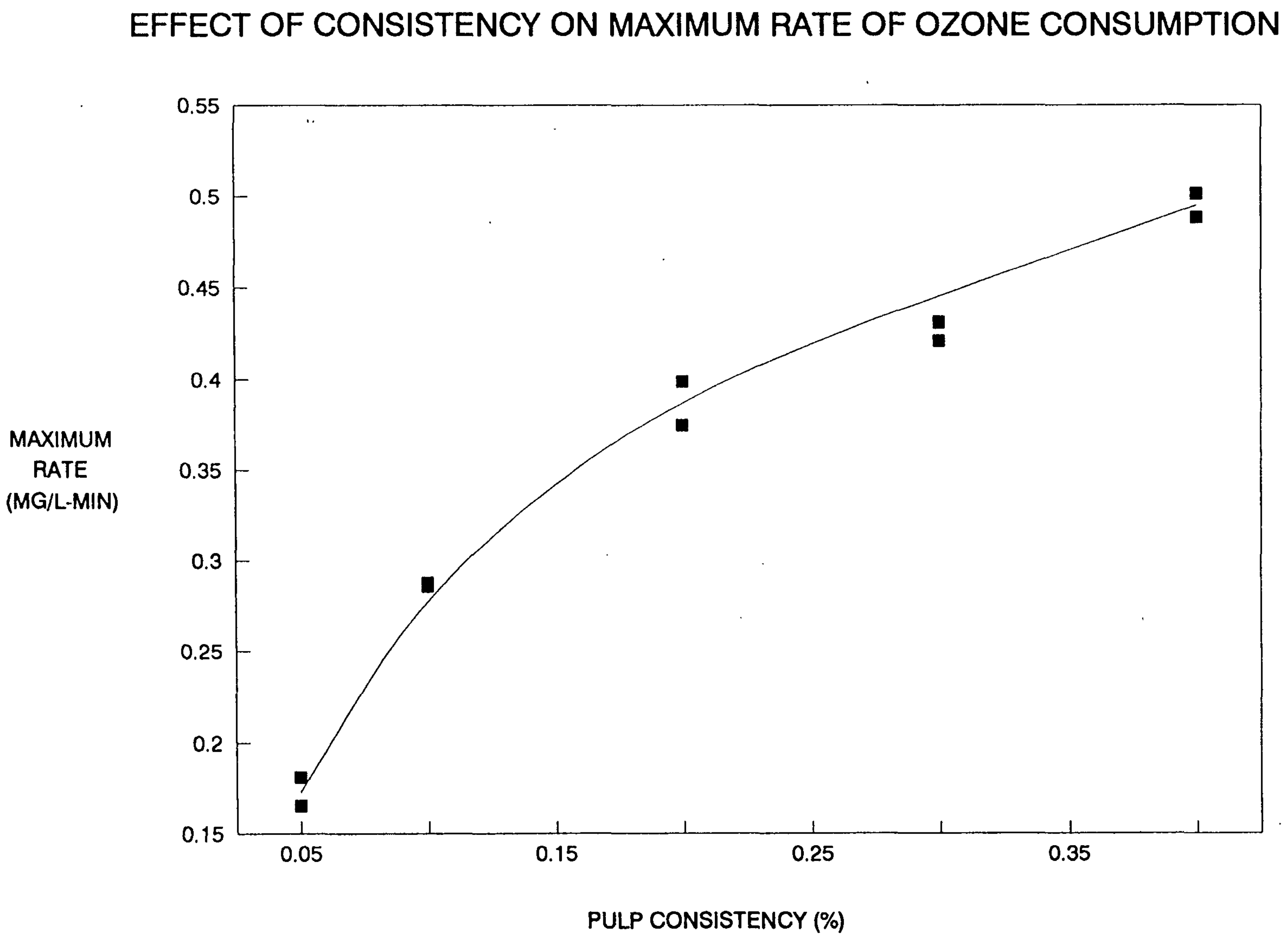


Figure 5. Effect of consistency on maximum rate

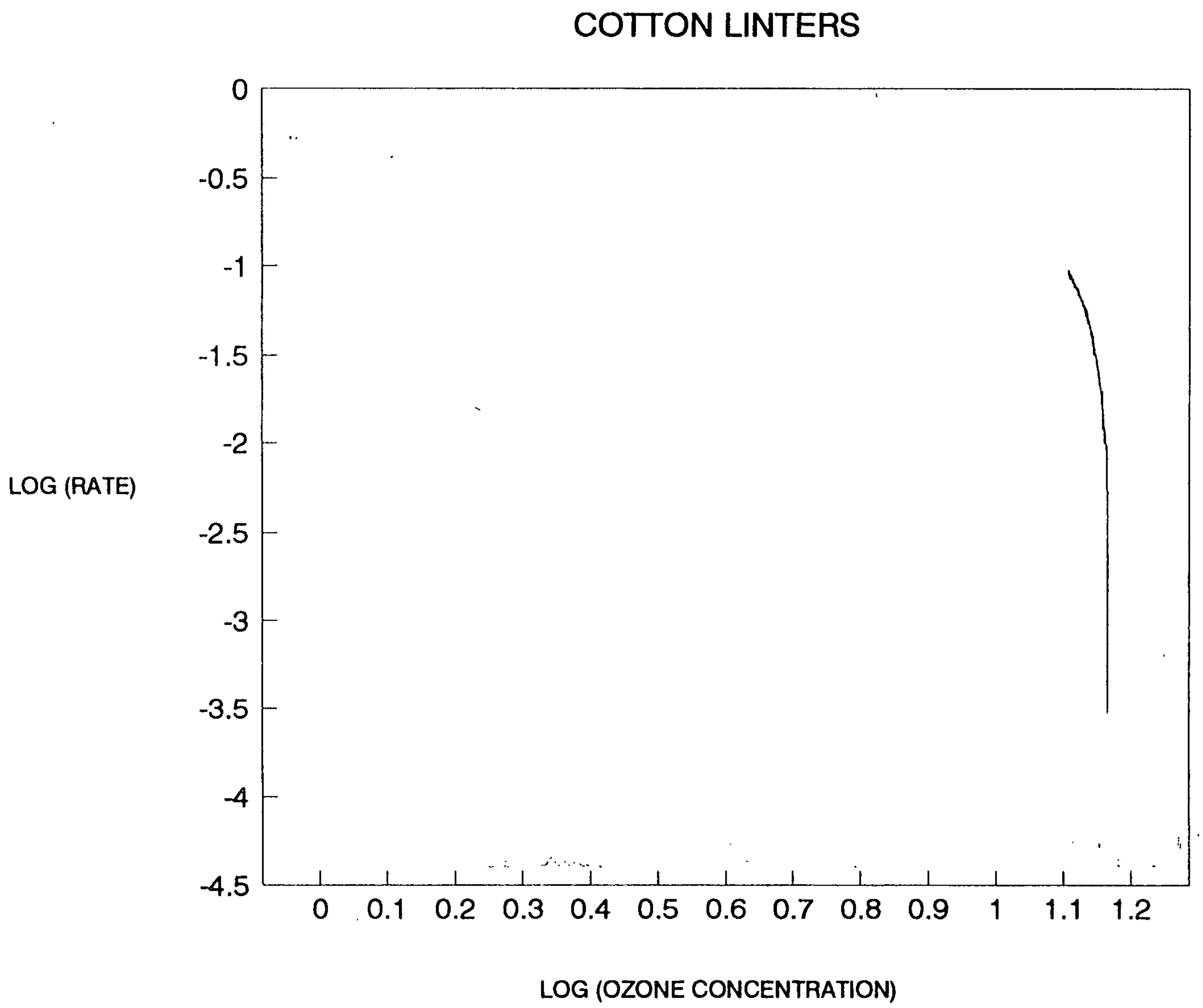


Figure 6. Log (rate) vs log (O_3 conc.) for cotton linters

Table 1. Kinetics of Ozone Bleaching of Oxygen Delignified Kraft Pulp[a]

	Run No.	Initial Ozone Concentration (mg/L)	Consistency (%)	Temperature (C)	Ozone Consumed (% on o.d. fiber)	Final Viscosity (cps)	log(-r) max	-r max	$\frac{d[\log(-r)]^b}{d[\log(\text{ozone conc})]}$
Temperature Varied	1	10.7	0.4	25	0.25	7.1	-0.32	0.48	-0.28
	2	11.8	0.4	25	0.26	6.8	-0.27	0.53	-0.33
	3	7.0	0.4	35	0.15	7.3	-0.42	0.39	0.34
	4	7.8	0.4	35	0.17	7.2	-0.41	0.39	-0.35
Consistency Varied	5	10.7	0.05	25	0.65	4.0	-0.78	0.17	-2.60
	6	10.9	0.05	25	0.81	4.0	-0.74	0.18	-2.03
	7	10.7	0.1	25	0.56	4.4	-0.54	0.29	-1.20
	8	10.5	0.1	25	0.58	4.5	-0.54	0.29	-1.08
	9	11.3	0.2	25	0.42	5.2	-0.40	0.40	-0.53
	10	10.2	0.2	25	0.42	5.5	-0.43	0.38	-0.42
	11	11.2	0.3	25	0.30	6.1	-0.38	0.42	-0.39
	12	10.6	0.3	25	0.30	8.3	-0.37	0.43	-0.30
	13	10.9	0.4	25	0.23	6.6	-0.31	0.49	-0.30
	14	11.9	0.4	25	0.26	9.9	-0.30	0.50	0.27

[a] Unbleached Pulp data: Oxygen bleached softwood kraft
Kappa number: 10.8
Viscosity: 18.7

[b] During period of increasing ozone concentration

ATTACHMENT 1

TOTALLY CHLORINE FREE BLEACHING WITH DIMETHYLDIOXIRANE

Thomas J. McDonough, Arnaud Marquis and Arthur J. Ragauskas
Institute of Paper Science and Technology
Atlanta, Georgia

INTRODUCTION

Dimethyldioxirane (DMD) is an organic peroxide that can be made by oxidizing acetone with the potassium salt of Caro's acid (peroxymonosulfuric acid, an oxidized form of sulfuric acid). The reaction effectively inserts an extra oxygen atom into the carbonyl group of acetone, giving a structure that has a three-membered ring containing two oxygen atoms and one carbon atom, the carbon atom bearing two methyl substituents, as shown in Figure 1. The strained ring structure and peroxidic character make DMD a powerful and reactive oxidizing agent.

The potential of DMD for pulp bleaching applications was independently recognized by Lee and co-workers at the Pulp and Paper Research Institute of Canada[1] and Ragauskas at the Institute of Paper Science and Technology[2]. Lee *et al.* showed that the kappa number of a hardwood kraft pulp was reduced from 16.4 to 3.4 (79% delignification) by 2.5% isolated DMD, and that of a softwood kraft pulp was reduced from 31.5 to 5.4 (83% delignification) by 12.5% in-situ-generated DMD followed by 3.3% NaOH. Ragauskas showed that the kappa number of a softwood kraft pulp was reduced from 39.5 to 12.5 (68% delignification) by 5% isolated DMD. In situ generation of DMD is accomplished by adding acetone, sodium bicarbonate, and potassium peroxymonosulfate to the pulp, the DMD charge being calculated from the amount of active oxygen added as peroxymonosulfate. The studies cited above also showed that DMD is very selective as a delignifying agent. For example, in reducing the kappa number of a softwood pulp from 31.5 to 5.4, the viscosity was reduced only from 33.5 to 21.0. This reflects the relative inertness of DMD toward saturated carbohydrates. The literature on bleaching with dioxiranes and the relevant chemistry has recently been reviewed by Ragauskas.[3]

Although the above studies have demonstrated the ability of DMD to effectively replace chlorine in the chlorination stage of multistage bleaching sequences, the emphasis has generally been on sequences employing chlorine dioxide in the later stages. Published data on chlorine compound free sequences consists of only three data points.[4] There is, however, cause for concern that the use of chlorine or any of its compounds, including chlorine dioxide, may be limited in the future. To guard against this possibility, research aimed at the development of totally chlorine free (TCF) bleaching technology is of increasing importance. Accordingly, we undertook the present study to explore the potential of DMD to play a role in TCF multistage bleaching sequences.

Our objectives were: first, to evaluate the potential benefits of combining a DMD stage with oxygen, chelant and peroxide stages; and secondly, to compare the utility of DMD as a delignification stage placed early in the sequence, with its effectiveness as a brightening stage at the end of the sequence. The two sequences compared were thus OIQP and OQPI in which I is used to denote a DMD stage. (The "I" designation is derived from the informal rule that a stage should be designated by the first letter in its name that is unlikely to be confused with an existing stage designator; the others are dictated by the TAPPI protocol.[5])

EXPERIMENTAL APPROACH

Any commercial implementation of DMD bleaching may well involve generation of the bleaching agent *in situ*. Nonetheless, the full potential of such systems is definable in terms of the results obtained by using pre-made, isolated DMD as the bleaching agent, and studies to date indicate that this potential is closely approached by generation *in situ*. For this reason, and to allow the DMD charge to be well defined, we chose to use isolated DMD in the present study. DMD was generated by adding potassium peroxymonosulphate (as the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ sold under the trade name "Oxone") to an aqueous acetone solution of sodium bicarbonate and vacuum distilling the DMD in acetone.[6] The DMD concentration, as determined iodometrically, was in the range 0.12-0.14M.

The pulp used was an oxygen-delignified softwood kraft from a southeastern U.S. mill. It had a kappa number of 14.1 and viscosity 16.4 cp. Bleaching was conducted in sealed polyester bags in a thermostatted water bath. DMD stages were conducted by adding the required quantity of DMD (0.12M in acetone) to pulp to give a consistency of 12%, sealing the bag and maintaining it at 25°C for 1 hour; the pH was in the range 5-7. Controls were run in which the DMD solution was replaced by acetone; the corresponding results are shown on the graphs as points plotted at a DMD charge of zero. Conditions for the chelant stage were 1 hour, 90°C, 10% consistency and pH 5-7, with an ethylenediaminetetraacetic acid (EDTA) charge of 0.2% (o.d. pulp basis). Conditions for the peroxide stage were 4 hours, 90°C, 20% consistency, and chemical charges (o.d. pulp basis) were 2% H_2O_2, 2% NaOH, 3% sodium silicate and 0.05% $MgSO_4$.

Kappa number, viscosity and PFI mill evaluations were conducted according to the corresponding TAPPI test methods. Brightness was determined by an ISO test method.

RESULTS AND DISCUSSION

The results are discussed under the headings of delignification, brightness, and selectivity.

Delignification

Figure 2 shows the effect on kappa number of applying varied amounts of DMD to the oxygen delignified starting pulp (resulting in an OI partial sequence) and to pulp which had previously been subjected to chelant and peroxide stages (resulting in an OQPI sequence). It is apparent that DMD has substantial delignifying power, and that the pulp continues to respond to incremental additions of DMD over the range shown. (Note that, in Figure 2 and elsewhere in this paper, DMD charge is expressed in terms of the actual chemical, not in terms of its content of active oxygen atoms, as has been done elsewhere.[1,4] The charge expressed as DMD is 4.26 times higher than when it is expressed as active oxygen, but is a more realistic reflection of the chemical requirement.)

Although increasing the DMD charge continues to decrease the kappa number, a levelling off is apparent in Figure 2. The levelling off can be described by assuming that the effectiveness of an incremental addition of DMD is proportional to the square of the amount of residual lignin remaining. This simple differential relationship, when expressed in integral form, implies a linear relationship between the reciprocal of the kappa number and the DMD charge, as shown in Figure 3. A similar relationship has been previously observed for oxygen delignification[7]. In both cases, it may be attributable to the diversity of residual lignin structural features and the corresponding variability in their ease of removal. The "easy" ones are effectively removed at low charges of oxidant, while the "difficult" ones remain to be removed less efficiently by additional oxidant.

Figure 4 compares the final extents of delignification achieved by the two TCF sequences that differ only in respect to the placement of the DMD (I) stage. At low DMD charges, a lower final kappa number is obtained by placing the I stage at the end of the sequence. On the other hand, using the I stage to accomplish the bulk of the delignification by placing it early in the sequence makes the DMD less subject to the levelling off effect described above. The result is that lower final kappa numbers are achieved by the OIQP sequence when the DMD charge is in the higher range likely to be needed for effective TCF bleaching. These observations can be interpreted in terms of synergism between the QP partial sequence and the I stage. Placing QP before I increases the % delignification achieved in I at any given DMD charge, as shown in Figure 5. Similarly, placing I before QP increases the % delignification in QP, and the larger the amount of DMD used the greater is the enhancement of the subsequent QP sequence, as shown in Figure 6. On the other hand, the enhancement of I by a preceding QP decreases as the DMD charge is increased, as indicated by the convergence of the OI and OQPI curves in Figure 5. The net result is superior delignification by OIQP at higher DMD charges.

Brightness

The effects on brightness of applying increasing amounts of DMD to both untreated oxygen stage pulp and pulp after OQP are shown in Figure 7. They can be interpreted in terms of two kinds of reactions that compete with each other - lignin removal and chromophore introduction. When oxygen delignified but otherwise untreated pulp is treated with DMD, the brightness continuously increases, albeit at a modest rate. Under these conditions of low brightness and high lignin content, lignin removal is the predominant effect. By contrast, application of limited amounts of DMD to the brighter, low kappa number pulp emerging from an OQP sequence results in a brightness decrease, as a result of chromophores created by DMD. Lignin removal becomes predominant at higher charges, but no net brightness gain is achieved. It is clear from these results that DMD is unsuitable as a final brightening stage. Attempts to reductively remove the chromophores introduced by DMD met with little success. Treatment with sulfur dioxide after bleaching had no effect, and a single experiment involving treatment of the 4% DMD OQPI pulp with 1% of a commercial hydrosulfite formulation increased the brightness only 3 units.

The effect of DMD on final brightness is much more positive when it is applied earlier in the sequence, as shown in Figure 8. Preceding the QP partial sequence with DMD improved the brightness gain achieved with a fixed amount of peroxide. Apparently the dominant effects of DMD in this role are delignification and "conditioning" of the remaining lignin to make it more responsive to peroxide treatment. The chromophores introduced by the DMD treatment are inconsequential in this sequence because they are susceptible to removal by hydrogen peroxide. Further evidence for this was provided by a separate experiment in which pulp bleached in the OQPI sequence with 4% DMD was subjected to an additional peroxide stage under the same conditions as the first one. The brightness was increased from 70 to 88.

Evidence for a lignin "conditioning" effect is the aforementioned increase in % delignification by peroxide following DMD treatment. Figure 9 was prepared to investigate the relationship between the improvement in delignification and the improvement in brightness response. Kubelka-Munk theory was used to convert the brightness data to k/s data, where k is the light absorption coefficient and s is the scattering coefficient. If it is assumed that there is no change in scattering coefficient during bleaching, the change in k/s may be interpreted as entirely due to a change in k, which is a measure of the effective concentration of chromophores in the fibers. This figure, together with Figure 6, suggests that the increased QP delignification associated with low charges of DMD results in higher rates of chromophore removal than at higher DMD charges.

The combined effects of the I stage on delignification and brightness are summarized in Figure 10, which makes the superiority of the OIQP sequence readily apparent.

Selectivity

One measure of selectivity, pulp viscosity, is shown in Figure 11 as a function of the charge of DMD applied after O and OQP, respectively. DMD in amounts up to 2% had virtually no effect on the viscosity of the oxygen stage pulp but a noticeable viscosity loss was seen at 4% DMD. After OQP, however, a continuous decrease in viscosity was observed as the DMD charge was increased. The difference in behavior may reflect increased vulnerability of cellulose to oxidative attack when less lignin is present to consume the oxidant. The practical implication is that application of DMD late in the sequence carries higher risk of pulp strength loss. Its use early in the sequence, however, does not appear to carry the same risk, as shown in Figure 12. Viscosity losses remain modest as the DMD charge is increased in the I stage of the OIQP sequence. The combined effects on brightness and viscosity are summarized in Figure 13; the OIQP sequence is seen to remain selective at high brightness levels, and the shape of the curve suggests that the selectivity limit on brightness was not reached.

To provide another measure of selectivity, the bleached pulps were beaten in a PFI mill and handsheets were prepared for zero-span tensile strength measurement. Each pulp was beaten to three different Canadian Standard Freeness levels in the range 190 - 700 mL, and handsheets were prepared and tested. The three results for any given pulp did not differ significantly and were averaged to give the final results plotted in Figure 14. It is apparent that there were no significant effects of bleaching conditions on strength retention.

CONCLUSIONS

1. Oxygen delignified softwood kraft pulp is effectively further delignified by treatment with DMD. In the present study, the kappa number was reduced from 14.1 to 5.8 by treatment with 4% DMD. Within this range, the effect of incremental additions of DMD was approximately proportional to the square of the remaining residual lignin content.

2. Totally chlorine-free bleaching with oxygen and peroxide can be enhanced by adding a DMD (I) stage to the sequence. Insertion of a 4% DMD I stage after the oxygen stage of an oxygen-chelant-peroxide (OQP) sequence reduced the kappa number after the P stage from 5.9 to 0.8 and increased the final brightness from 66 to 85.

3. Adding the I stage to the end of the OQP sequence was less successful, resulting in a final brightness of only 69 with 4% DMD, in spite of the fact that extensive lignin removal occurred in the I stage. The OQPI sequence also resulted in lower viscosity than the OIQP sequence.

4. A synergistic effect on delignification may be observed upon combining a QP partial sequence with an I stage. Preceding I by QP increases the relative extent of delignification that occurs in I, and preceding QP by I does the same for QP. The latter effect is greater at DMD charges greater than 2%.

5. Dimethyldioxirane is not an effective brightening agent, apparently because it introduces chromophores into the remaining lignin. However, it has a positive effect on the brightening power of a subsequent peroxide stage. Peroxide not only removes the chromophores formed by DMD but benefits from the prior DMD treatment.

6. Application of up to 2% DMD to oxygen delignified pulp had no effect on viscosity, but a modest viscosity decrease was observed at higher DMD levels. DMD decreased the viscosity of OQP pulp over the whole range of application. None of the viscosity decreases was manifested as a loss in zero-span tensile strength.

LITERATURE CITED

1. Lee, C.-L., Hunt, K. and Murray, R.W., "A Novel Non-Chlorine Agent for Chemical Pulp Bleaching," 1992 TAPPI Pulping Conference Proceedings, TAPPI PRESS, Atlanta, Book 3, p. 1237; "Dimethyldioxirane as a Nonchlorine Agent for Chemical Pulp Bleaching," *Tappi J.* **76**(11):137 (1993).

2. Ragauskas, A.J., " Investigation of Dimethyldioxirane as a Bleaching Reagent for Kraft Pulp," *Tappi J.* **76**(7):87 (1993).

3. Ragauskas, A.J., "Bleaching of Kraft Pulps via Dioxiranes," American Chemical Society, in press.

4. Lee, C.-L., Hunt, K., and Murray, R.W., "Activated Oxygen, A Selective Bleaching Agent For Chemical Pulps. Part 1. Laboratory Bleaching with Isolated and In-Situ-Generated Activated Oxygen," Preprints, 79th Annual Meeting, Technical Section, CPPA, p. B1 (1993).

5. TAPPI Technical Information Sheet TIS 0606.21 (1993).

6. Adam, W., Yuk-Yee, C., Cremer, D., *et al.*, *J. Org. Chem.* **52**:2800 (1987).

7. McDonough, T.J., Cukier, M., and Nelson, D.A., "Effects of Kraft Pulping Conditions on Oxygen Delignification and Subsequent (CD)ED Bleaching. 1983 TAPPI Pulping Conference Preprints, TAPPI PRESS, Atlanta.

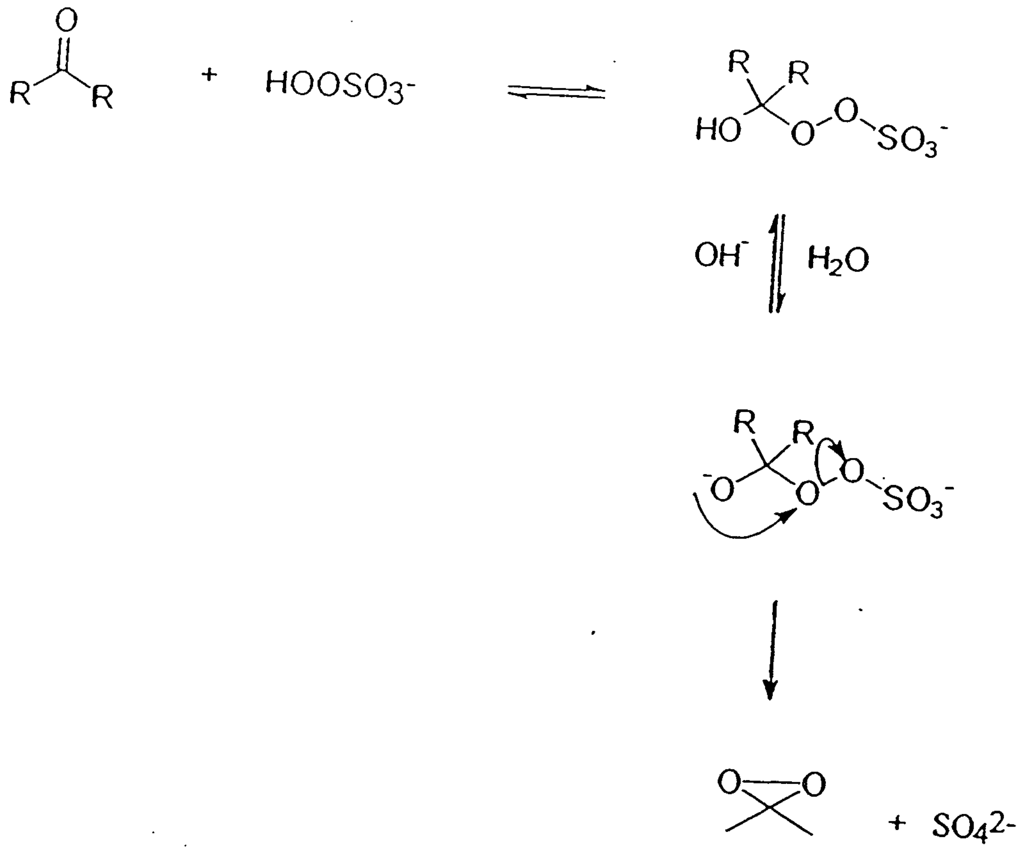


Fig. 1. Formation of dimethyldioxirane.

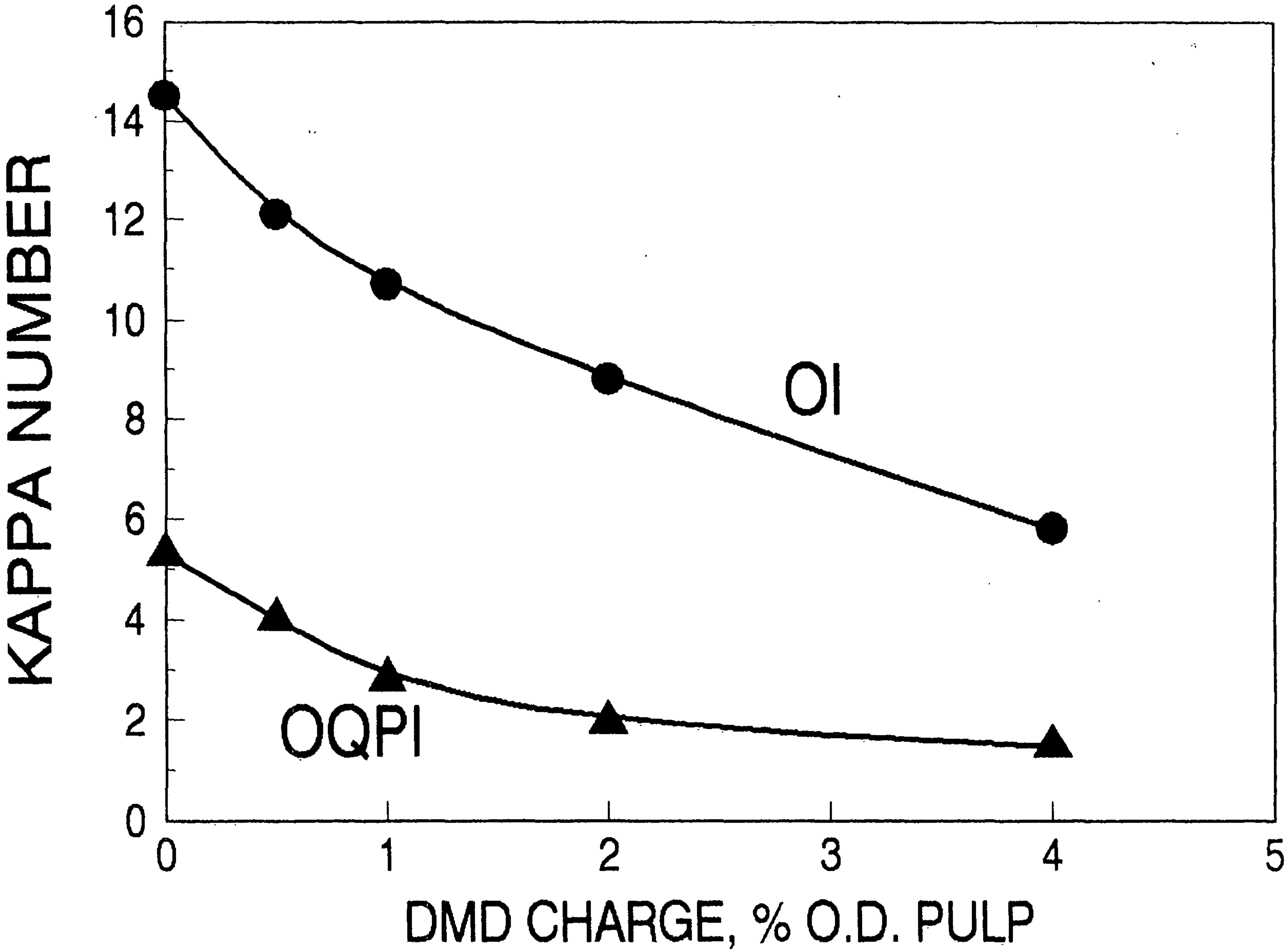


Fig. 2. Kappa number vs. DMD charge for the OI and OQPI sequences.

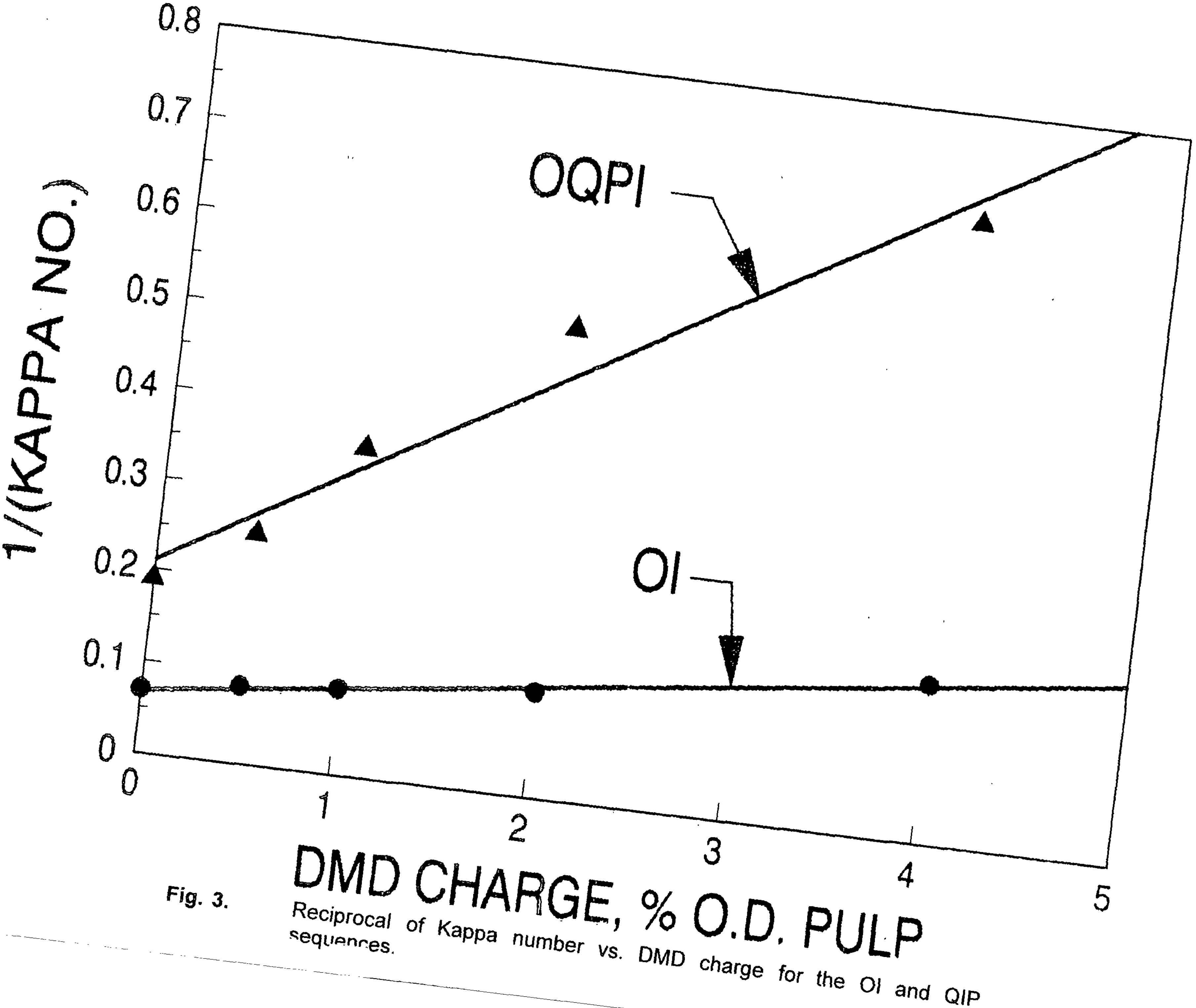


Fig. 3. Reciprocal of Kappa number vs. DMD charge for the OI and QIP sequences.

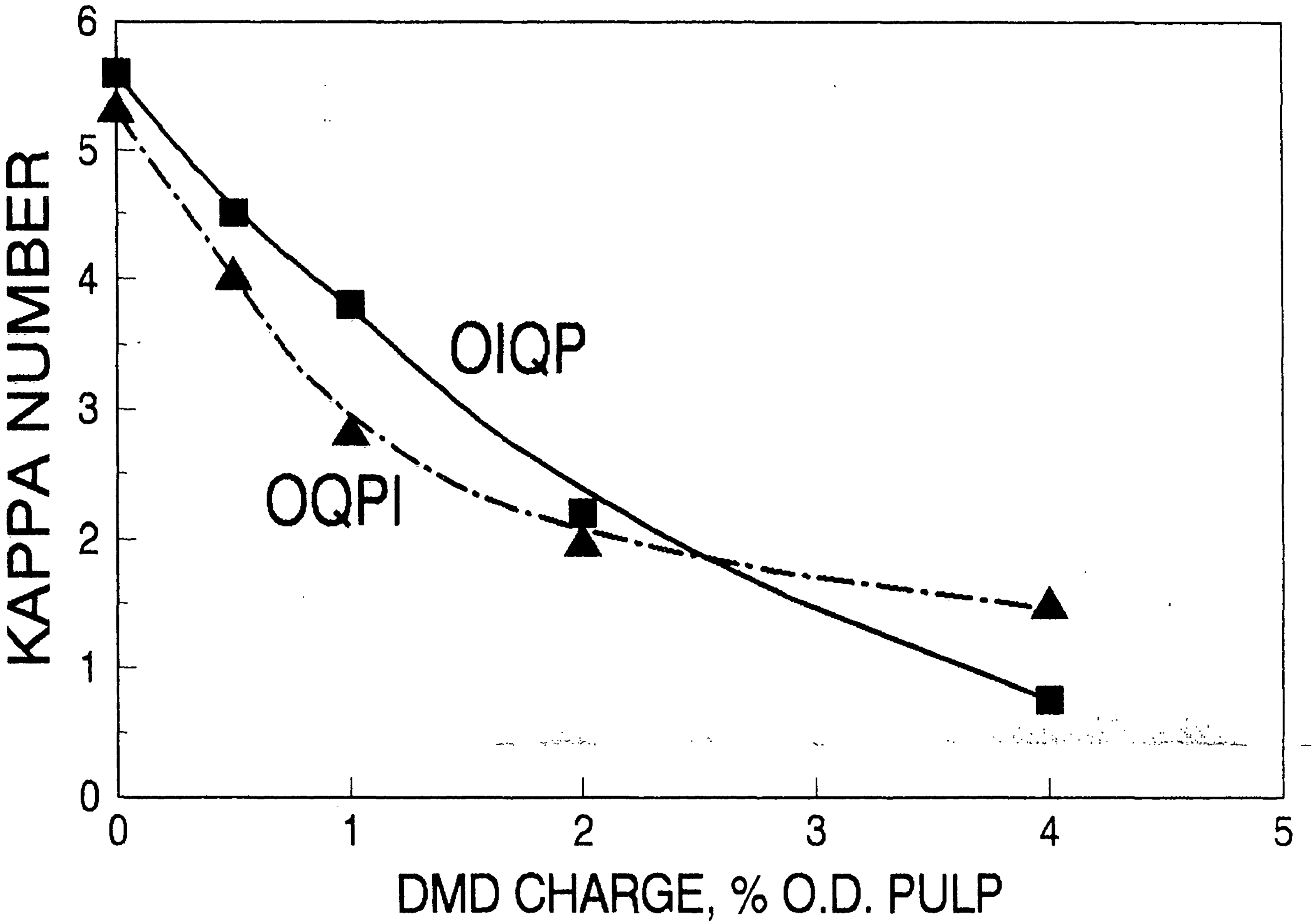
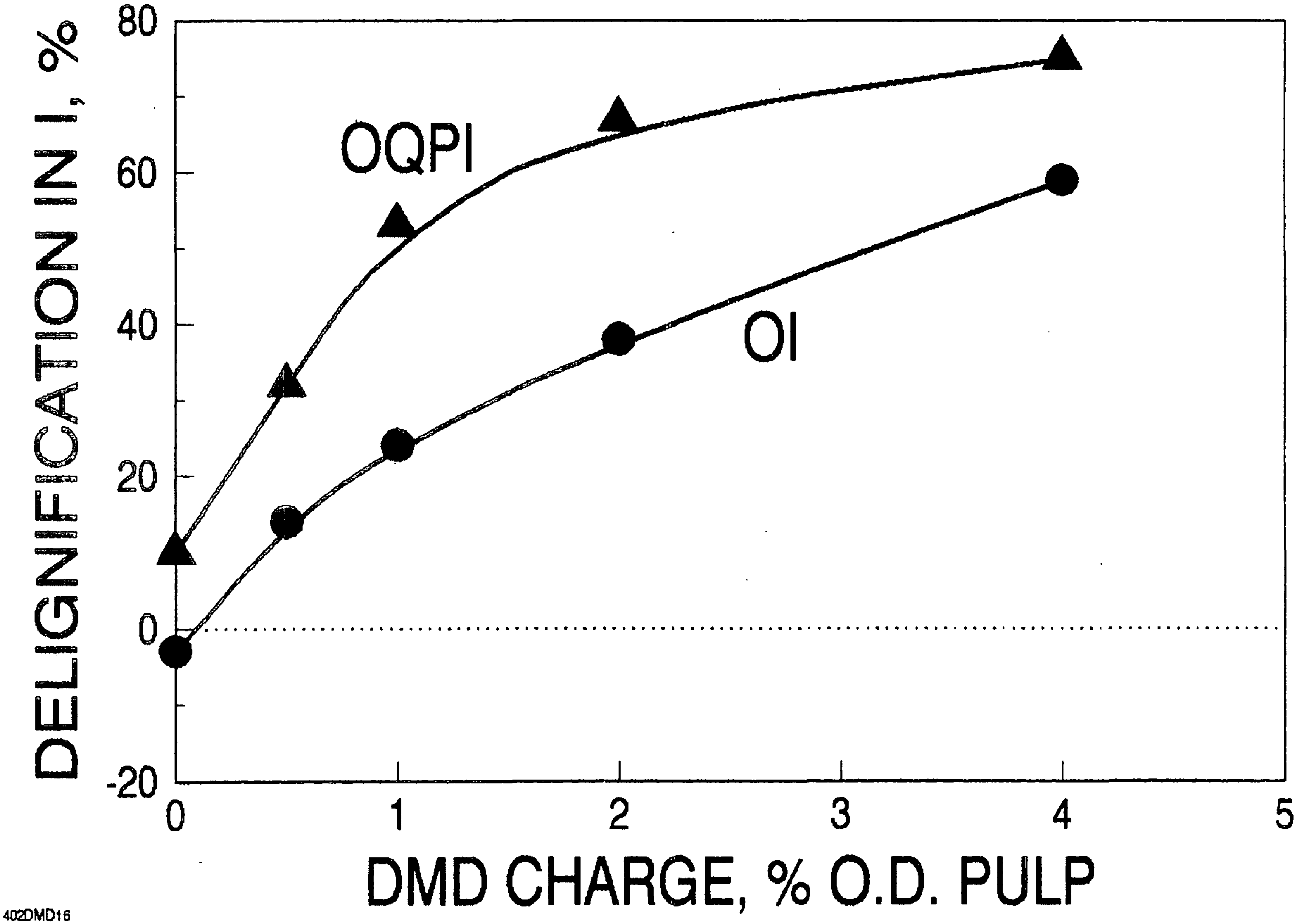


Fig. 4. Kappa number vs. DMD charge for OQPI and OIQP sequences.



402DMD16

Fig. 5. Extent of delignification in the I stage vs. DMD charge for the OI and OQPI sequences.

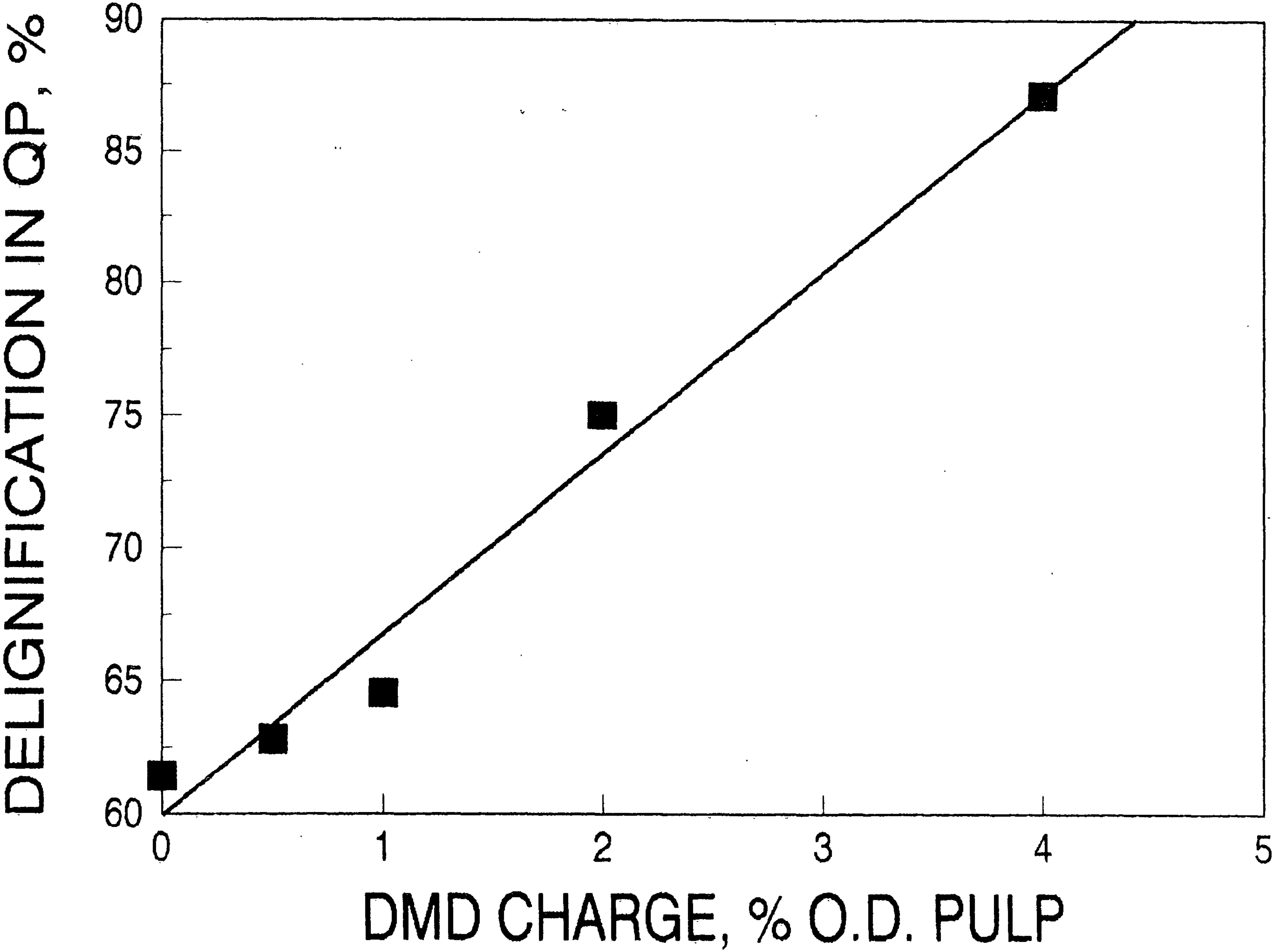
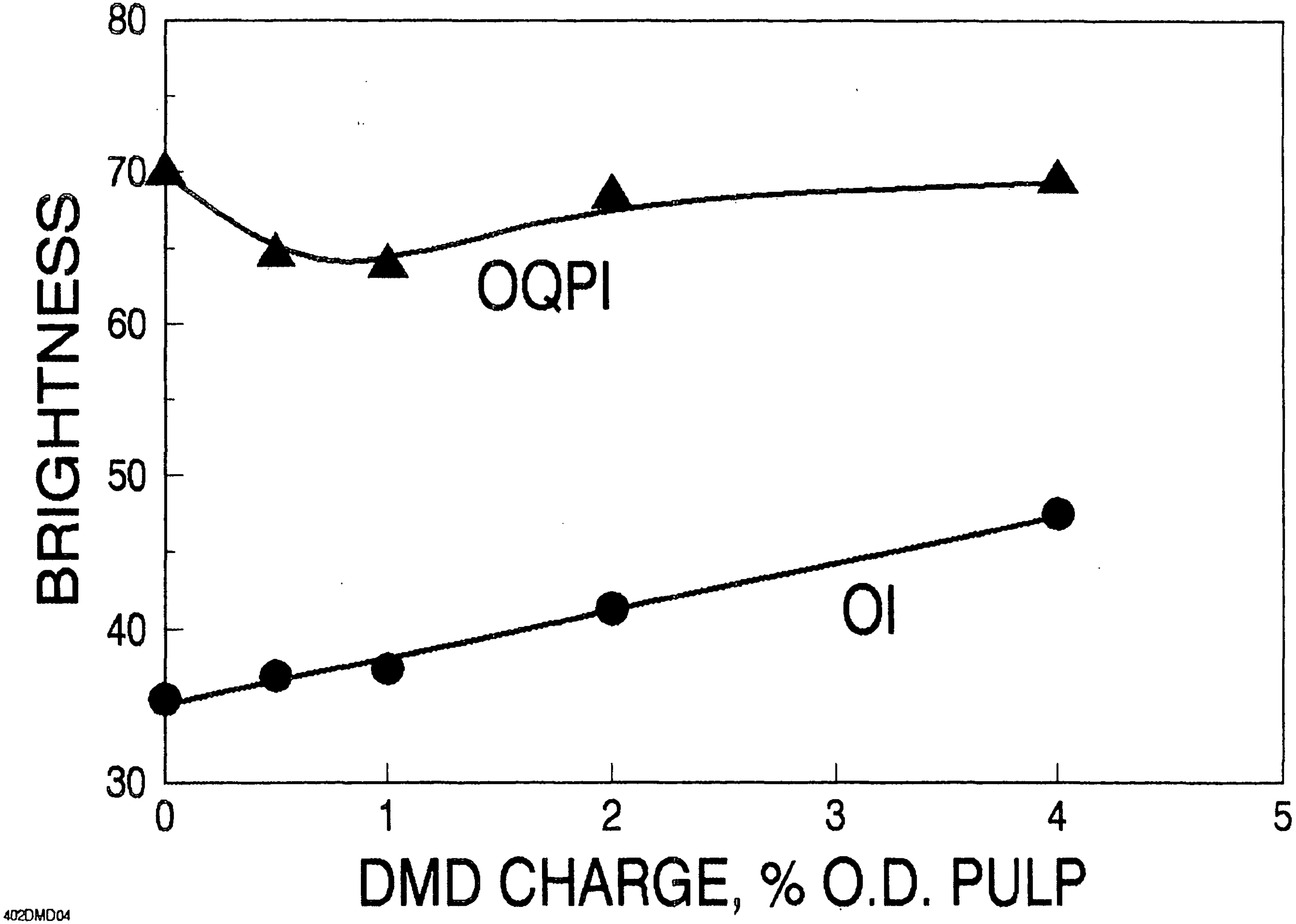
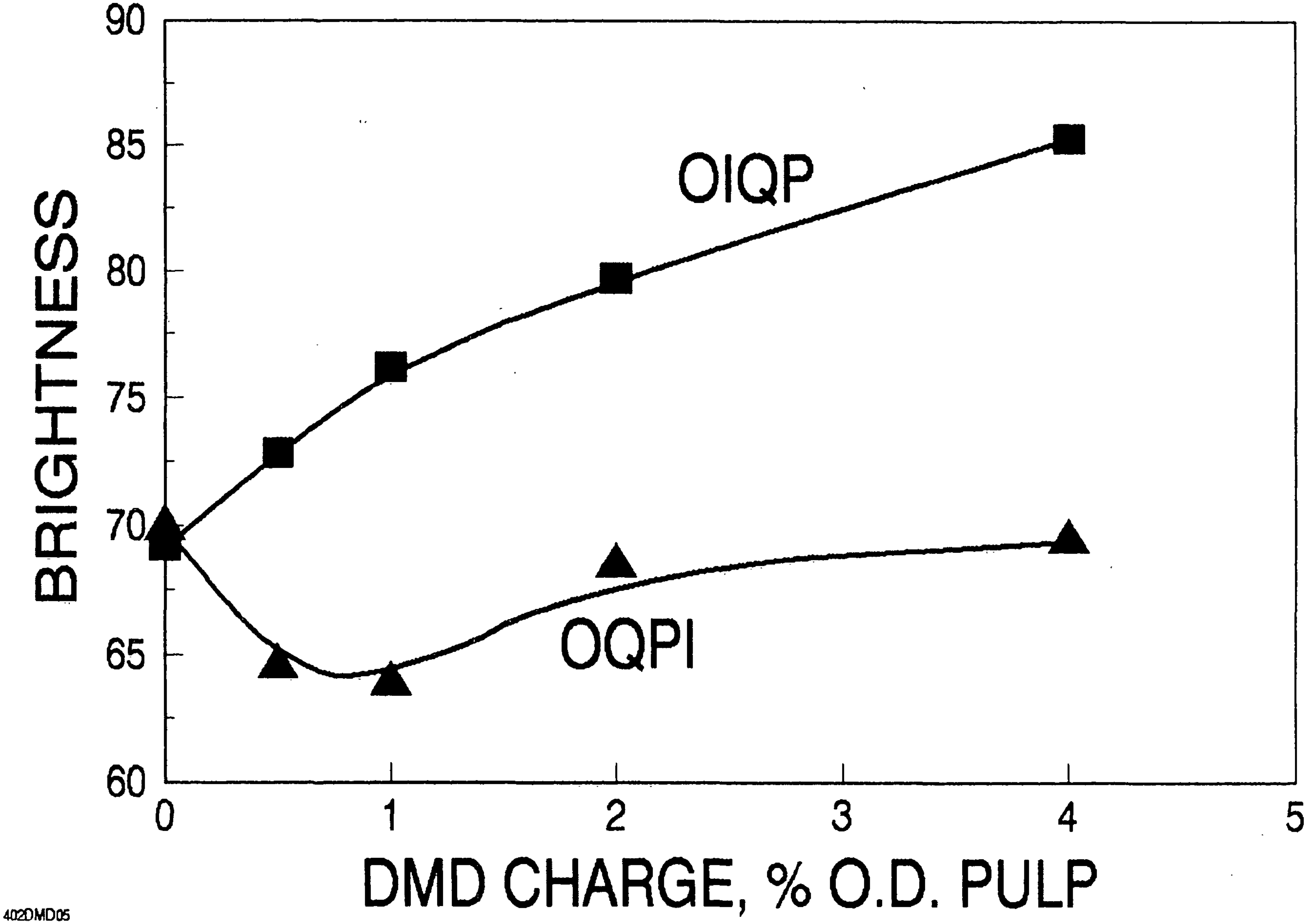


Fig. 6. Extent of delignification in the QP partial sequence vs. DMD charge in the preceding I stage.



402DMD04

Fig. 7. Brightness vs. DMD charge in the OI and OQPI sequences.



402DMD05

Fig. 8. Brightness vs. DMD charge in the OQPI and OIQP sequences.

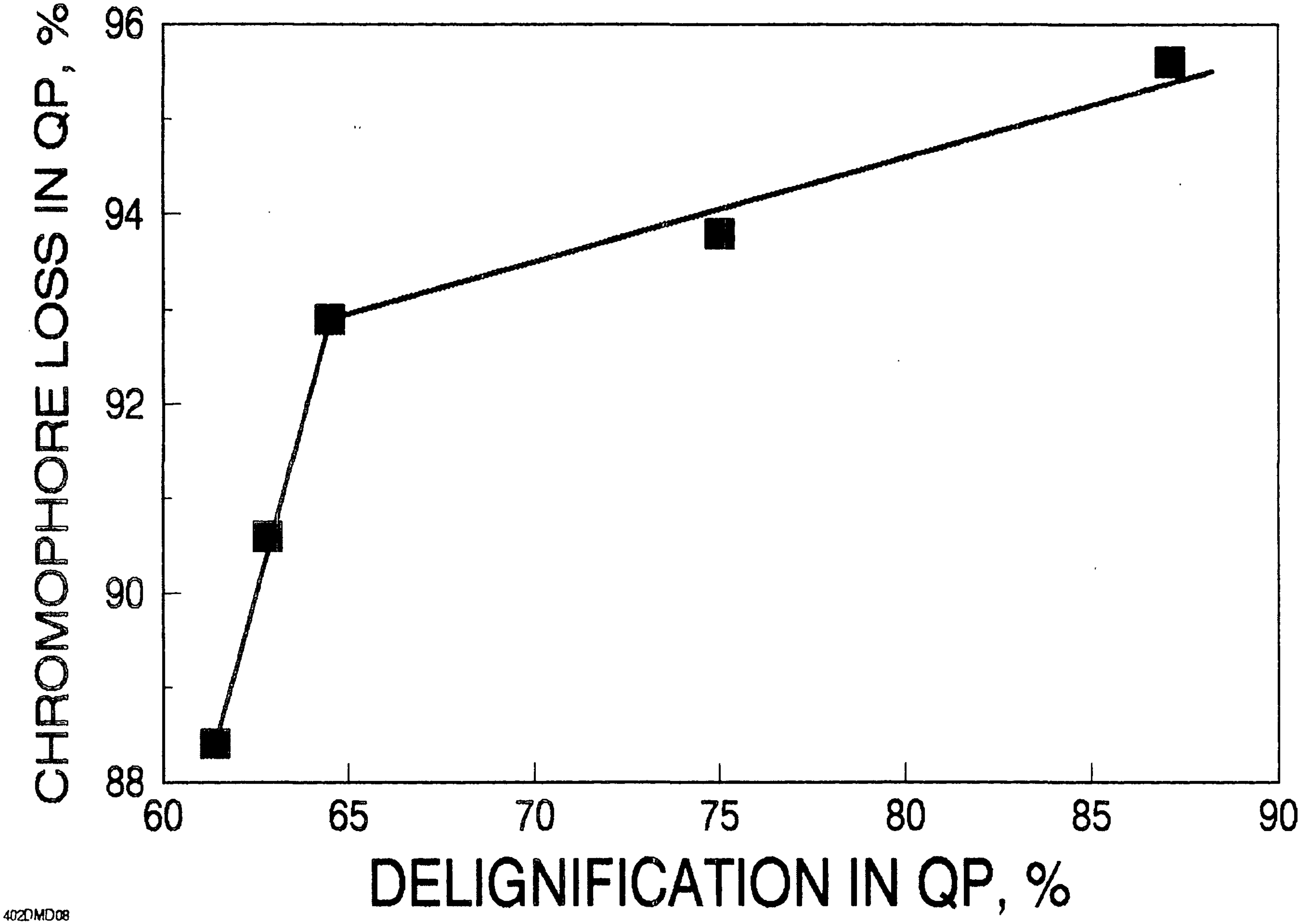


Fig. 9. Chromophophore loss vs. delignification in the QP partial sequence following an I stage.

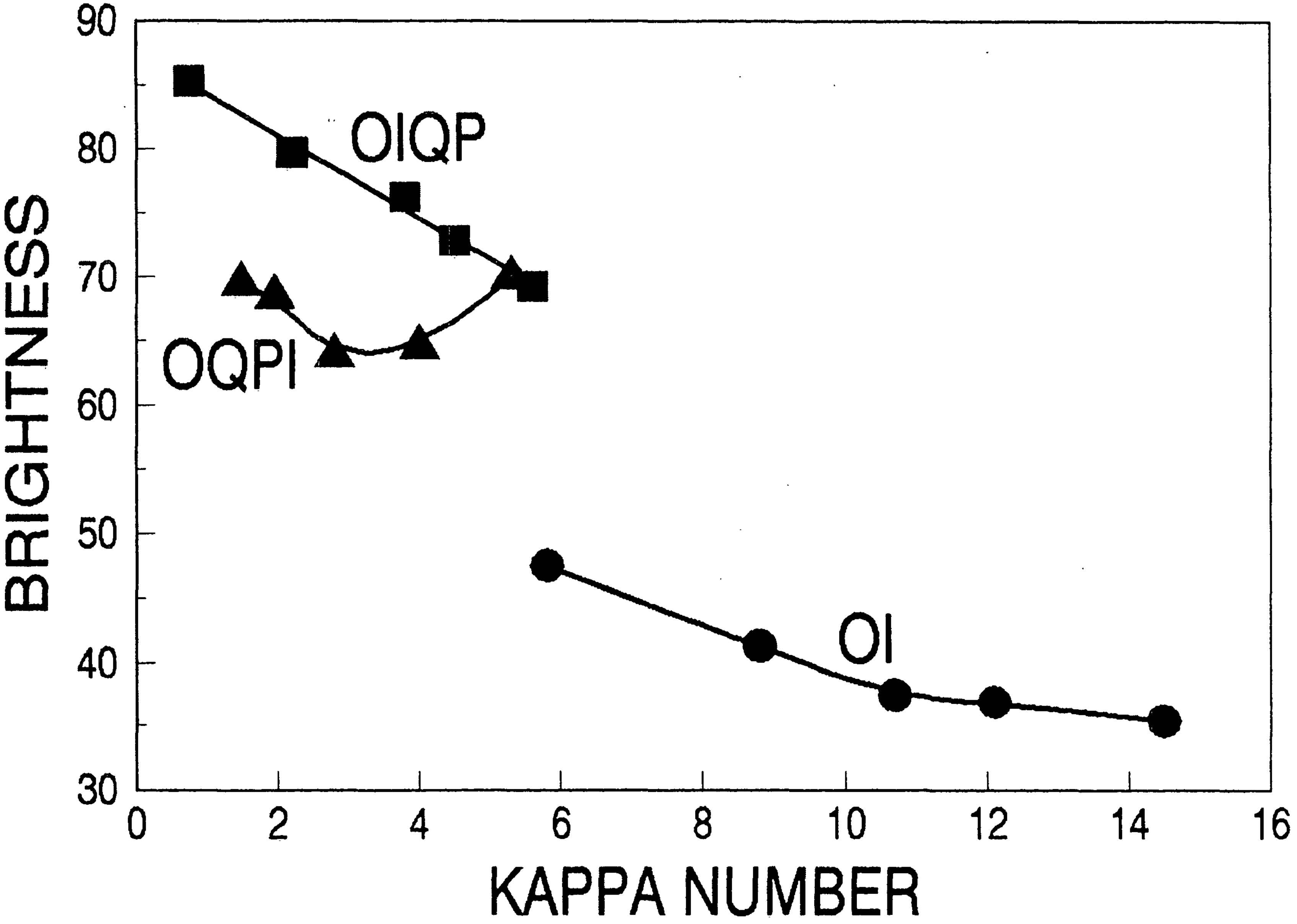
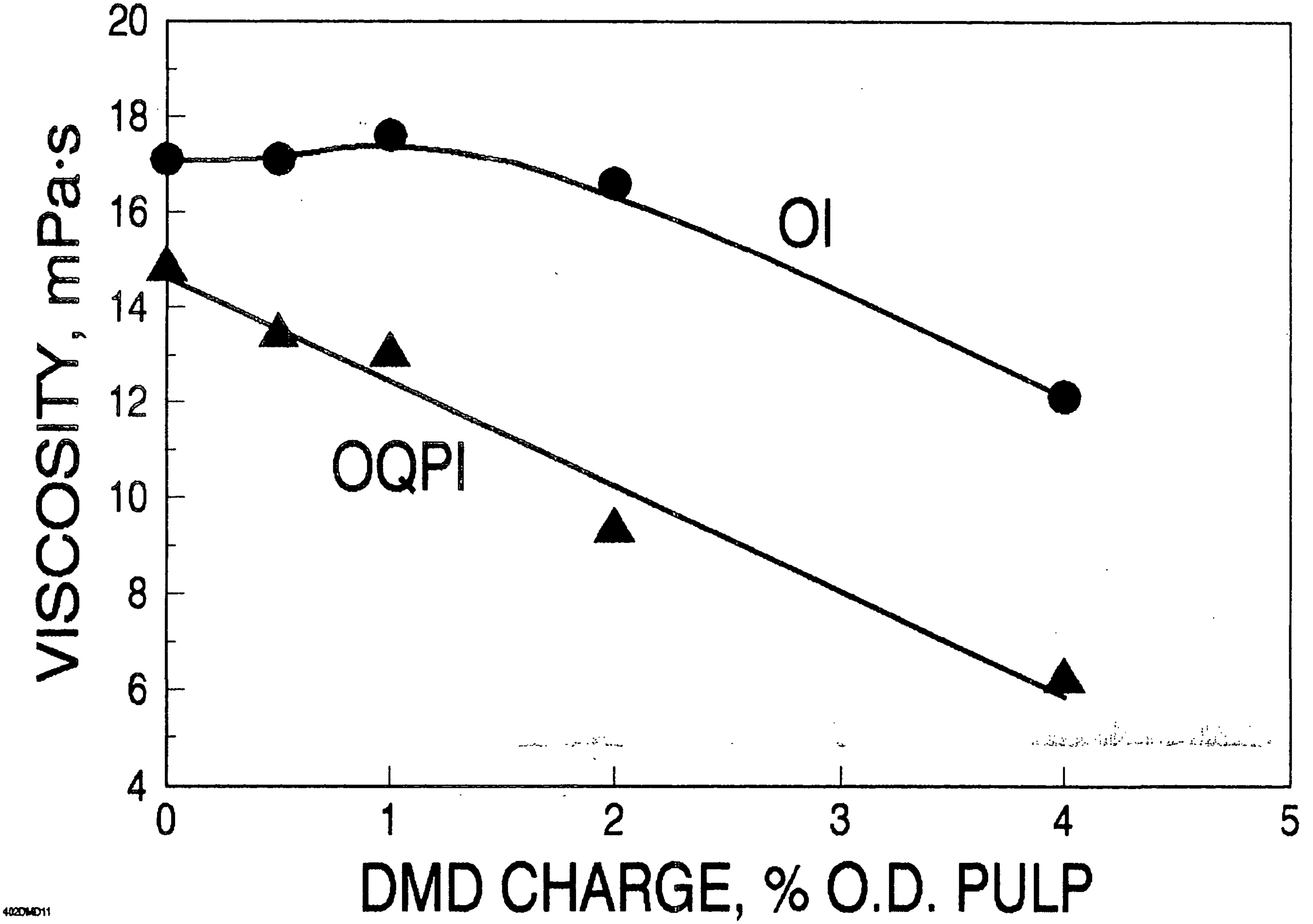
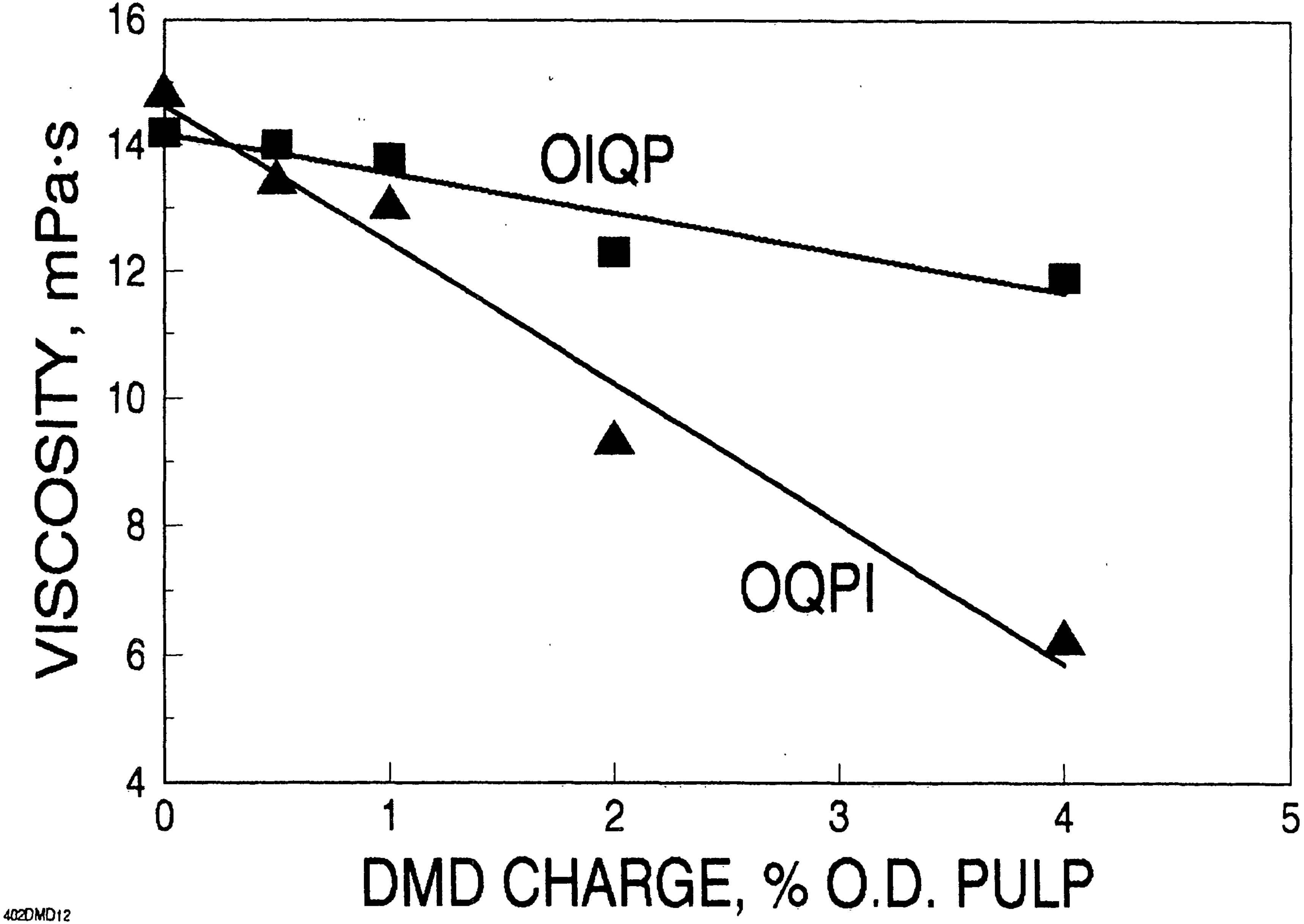


Fig. 10. Brightness vs. Kappa number.



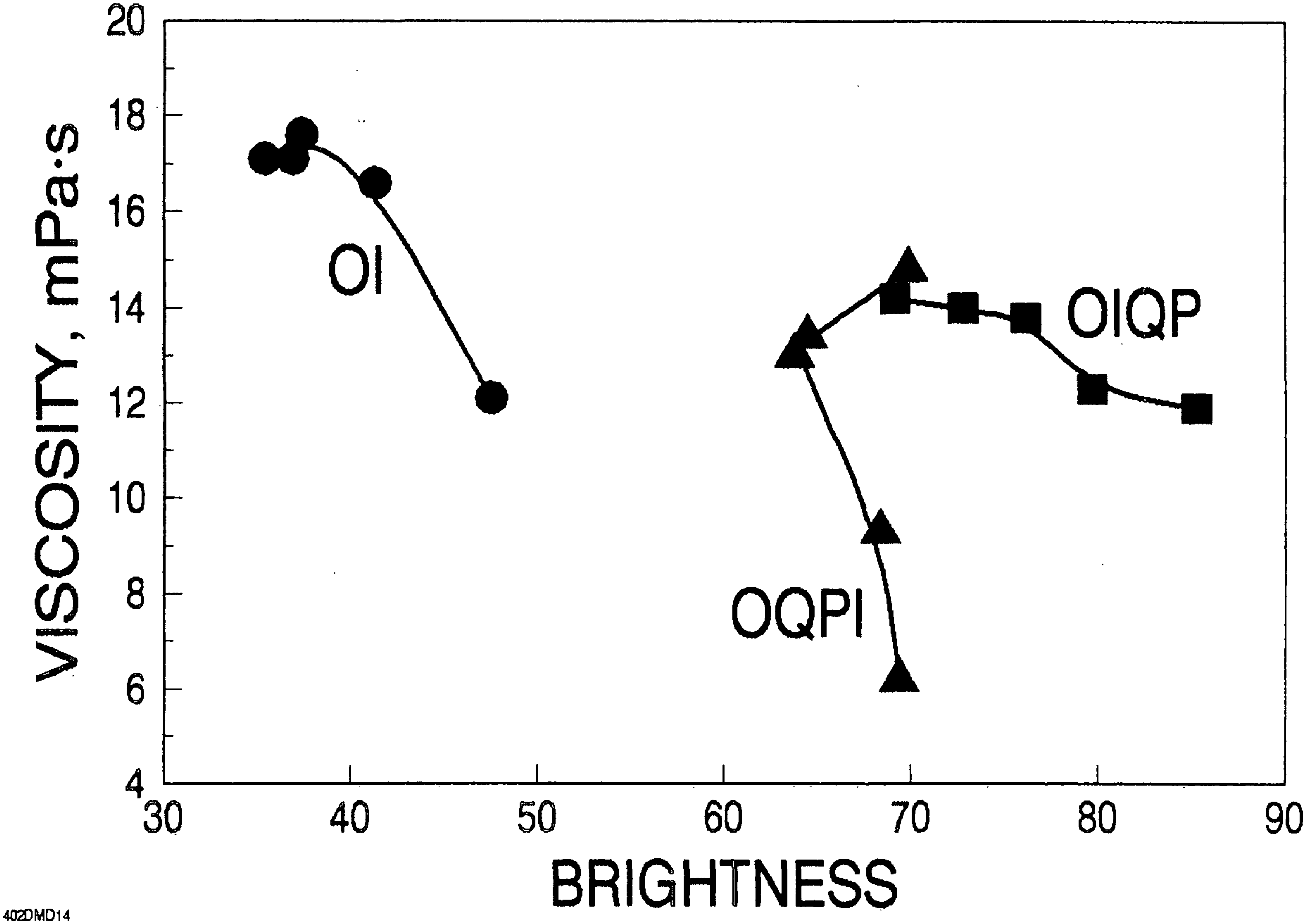
402DMD11

Fig. 11. Viscosity vs. DMD charge for the OI and OQPI sequences



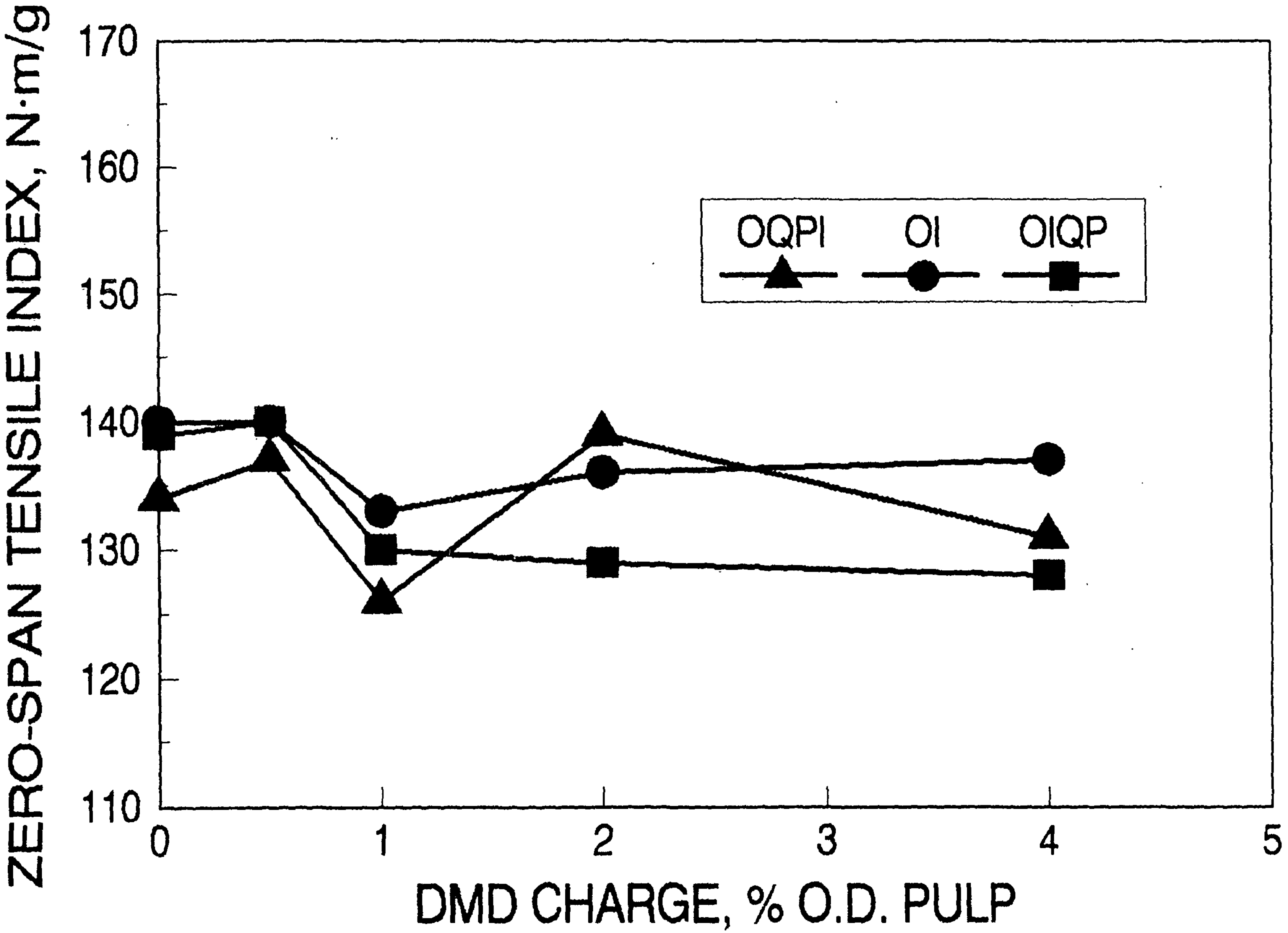
402DMD12

Fig. 12. Vicosity vs. DMD charge for the OQPI and OIQP sequence.



402DMD14

Fig. 13. Viscosity vs. brightness.



402DMD15

Fig. 14. Zero-span tensile strength vs. DMD charge.

ATTACHMENT 2

Catalytic Reactions in a Polymeric Model System for Hydrogen Peroxide Delignification of Pulp

Colleen C. Walker, Graduate Student
Thomas J. McDonough, Professor of Engineering
Ronald. J. Dinus, Professor of Biology
Institute of Paper Science and Technology
500 10th Street, NW
Atlanta, GA 30318

Karl.-Erik L. Eriksson
Professor of Biochemistry
Life Sciences Building
University of Georgia
Athens, GA 30602

ABSTRACT

A unique experimental system has been developed to study the effect of three iron-based catalysts on the hydrogen peroxide oxidation of polymeric models of lignin and carbohydrate. Iron chelated by sequestering agents or bound in porphyrin structures, in the presence of hydrogen peroxide or other oxidants, mimics the delignifying action of lignin peroxidase. The selectivity of these so-called biomimetic compounds for lignin over carbohydrate is the subject of this study.

Lignosulfonate and hydroxyethyl cellulose (HEC) have been chosen as the polymeric models for lignin and carbohydrate. Molecular weights of these substrates were measured by High Performance Size-Exclusion Chromatography and viscometry, respectively. Reactions were performed at pH 3.0, the optimum for lignin peroxidase activity. The three catalysts evaluated were $FeSO_4$, Fe-EDTA and hemoglobin.

Rates of lignosulfonate and hydroxyethyl cellulose degradation were separately determined in the presence of each catalyst. The two were then compared to determine the selectivity of each catalytic system. In experiments in which both lignosulfonate and HEC were combined in reaction solutions, the formation of a large molecular weight product was observed. This product is presumably the result of a condensation reaction between the lignin and cellulose models. Its formation is significant inasmuch as it models a counterproductive process that may be responsible for the limited effectiveness of enzymatic delignification systems.

INTRODUCTION

Environmental concerns have forced the pulp and paper industry to examine alternatives to the bleaching of pulp with chlorine and chlorine-containing compounds. Delignification with oxygen-containing agents, such as oxygen, hydrogen peroxide and ozone, have necessarily become more attractive bleaching technologies. Biotechnological applications are also receiving increased attention as viable alternatives for traditional chlorine bleaching (Yang et al. 1992).

The isolation and subsequent characterization of enzymes which are capable of degrading wood components has created numerous opportunities for applications of biotechnology to the production of pulp and paper. Lignin peroxidase, isolated from the white-rot fungus Phanerochaete chrysosporium, is a lignin-degrading enzyme which has been widely studied (Eriksson et al. 1990; Higuchi 1985). This enzyme possesses an iron protoporphyrin IX prosthetic group, the non-amino acid portion of the enzyme, and is dependent on hydrogen peroxide for activity (Tien et al. 1983; Glenn et al. 1983).

Researchers have used various iron complexes to mimic the heme group of lignin peroxidase, both to obtain a better understanding of the enzymatic mechanisms involved in lignin biodegradation, and to investigate their potential as bleaching agents. Combinations of these so-called biomimetic compounds with hydrogen peroxide and other oxidants have been applied to lignin model compounds (Shimada et al. 1989; Huynh 1986), wood pulp (Pettersson et al. 1988; Crawford and Paszczynski 1989; Paszczynski et al. 1988; Skerker et al. 1989) and chips (Paszczynski et al. 1988).

For biomimetic bleaching systems to be considered commercially feasible, they must demonstrate a selectivity which favors lignin removal. Hydroxyl radicals have been observed in solutions containing both hydrogen peroxide and iron (Walling 1975) or iron complexes (Sepp, et al. 1992; Puppo and Halliwell 1988). It is well known that $FeSO_4$ and hydrogen peroxide, more commonly known as Fenton's reagent, readily produce hydroxyl radicals (Walling 1975). The hydroxyl radical is known for its high reactivity and lack of selectivity. Evidence exists, however, that the hydroxyl radical reacts more rapidly with aromatic structures than with carbohydrates (Ek et al. 1989). The hydroxyl radical is believed to be a key radical species involved in alkaline hydrogen peroxide bleaching (Smith and McDonough 1985; Hobbs and Abbot 1991). Similar evidence is inconclusive for hydrogen peroxide delignification of pulp under acidic conditions (Hobbs and Abbot 1991).

The objective of this work was to evaluate the selectivity of three different types of biomimetic compounds. Soluble polymeric models for lignin and carbohydrate were selected to provide a homogeneous, yet realistic reaction system. Depolymerization rates were determined for each substrate separately and then compared. Preliminary results from experiments in which both substrates were combined in reaction solutions are briefly discussed.

EXPERIMENTAL APPROACH

Three different types of biomimetic, iron-based catalysts were chosen for evaluation: $FeSO_4$, Fe-EDTA and hemoglobin. $FeSO_4$ represents the simplest form of a biomimetic compound, and is known to generate hydroxyl radicals, if combined with hydrogen peroxide under the right conditions. Fe-EDTA represents biomimetic compounds in which iron is strongly sequestered, in this case by EDTA (Bell 1977). The third model catalyst, hemoglobin, perhaps most resembles the enzyme lignin peroxidase, since its iron is surrounded by a complex matrix of protein.

Homogeneous reaction conditions in aqueous solution were desired; therefore water-soluble model compounds representing wood pulp as closely as possible were considered. Lignosulfonate was chosen as a residual lignin model compound; hydroxyethyl cellulose (HEC) was chosen as a model for pulp carbohydrates. Changes in lignosulfonate molecular weight were measured using High Performance Size Exclusion Chromatography (HPSEC). Changes in HEC molecular weight were measured by viscometry.

The reactor system used for these experiments was designed to measure the amount of hydrogen peroxide consumed in the chemical reactions as well as that which is catalytically decomposed to oxygen. Evolved oxygen was collected in an expandable column, which allows atmospheric pressure to be maintained in the reactor. By measuring the amount of oxygen evolved, the amount of hydrogen peroxide decomposed to oxygen was determined. Residual hydrogen peroxide was determined by titration. The amount of hydrogen peroxide consumed in the chemical reaction was then considered to be the difference.

Reaction conditions for experiments discussed in this paper are listed in Table I. Concentrations of substrates and reactants were selected to resemble those commonly found in typical bleaching applications, while remaining within the constraints dictated by the analytical techniques. A pH of 3.0 was selected as it is that which the enzyme lignin peroxidase exhibits maximum activity (Aitken and Irvine 1989).

Table I. Reaction conditions for catalyzed hydrogen peroxide oxidation of lignosulfonate and hydroxyethyl cellulose (HEC). All reactions were carried out at pH 3.0 and 45°C.

			CATALYST	
SUBSTRATE	**SUBSTRATE CONC. (g/l)**	**H_2O_2 (mM)**	**TYPE**	**CONC. (mM)**
Lignosulfonate	3.4	50.0	$FeSO_4$ Fe-EDTA Hemoglobin	0.5 0.5 0.062 (Fe)
Hydroxyethyl Cellulose	3.0	20.0	$FeSO_4$ Fe-EDTA Hemoglobin	0.2 0.2 0.025 (Fe)

The molar concentration of iron in hemoglobin was estimated from its structure. Hemoglobin has a molecular weight of 64,500 units with each molecule possessing four iron atoms. An extremely large concentration of hemoglobin (8.1 g/l) would be needed to match the 0.5 mM iron concentration used in the $FeSO_4$ and Fe-EDTA experiments. Consequently, the concentration of hemoglobin used in these experiments was arbitrarily selected.

RESULTS AND DISCUSSION

Catalyzed Oxidation of Lignosulfonate

The weight-average molecular weight of lignosulfonate versus reaction time for each catalyst is shown in Figure 1. Results from a control reaction, in which no catalyst was present, are also shown. All catalysts promote significant degradation of lignosulfonate as compared to the control. $FeSO_4$ causes the largest decrease in the molecular weight of lignosulfonate within the 400 minute reaction time.

Although not clearly visible in Figure 1, when hemoglobin is added to solutions containing lignosulfonate, prior to the addition of hydrogen peroxide, a reduction in the weight average molecular weight of lignosulfonate is observed (a decrease of approximately 1000 units). This gives the appearance of a larger overall reduction in lignosulfonate molecular weight for this reaction. Control experiments with hemoglobin and lignosulfonate, in the absence of hydrogen peroxide, showed that no significant degradation of the lignosulfonate occurred after this initial drop.

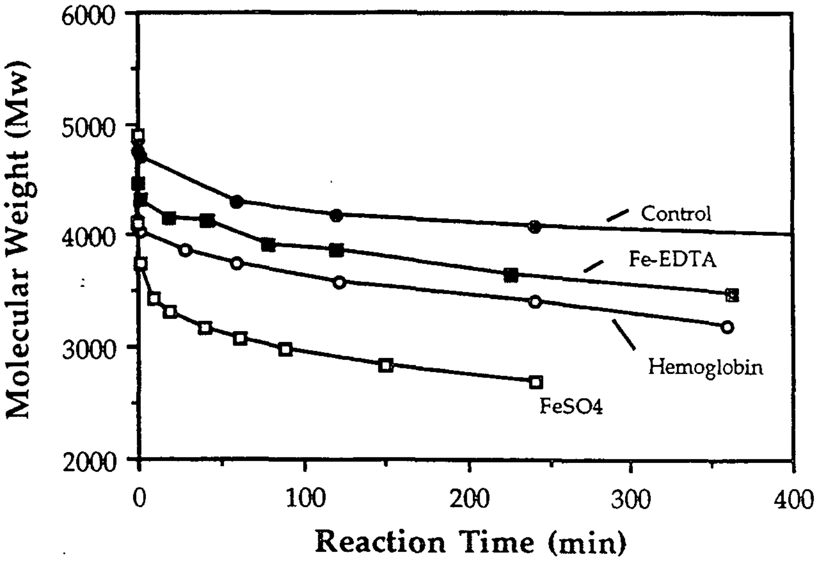


Figure 1. Weight-average molecular weights of lignosulfonate versus reaction time for each catalyst and a control, with H_2O_2 and no catalyst. See Table 1 for reaction conditions.

This initial decrease in molecular weight was not observed in either the $FeSO_4$ or Fe-EDTA catalyzed reactions. Similar control experiments with lignosulfonate and $FeSO_4$ or Fe-EDTA in the absence of hydrogen peroxide showed no degradation of the lignosulfonate.

Two possible explanations can be presented for this apparent decrease in molecular weight. In the presence of hemoglobin, the natural conformation of the lignosulfonate may be affected. As lignosulfonate then passes through the size-exclusion column, it appears to have a lower molecular weight. Alternatively, the hemoglobin may possess enough oxidizing potential to break only certain weak bonds in the lignosulfonate polymer, resulting in a decrease in the molecular weight. Efforts are continuing to determine the reason for this apparent decrease in molecular weight.

Corresponding changes in residual hydrogen peroxide concentration for the reactions shown in Figure 1 are shown in Figure 2. Here, with regard to the reaction of hydrogen peroxide, the addition of $FeSO_4$ results in the largest apparent consumption of hydrogen peroxide. Fe-EDTA and hemoglobin both catalyze the disappearance of hydrogen peroxide, but not to the same extent as $FeSO_4$.

The ratio of the amount of hydrogen peroxide decomposed to that consumed by reaction is plotted against the total amount of hydrogen peroxide reacted in Figure 3. The data for the control run shown in Figure 3 lack precision because oxygen evolution is minimal during the control run and little hydrogen peroxide reacts. However, it can be concluded that most of the hydrogen peroxide that disappeared in the control run was lost by conversion to oxygen.

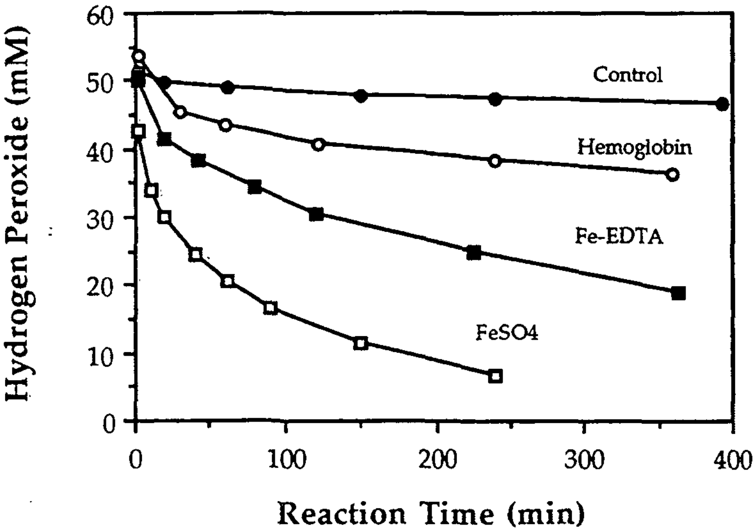


Figure 2. Residual hydrogen peroxide concentration versus reaction time for those experiments shown in Figure 1. See Table 1 for reaction conditions

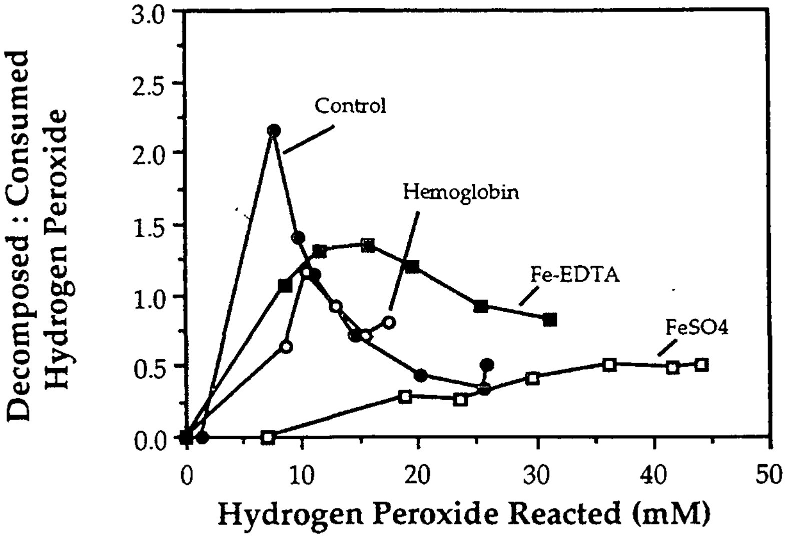


Figure 3. Ratio of hydrogen peroxide decomposed (to oxygen) to hydrogen peroxide consumed (by oxidation of lignosulfonate) versus total hydrogen peroxide reacted for those experiments shown in Figure 1.

$FeSO_4$ utilizes reacted hydrogen peroxide better than Fe-EDTA or hemoglobin. At a given amount of hydrogen peroxide reacted, for instance 20 mM H_2O_2, the ratio of decomposed to consumed hydrogen peroxide is significantly less than 1.0 for $FeSO_4$, indicating that most of the hydrogen peroxide has been consumed in the reaction. For Fe-EDTA and hemoglobin this ratio is near 1.0, indicating that equal amounts of hydrogen peroxide are consumed and decomposed.

Kinetics of Lignosulfonate Depolymerization

The lignosulfonate polymer can be broken either by random chain scission or non-random processes such as bond-splitting at weak points in the polymer. If the process is random, the rate at which bonds are broken would not change with time. It can be shown that the number of chain scissions, N, can be determined from the degree of polymerization, DP, by :

$$N = \frac{1}{DP_t} - \frac{1}{DP_o} \tag{1}$$

As DP is proportional to the weight-average molecular weight, Mw, Equation 1 can be rewritten in terms of Mw to give:

$$N = \frac{1}{Mw_t} - \frac{1}{Mw_o} \tag{2}$$

The number of chain scissions plotted versus reaction time for all three catalysts and the control are shown in Figure 4. A straight line on this plot indicates that the rate of chain scission is constant throughout the reaction. It is apparent that this rate for the ferrous sulfate catalyzed oxidation of lignosulfonate varies greatly with time. For the Fe-EDTA and hemoglobin catalyzed reactions, the rate of chain scission decreases only slightly with respect to reaction time. The control experiment also shows a slight decrease in the rate of chain scission with reaction time.

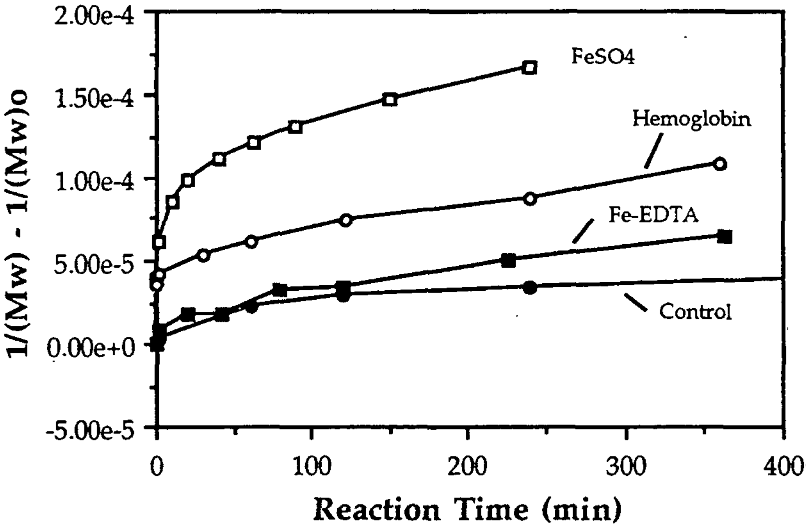


Figure 4. Number of chain scissions versus reaction time for those experiments shown in Figure 1.

In general the rate of chain scission is expected to be dependent on the number of bonds present and the concentration of hydrogen peroxide. The rate equation applicable to all four reactions is therefore:

$$-\frac{d\,[\text{bonds}\}}{dt} = k_1\,[\text{bonds}]^a[\,C_H]^b$$

where **k1** represents the overall rate constant, **a** the reaction order in bonds, and **b** the reaction order in hydrogen peroxide. For these systems, it is most likely that bonds are broken randomly, independent of the total concentration of bonds present. Therefore, the rate of chain scission is zero order in bonds. The rate equation then simplifies to:

$$-\frac{d\,[\text{bonds}\}}{dt} = k_1\,[\,C_H]^b \tag{3}$$

The differential method was used to evaluate the reaction order **b** for the dependence of the rate on the hydrogen peroxide concentration. Reaction rates were determined from [bonds] versus time plots, where [bonds] = 1 - (1/Mw). Once the reaction order **b** was determined, the rate constant $\mathbf{k_1}$ was calculated. Values of all parameters obtained for each catalyst are summarized in Table 2. For all reactions, the data fit the derived equations very well.

Table 2. Rate laws for the catalyzed hydrogen peroxide depolymerization of lignosulfonate.

CATALYST	H_2O_2 RANGE	RATE LAW
Control	50 - 30 mM	$r = 2.50 \times 10^{-10} [H_2O_2]^{1.3}$
$FeSO_4$	$[H_2O_2]$ 50 - 21 mM $[H_2O_2] < 21$ mM	$r = 2.35 \times 10^{-11} [H_2O_2]^{3.1}$ $r = 3.39 \times 10^{-11} [H_2O_2]^{0.86}$
Fe-EDTA	50 - 20 mM	$r = 2.10 \times 10^{-11} [H_2O_2]^{2.6}$
Hemoglobin	50 - 20 mM	$r = 7.90 \times 10^{-12} [H_2O_2]^{2.7}$

Catalyzed Oxidation of Hydroxyethyl Cellulose

Table I lists the reaction conditions used for these experiments. Viscosity-average molecular weights were determined using the Mark-Houwink equation, which relates intrinsic viscosity to molecular weight. Figure 5 shows the changes in viscosity-average molecular weight of HEC during the three catalyzed reactions and a control.

The $FeSO_4$ catalyzed reaction resulted in the greatest degradation of HEC. Fe-EDTA provides a sufficient catalytic environment to also degrade the HEC polymer. Hemoglobin, even at it's relatively low molar iron concentration, also catalyzes the degradation of the HEC polymer.

For these experiments a small change in the hydrogen peroxide concentration (< 20%) was observed during all reactions. It was therefore difficult to obtain information on the relative amounts of hydrogen peroxide which was consumed by reaction versus that decomposed to oxygen.

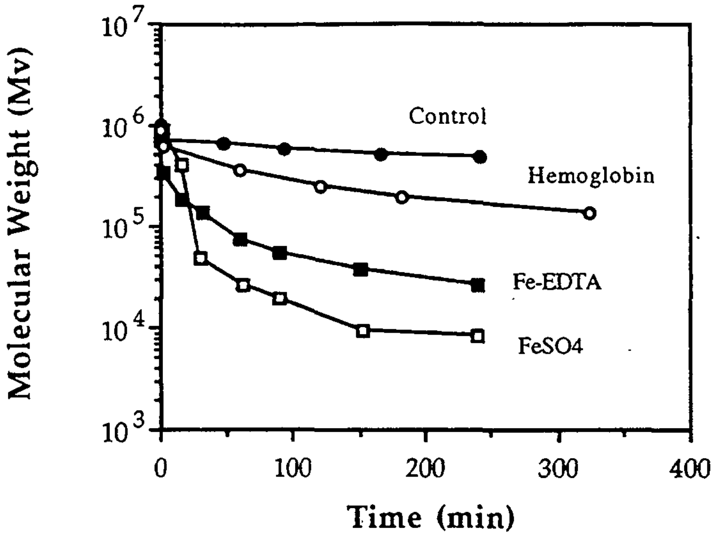


Figure 5. Viscosity average molecular weight versus reaction time for each catalyst and a control with H_2O_2 but no catalyst. See Table 1 for reaction conditions.

Kinetics of HEC Depolymerization

A plot of the number of chain scissions (Equation 2) during the reaction versus reaction time is shown in Figure 6 for each catalyst as well as the control (no catalyst). The straight lines in Figure 6 indicate that the depolymerization of HEC occurs at a constant rate throughout the reaction.

The generalized rate equation given above (Equation 3) can also be applied to the data from these experiments. For the depolymerization of HEC, the rate of chain scission is zero order in bonds, as shown in Figure 6. As mentioned previously, the hydrogen peroxide concentration remains relatively constant during these reactions. Consequently, a first order dependence on the hydrogen peroxide concentration has been assumed. Experiments are being performed to verify this assumption. Table II lists values for $\mathbf{k_1}$ determined from slopes in Figure 6.

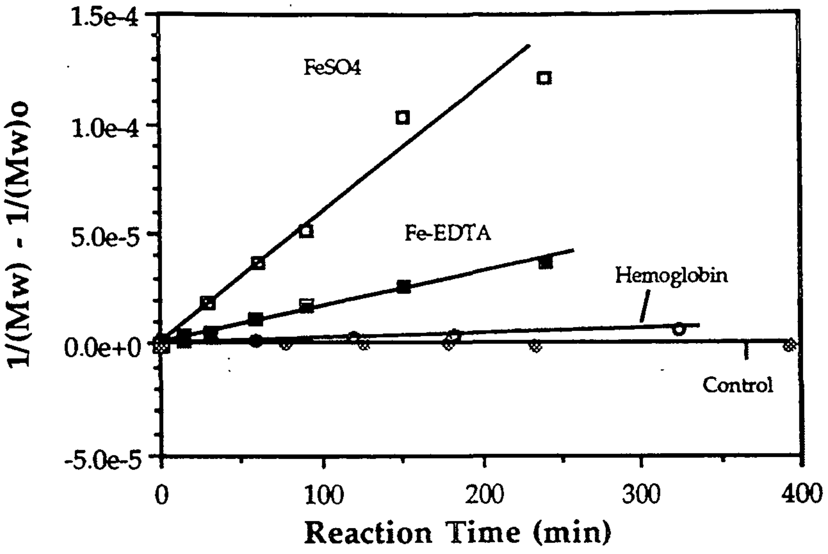


Figure 6. Number of chain scissions versus reaction time for each catalyst and a control (no catalyst). See Table 1 for reaction conditions.

TABLE 3. Rate constants for the catalyzed hydrogen peroxide depolymerization of HEC. Reaction conditions as given in Table 1.

CATALYST	RATE CONSTANT, k_1 ($H_2O_2^{-1}$ min^{-1})
Control	0.15×10^{-9}
$FeSO_4$	27.50×10^{-9}
Fe-EDTA	7.70×10^{-9}
Hemoglobin	0.94×10^{-9}

Selectivity

Selectivity is most appropriately evaluated by comparing rate constants for the involved reactions. For the work presented here, a simple comparison of rate constants is meaningless since the rate laws for each catalyst in the lignosulfonate and HEC system are not identical. However, a point selectivity can be calculated and compared. A point selectivity is defined as the ratio of the two rates of interest evaluated at a certain point in the reaction.

Point selectivities were determined at a concentration of 20 mM hydrogen peroxide, as HEC reactions were performed at 20 mM. Rates of lignosulfonate depolymerization were calculated from the determined rate laws (Table 2), substituting a value of 20 mM for the hydrogen peroxide concentration. Results from this comparison are shown in Table 4. These results indicate that the ratio of the rate of lignosulfonate degradation to that of HEC degradation at 20 mM H_2O_2 is greatest in the case when hemoglobin is the catalyst. Fe-EDTA is next in its ability to degrade lignosulfonate more rapidly than HEC. $FeSO_4$ exhibits the least ability to degrade lignosulfonate over HEC.

Table 4. Point selectivities for the rate of bond cleavage in lignosulfonate to HEC determined at 20 mM H_2O_2.

CATALYST	POINT SELECTIVITY
$FeSO_4$	0.02
Fe-EDTA	6.49
Hemoglobin	26.6

These results may reflect the ability of these catalysts to generate radical species. The efficiency of hydrogen peroxide utilization must also be considered. The molecules or "cages" surrounding the iron may also contribute to the ability of the catalysts to associate with either substrate.

Combined Substrate Experiments

To provide a realistic reaction environment, lignosulfonate and HEC were combined in reaction solutions. The effect on reaction rates of the same three catalysts was evaluated. These results will be briefly described, with a more detailed description and discussion to be presented in a subsequent publication.

In all reactions, including that with hydrogen peroxide alone (no catalyst), analysis of reaction samples by HPSEC indicated the formation of a large molecular weight product. This product is believed to be produced by condensation of the lignosulfonate onto the HEC polymer.

Significant experimental evidence exists to support this hypothesis. This large molecular weight product was not observed to form in reactions with lignosulfonate in the absence of HEC.

Figure 7 shows chromatograms from several samples taken during the $FeSO_4$ catalyzed reaction. The molecular weight distribution of this condensation product changes during the reaction, shifting towards lower molecular weights, indicating that degradation has occurred.

For the $FeSO_4$ catalyzed reaction, the condensation product appears immediately (within 1 minute of reaction initiation). In the presence of Fe-EDTA, the condensation product appears a little more slowly, with full condensation of the lignosulfonate occurring after 10 minutes. In the presence of hemoglobin, only a small portion of the lignosulfonate condenses onto the HEC polymer.

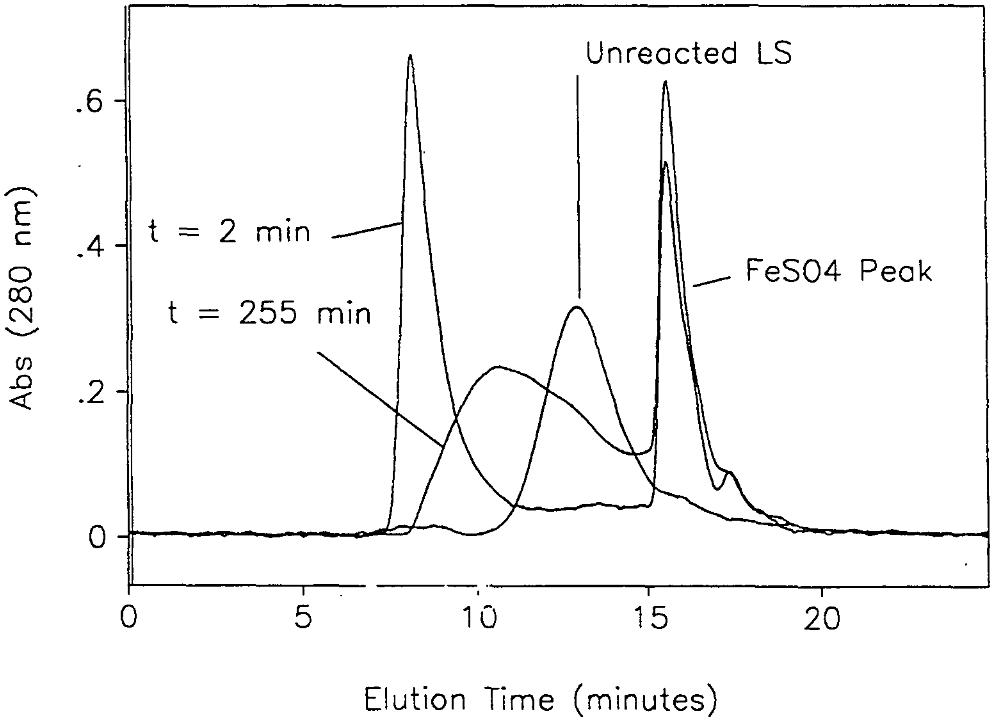


Figure 7. Size-exclusion chromatograms (UV Detector at 280 nm) from several reaction samples showing the large molecular weight product and the change in molecular weight distribution during reaction time. Reaction conditions: 3.0 g/l HEC, 0.5 g/l Lignosulfonate, 20 mM H_2O_2, 0.2 mM $FeSO_4$, pH 3.0 and 45°C.

CONCLUSIONS

Rate laws for the catalyzed hydrogen peroxide oxidation of lignosulfonate by three iron-containing catalysts were determined. Although the dependence on the hydrogen peroxide concentration differs for each catalyst, these values are relatively close together in magnitude. Rate laws were also determined for the hydrogen peroxide oxidation of HEC by the same three catalysts. For these reactions, it was necessary to assume a first order dependence on hydrogen peroxide concentration, which is presently under investigation.

Point selectivities were determined from these rate equations at a concentration of 20 mM hydrogen peroxide. The ratio of the rate of chain scission in lignosulfonate to that of HEC was evaluated for each catalyst. These results indicate the $FeSO_4$ exhibits the highest selectivity at the chosen concentration. $FeSO_4$ is followed by Fe-EDTA and then hemoglobin.

In combined substrate experiments, the formation of a large molecular weight product was observed. This may provide new insight to the efficiency of hydrogen peroxide delignification of pulp. It is possible that the generation of hydroxyl radicals, and other active species, cause a polymerization to occur. This limits the efficiency of the bleaching agent to remove lignin from the pulp without also removing carbohydrate. Experimental conditions in which the formation of this condensation product is minimized may produce a more efficient bleaching agent.

EXPERIMENTAL METHODS

Chemicals and Substrates

Chemicals and Water

Ultrapure water was obtained from a Barnestead Reverse Osmosis Water Purifier configured to provide Class Type II lab water. Hydrogen peroxide (J. T. Baker) and hydrochloric acid were also of ultrapure quality. Hemoglobin (Sigma Chem. Co.) was bovine hemoglobin, unpurified. All other chemicals were of reagent grade.

Lignosulfonate

Lignosulfonate at ~ 50% solids was obtained from Daishowa Chem. Inc., Rothschild, Wisconsin. This solution was diluted, passed through a 0.22 µm Whatman filter, and then ultrafiltered using 30,000 and 10,000 daltons filters to obtain a fraction of relatively narrow molecular weight. Concentration of stock solutions were determined by spectrometry; a standard calibration was made by using a solution whose solids content had been determined.

Hydroxyethyl Cellulose (HEC)

Hydroxyethyl cellulose was obtained from Aqualon Chem. Co., Wilmington Delaware. Solutions were prepared by dissolving a preweighed amount of HEC into a known quantity of ultrapure water (usually 300 ml). Solutions were allowed to mix for one hour at room temperature, and then overnight at 4°C to ensure complete swelling of the substituted cellulose.

Reactor and Reaction Sampling

All experiments were performed in a 300 ml teflon-lined, magnetically stirred batch reactor. The reactor was equipped with an air-tight lid, a sampling line, pH probe and gas exit line. Samples were periodically removed and immediately placed on ice. Once cooled, aliquots were removed for titration, chromatography or viscometry measurements.

High Performance Size Exclusion Chromatography

A Bio-Rad Bio-Sil SEC 125 Size Exclusion Column was used on a Varian 5060 High Performance Liquid Chromatograph equipped with a Varian UV-50 Variable Wavelength Detector and an Hewlett-Packard Integrator. The mobile phase (eluent) was 50 mM citric acid-disodium hydrogen phosphate buffer (Lewis and Yean 1985), pH 3.0 and flowed at 0.8 ml/min.

Viscometry

An existing correlation between intrinsic viscosity and molecular weight (the Mark-Houwink equation) was used to obtain molecular weight values. Mark-Houwink parameters for dilute HEC solutions was obtained from Brown et al. (1963). Samples were introduced into the viscometer (usually 1.0 ml) via pipet and allowed to equilibrate for 5 minutes (hydrogen peroxide was removed by addition of sodium bisulfite). Water was then added to reach the minimum volume necessary for measurement. Flow time was recorded for two passes, then additional water was added.

ACKNOWLEDGMENTS

Funding for this work was provided by the Institute of Paper Science and Technology and its member companies. Portions of the work will be used by C. W. as partial fulfillment of the requirements of the degree of Ph.D. at the Institute of Paper Science and Technology.

LITERATURE CITATIONS

Aitken, M. D., Irvine, R. L. Stability Testing of Ligninase and Mn-Peroxidase from Phanerochaete chrysosporium. Biotech. Bioengg. 34(12):1251-1260(1989).

Bell, C. F. Principles and Applications of Metal Chelation. Oxford University Press 1977.

Brown, W., Henley, D., Ohman, J. Studies on Cellulose Derivatives Part II: The Influence of Solvent and Temperature on the Configuration and Hydrodynamic Behavior of Hydroxyethyl Cellulose in Dilute Solutions. Makro. Chem. 64:49-67(1963).

Crawford, R. L., Paszczynski, A. Delignification and Bleaching of Pulps Using H2O2 and Iron Organic Chelant Complexes Under Acidic Conditions as a Biomimetic Approach. Fourth International Conference on Biotechnology in the Pulp and Paper Industry, pp. 50 (May 1989).

Ek, M., Gierer, J., Jansbo, K. Study of the Selectivity of Bleaching with Oxygen-Containing Species. Holzforschung 43:391-396(1989).

Eriksson, K. - E. L., Blanchette, R. A., Ander, P. Microbial and Enzymatic Degradation of Wood and Wood Components. Springer-Verlag, New York, 1990.

Glenn, J. K., Morgan, M. A., Mayfield, M. B., Kuwahara, M., Gold, M. H. An extracellular H2O2-Requiring Enzyme Preparation Involved in Lignin Biodegradation by the White-rot Basidiomycete Phanerochaete chrysosporium. Biochem. Biophys. Res. Comm. 114(3):1077-1083(1983).

Higuchi, T., Ed. Biosynthesis and Biodegradation of Wood Components. Academic Press, Inc., New York (1985).

Hobbs, G. C., Abbot, J. Peroxide Bleaching Reactions Under Alkaline and Acidic Conditions. J. Wood Chem. Tech. 11(2):225-246 (1991).

Huynh, V.-B. Biomimetic Oxidation of Lignin Model Compounds by Simple Inorganic Complexes. Biochem. Biophys. Res. Comm. 139(3):1104-1110(1986).

Lewis, N. G., Yean, W. Q. High-Performance Size-Exclusion Chromatography of Lignosulphonates. J. Chrom. 331:419-424(1985).

Paszczynski, A., Crawford, R. L., Blanchette, R. A. Delignification of Wood Chips and Pulps by Using Natural and Synthetic Porphyrins: Models for Fungal Decay. Appl. Envir. Microbio. 54(1):62-68(1988).

Pettersson, B., Yang, J., Eriksson, K.-E.. Biotechnical Approaches to Pulp Bleaching. Nordic Pulp Paper Res. J. (4):198-202(1988).

Puppo, A., Halliwell, B. Formation of Hydroxyl Radicals from Hydrogen Peroxide in the Presence of Iron: Is Haemoglobin a biological Fenton Reagent? Biochem. J. 249:185-190(1988).

Sepp, R. G., Faust, B. C., Holgne, J. Hydroxyl Radical Formation in Aqueous Reactions (pH 3-8) of Iron (II) with Hydrogen Peroxide: the Photo-Fenton Reaction. Environ. Sci. Technol. 26(2):313-319(1992).

Shimada, M., Habe, T., Higuchi, T., Okamoto, T., Panijpan, B. Biomimetic Approach to Lignin Degradation II. The Mechanism of Oxidative C-C bond Cleavage Reactions of Lignin Model Compounds with Natural Iron (III) Porphyrin chloride as a Heme-Enzyme Model System. Holzforschung. 41(5):277-285(1989).

Skerker, P. S., Farrell, R. L., Dolphin, D., Cui, F., Wijesekera, T. Biomimetic Bleaching of Kraft Pulp. Fourth International Conference on Biotechnology in the Pulp and Paper Industry, pp. 48-49 (May 1989).

Smith, P. K., McDonough, T. J. Transition Metal Ion Catalysis of the Reaction of a Residual Lignin-related Compound with Alkaline Hydrogen Peroxide. Svensk Papperstidning. 88(12):R106-R112 (1985).

Tien, M., Kirk, T. K. Lignin-Degrading Enzyme from the Hymenomycete Phanerochaete chrysosporium Burds. Science. 221:661-663(1983).

Walling, C. Fenton's Reagent Revisited. Accts. Chem. Res. 8:125-131(1975).

Yang, J. L., Lou, G., Eriksson, K.-E. L. The Impact of Xylanases on Bleaching of Kraft Pulps. TAPPI J. 75(12):95-101(1992).

ATTACHMENT 3

Catalytic Reactions in a Polymeric Model System for Hydrogen Peroxide Delignification of Pulp. Part II. Formation of Condensation Products

Colleen C. Walker, Graduate Student
Thomas J. McDonough, Professor of Engineering
Ronald. J. Dinus, Professor of Biology
Institute of Paper Science and Technology
500 10th Street, NW
Atlanta, GA 30318

Karl.-Erik L. Eriksson
Professor of Biochemistry
Life Sciences Building
University of Georgia
Athens, GA 30602

A unique experimental system has been developed to study the effect of three iron-based catalysts on the hydrogen peroxide oxidation of polymeric models of lignin and carbohydrate. Iron chelated by sequestering agents or bound in porphyrin structures, in the presence of hydrogen peroxide or other oxidants mimic the delignifying action of lignin peroxidase. The selectivity of these so-called biomimetic compounds for lignin over carbohydrate is the subject of this study.

Lignosulfonate and hydroxyethyl cellulose (HEC) have been chosen as polymeric models of lignin and carbohydrate. Molecular weights of these substrates were measured by High Performance Size-Exclusion Chromatography (HPSEC) and viscometry, respectively. Reactions were performed at pH 3.0, the optimum for lignin peroxidase activity. The three catalysts evaluated were FeSO4, Fe-EDTA and hemoglobin.

Lignosulfonate and HEC were combined in reaction solutions to provide a realistic reaction environment. In all reactions, including that with hydrogen peroxide alone (no catalyst), analysis of reaction samples by HPSEC indicated the formation of a large molecular weight product. This product is believed to be produced by condensation of the lignosulfonate onto the HEC polymer.

Figure 1 shows HPSEC chromatograms from several samples taken during the FeSO4 catalyzed reaction. Reaction conditions are listed in the figure caption. The first sample, taken prior to reaction initiation, shows the unreacted lignosulfonate peak. The sample at 2 minutes shows the immediate formation of the condensation product, with no "free" lignosulfonate remaining. The molecular weight distribution of this condensation product changes during the reaction, shifting towards lower molecular weights, indicating that degradation has occurred. The sample at 255 minutes shows the condensation product at the end of the reaction when all hydrogen peroxide has been consumed.

As noted above for the FeSO4 catalyzed reaction, the condensation product appears immediately (within 1 minute of reaction initiation). In the presence of Fe-EDTA, the condensation product appears more slowly, with full condensation of the lignosulfonate occurring after 10 minutes. In the presence of hemoglobin, however, only a small portion of the lignosulfonate condenses onto the HEC polymer. In addition, during this reaction the degradation of the uncondensed lignosulfonate is visible.

When the concentration of lignosulfonate is increased from 0.5 to 3.0 g/l, equal to that of HEC, different results are obtained. Figure 2 shows the HPSEC chromatograms from a $FeSO4$ catalyzed reaction. Only a small amount of the lignosulfonate condenses onto the HEC polymer, as seen by the relatively small area of the high molecular weight product. (Reaction conditions are identical to those stated in Figure 1 except for the increased concentration of lignosulfonate, from 0.5 to 3.0 g/l.) These results indicate that only a certain amount of condensation can occur.

The formation of the large molecular weight condensation product in these reactions may provide some insight to the efficiency of acidic hydrogen peroxide bleaching with biomimetic compounds. It is possible that the generation of hydroxyl radicals, and other active species, cause a polymerization of the two substrates. This limits the efficiency of the bleaching agent to remove lignin from the pulp without also removing carbohydrate. Experimental conditions in which the formation of this condensation product is minimized may produce a more efficient bleaching agent.

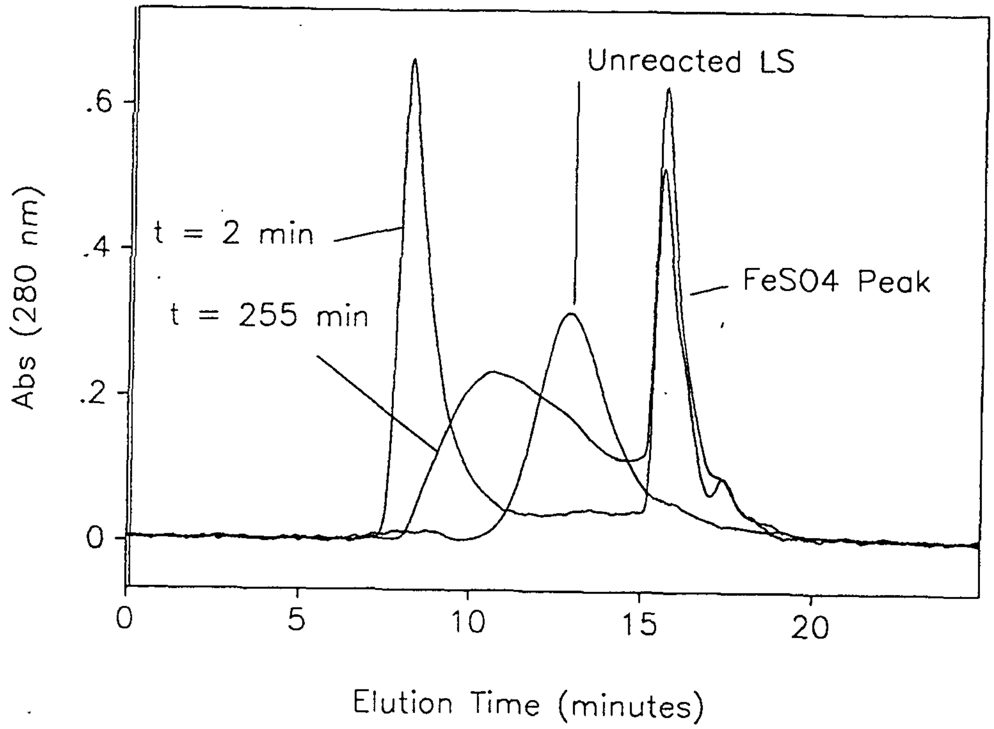


Figure 1. Size-exclusion chromatograms (UV Detector at 280 nm) from several reaction samples showing the large molecular weight product and the change in molecular weight distribution during reaction time. Reaction conditions: 3.0 g/l HEC, 0.5 g/l Lignosulfonate, 20 mM H_2O_2, 0.2 mM $FeSO_4$, pH 3.0 and 45°C.

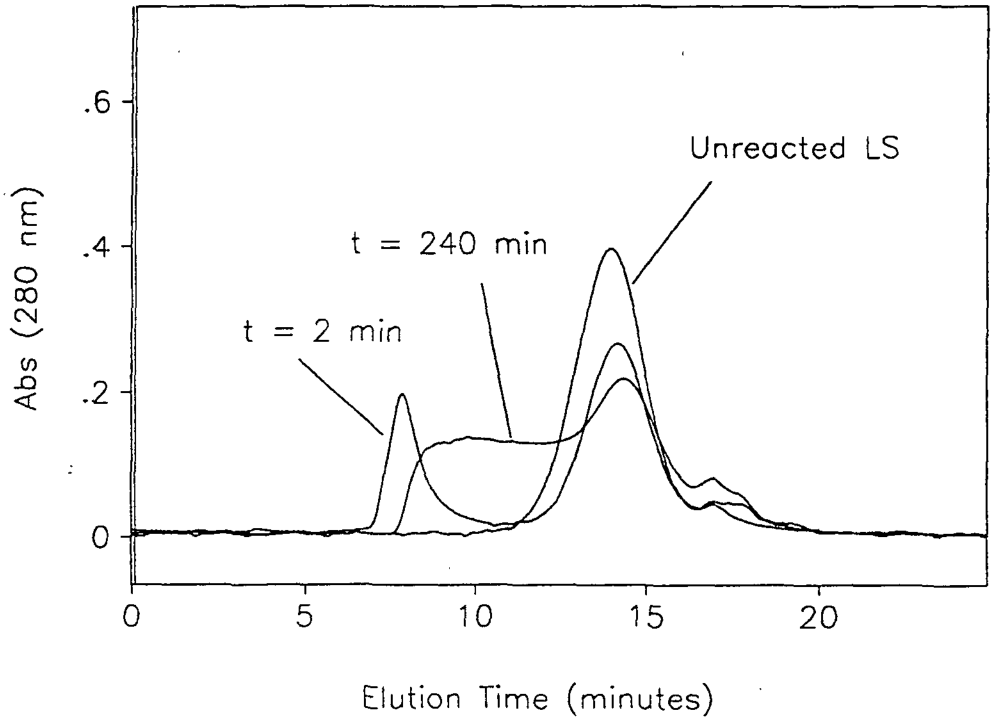


Figure 2. Size-exclusion chromatograms (UV Detector at 280 nm) from several reaction samples showing the large molecular weight product and the change in molecular weight distribution during reaction time. Reaction conditions: 3.0 g/l HEC, 3.0 g/l Lignosulfonate, 20 mM H_2O_2, 0.2 mM $FeSO_4$, pH 3.0 and 45°C.

CHARACTERIZATION OF EFFLUENT FRACTIONS FROM ClO_2 AND Cl_2 BLEACHING OF UNBLEACHED AND O_2 BLEACHED SOFTWOOD KRAFT PULPS

T. A. Schwantes
Graduate Student
Institute of Paper Science and Technology
Atlanta, GA

T. J. McDonough
Professor of Engineering
Institute of Paper Science and Technology
Atlanta, GA

ABSTRACT

Effluents from OC(EO), OD(EO), and D(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the effluents and effluent fractions from each stage, with the exception of the oxygen stage. Each fraction was characterized in terms of its size, and in terms of its ratio of chlorine to carbon - an environmentally significant parameter. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions.

Replacement of chlorine with chlorine dioxide after oxygen bleaching sharply reduced the AOX, TOC, and chlorine to carbon ratio (expressed as the number of chlorine atoms per 100 carbon atoms, Cl/C_{100}) of the whole effluents. Larger AOX and TOC reductions were seen in the ether soluble fraction and in the phenolic subfraction of the ether soluble material. Since both Cl/C_{100} and the size of the ether soluble fractions may be expected to correlate with the potential of an effluent for negative environmental effects, these observations show that replacement of chlorine by chlorine dioxide may be more beneficial than the resulting reductions in whole effluent AOX would suggest.

Oxygen delignification prior to a 100% chlorine dioxide stage reduced whole effluent AOX and TOC in rough proportion to the amount of lignin removed in the oxygen stage, but did not affect the overall Cl/C_{100}. The reductions in AOX and TOC in the environmentally significant ether soluble neutral and phenolic fractions were slightly larger. There was also a significant reduction in Cl/C_{100} in these fractions. Oxygen delignification, like chlorine dioxide substitution, may therefore be more beneficial than the overall AOX reduction would suggest.

INTRODUCTION

During the past decade, the possibility that pulp bleaching effluents may harm the environment has become a major issue with environmentalists and the general public alike. Total chlorinated organic material (measured as AOX) is currently of considerable interest. In fact, environmental pressures have led to either proposed or implemented AOX limits in several European countries and Canadian provinces (1, 2). Similar limits are likely in the U. S.

AOX regulation, together with the consumer's desire to buy "environmentally friendly" products, has led pulp mills to implement AOX reduction strategies. The AOX in pulp bleaching effluents may be decreased by one or more of the following process changes: improved brownstock washing (3-5), extended kraft delignification (6-8), O_2 delignification (3, 6, 9, 10), substitution of chlorine dioxide for chlorine (6, 9, 11-16), and oxidative caustic extraction (11, 17-19).

Although process changes can reduce the AOX, their effect on the environment remains uncertain since AOX reduction does not necessarily imply environmental impact reduction (20, 21). Because much of the effluent AOX is believed to be innocuous and only a small fraction potentially harmful, reducing the overall AOX may or may not reduce its environmental effects. The small, potentially harmful fraction is of low molecular weight and consists of hundreds or perhaps thousands of compounds, including certain environmentally troublesome ones. Such compounds or groups of them have been isolated and identified in pulp bleaching effluents. These include chlorophenolics (12, 16, 22-28), chlorinated dioxins (12, 25, 29), chlorinated neutral compounds (28, 30, 31), chlorinated carboxylic acids (28, 32) and chloroform (23, 33).

The complexity of pulp bleaching effluents complicates the task of developing a bleaching process that eliminates the potential for harmful effects on the environment. In an ideal world, a full chemical characterization would be done on effluents from a variety of process alternatives, and data on the environmental effects of each component would be available. It would then be a simple task to choose the alternative that results in minimum environmental effect. Effluents are, however, sufficiently complex to defy full chemical characterization. For example, the toxicity of effluents can only be partially accounted for by identified components (24).

A practical alternative to the impossible ideal of complete analysis, is fractionation of the effluents from candidate bleaching processes and characterization of the fractions in terms that will allow prediction of environmental effects. Such an approach was adopted in the present study. Fractionation was conducted on the basis of ether solubility, volatility and acidity, and the fractions were characterized in terms of their relative amounts and chlorine to carbon ratios. Ether solubility implies low molecular weight (34, 35) and low molecular weight material may be correlated with acute and chronic toxicity (21, 36). The ether extract contains most of the effluent's mutagenicity (30, 37, 38) and toxicity (34). For example, Dence and co-workers (34) found that 92% of the C stage toxicity and 75% of the E stage toxicity resides in the corresponding ether extracts. Furthermore, the toxicities of the extracts were concentrated in the phenolic and neutral subfractions. The amounts of these subfractions therefore assume corresponding significance. The chlorine to carbon ratio may be used as a predictor of toxicity (24, 39) and lipophilicity (40).

EXPERIMENTAL APPROACH

Pulp Bleaching

Three different pulp bleaching sequences were considered in this work: OC(EO), OD(EO), and D(EO). The unbleached pulp was a mill produced kraft with a kappa number of 26.0 before the oxygen stage. The oxygen bleached pulp (kappa 14.1) was collected after the oxygen stage at the same mill. Kappa numbers after bleaching are given in Table I. Only the first two stages of pulp bleaching were done, since they effect the majority of the delignification, and therefore produce most of the effluent load. The D and C stages (referred to collectively as D/C stages throughout this report) were done in a batch reactor at 2% consistency, at 45°C, for 30 minutes, and with a kappa factor of 0.25; the (EO) stages were done in a high shear mixer at 10% consistency, at 70°C, and for 70 minutes.

Effluent Fractionation and Characterization

For the reasons mentioned above, effluent characterization was based on ether extraction. The ether extractable material was further separated into an acidic fraction, a phenolic fraction, and a neutral fraction. This type of procedure has been used in previous studies of mutagenicity (38, 41) and toxicity (34), and analyses of chlorophenols (26, 39), chlorinated neutral compounds (31, 42), and chlorinated carboxylic acids (32).

The TOC-normalized AOX, expressed as organically bound chlorine atoms per hundred carbon atoms (Cl/C_{100}), was determined for each effluent and effluent fraction. To measure Cl/C_{100} on the ether extract and extract fractions, the ether was first completely removed, then AOX and TOC measured on each fraction. The removal of ether was accomplished by evaporation of the sample to dryness or very near to dryness. During this process, other volatiles were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted exhaustively with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction, and two ether extractable fractions. The first ether fraction is material readily extracted and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

All bleaching sequences were performed in duplicate, and the individual stage effluents from each replication were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. The D/C and (EO) stage data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represents TOC and AOX mass balances around the fractionation scheme and were determined as the sums of the AOX and TOC determinations of the neutrals, the phenolics, the acids, the polar fraction, the hydrophilic fraction, and the volatiles.

In this report emphasis will be placed on the whole effluents and on the ether soluble fraction, the phenolics, and the neutrals, since evidence in the literature indicates these fractions may be more environmentally important than the others. The Cl/C_{100} and the percentage of total TOC are also emphasized, since all needed information can be gained from these two results. The Cl/C_{100} gives an estimate of the relative environmental behavior of the material, and the percentage of the total TOC gives a measure of the total amount of material. The percentage of total TOC is used in order to normalize the TOC data for different levels of removed material.

Analyses of variance (AOV) were done on the data from each fraction, to assess the significance of differences between sequences and between stages. Since data with high Cl/C_{100} clearly had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between bleaching sequences, least significant differences were determined using Duncan's multiple range test (43).

RESULTS AND DISCUSSION

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-17 kg/t TOC and 0.1-2.8 kg/t AOX, depending on the stage and sequence.

Figure 2 compares the three partial bleaching sequences with respect to mean TOC production. TOC provides a measure of the total organic load produced by each sequence. As expected, based on the higher pulp kappa number entering the sequence, the D(EO) sequence produces the greatest quantity of TOC. In the case of the oxygen based sequences about half of the organic material has already been removed in the oxygen stage prior to delignification with chlorine based chemicals. This material is recycled to the mill's recovery system and is therefore without environmental significance in the wastewater stream.

A comparison of the oxygen based sequences shows that chlorine produces more TOC than chlorine dioxide in both the D/C and (EO) stages. This is in part due to the more effective delignification done by chlorine, but the difference is too great to be due to this effect alone. The data suggest that the OD(EO) sequence gives a higher carbohydrate yield. This is discussed further below.

Figure 3 presents a similar comparison of mean Cl/C_{100}. In both stages the material released by chlorine bleaching is much more extensively chlorinated than that released by chlorine dioxide bleaching. This is expected since chlorine reacts by both oxidation and substitution while chlorine dioxide only reacts by oxidation (44, 45). The ClO_2 bleaching produces some chlorinated organics as well, as a result of the formation and reaction of HOCl and Cl_2 during the process (46-48).

Insertion of an O_2 stage before ClO_2 has little effect on the extent of chlorination of effluent compounds, although some decrease is seen in the case of the (EO) stage effluents. This may be a result of the action of O_2 delignification. Oxygen in alkaline solution oxidizes free phenolic structures (44, 49), thus reducing the number of sites that are readily substituted by chlorine. Another possible explanation is that material from the OD(EO) sequence is more readily dechlorinated in the caustic extraction stage than that material from the D(EO) sequence.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-1.4 kg/t TOC, representing 4-13% of the total TOC and 0.01-0.79 kg/t AOX, representing 7-35% of the total AOX. A change from chlorine to chlorine dioxide bleaching reduces both TOC and AOX in this fraction to a greater extent than occurs in the whole effluent.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for each bleaching sequence. For both the D/C and (EO) stages, chlorine results in a higher ether soluble TOC content than chlorine dioxide. The D(EO) sequence has a smaller percentage of total TOC in this fraction than OD(EO). Because of the increased lignin removal however, the absolute amounts of removed AOX and TOC in this fraction are greater for D(EO).

Figure 5 similarly compares the sequences with regard to Cl/C_{100}. For both the D/C and (EO) stages, this fraction contains increased chlorine per unit carbon compared to the whole effluents. This further supports the contention that the ether soluble fraction is of environmental interest. The ether soluble fraction is also chlorinated to a much greater extent when chlorine is used rather than chlorine dioxide. In fact the increased degree of chlorine substitution on the organic material in the case of chlorine results in a more hydrophobic effluent and is the likely cause of the increased ether soluble TOC that is also seen when chlorine is used. Use of chlorine dioxide provides two environmental benefits over chlorine use, in the case of the ether soluble material: a large reduction in the amount of organically bound chlorine per unit carbon, and a reduced amount of material within the fraction. There is no significant Cl/C_{100} effect seen between the OD(EO) and D(EO) sequences.

Phenolic Fraction

Detailed results of analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.12 kg/t TOC or 0.5-1.5% of the total TOC, and 0.002-0.09 kg/t AOX or 0.8-4.1% of the total AOX. Both TOC and AOX are again reduced to a greater extent in this fraction than in the whole effluent, when the change is made from chlorine to chlorine dioxide bleaching.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the three sequences. Chlorine bleaching results in an increased content of phenolic TOC relative to chlorine dioxide for both the D/C and (EO) stages. The reduced amount of phenolic material with ClO_2 bleaching is in accordance with other studies in which the amount of measured chlorophenolics decreased as ClO_2 substitution increased (22, 24, 28, 50).

Figure 7 compares the phenolic fraction Cl/C_{100} for the three bleaching sequences and for both stages. Chlorine produces a much more extensively chlorinated phenolic fraction than does chlorine dioxide. The two benefits from the use of chlorine dioxide rather than chlorine are again seen here: decreased phenolic AOX per unit carbon, as well as a decreased amount of material in the phenolic fraction.

No significant differences were seen between the OD(EO) and D(EO) sequences by the normal AOV. However if only the OD(EO) and D(EO) data are included in the analysis, a significantly greater Cl/C_{100} is seen for D(EO) bleaching compared to OD(EO).

Neutral Fraction

Complete data on the neutral fraction are shown in Table VI. The fraction contains 0.05-0.14 kg/t TOC (0.4-1.2% of the total TOC) and 0.001-0.006 kg/t AOX (0.3-1.4% of the total AOX).

Figure 8 compares the bleaching sequences with regard to neutral fraction TOC as a percentage of the total TOC. There are no statistically significant differences between any of the bleaching sequences, due to scatter in the replicate data.

Figure 9 compares the neutral fraction Cl/C_{100} for the sequences. Again chlorine produces a more highly chlorinated material than does chlorine dioxide, for both D/C and (EO) stages. The D(EO) sequence also produces a more highly chlorinated material than the OD(EO) sequence. This is another indication that oxygen delignification leaves a residual lignin that is less susceptible to chlorine substitution reactions than unoxidized lignin.

Acid Fraction

Table VII presents the detailed results for the acid fraction of the ether soluble material. About 0.2-1.1 kg/t TOC, representing 3-10% of the total TOC and 0.01-0.46 kg/t AOX, representing 6-20% of the total AOX, is contained within this fraction.

Figures 10 and 11 show the acid fraction TOC as a percent of the total, and the acid fraction Cl/C_{100}. Replacement of chlorine with chlorine dioxide results in a decreased percentage of total TOC in the (EO) stage fraction and reduces the Cl/C_{100} for both stages. Oxygen bleaching prior to chlorine dioxide treatment results in a decreased Cl/C_{100} for the (EO) stage fraction, but an increased percentage of TOC in the fraction for both stages. The absolute amounts of TOC and AOX in the acid fraction are again greater for D(EO) bleaching, however.

Polar Fraction

Complete data for the polar fraction, or difficultly ether extractable material, are shown in Table VIII. The fraction contains 0.2-1.1 kg/t TOC or 3-11% of total TOC, and 0.003-0.09 kg/t AOX or 2-20% of the total AOX.

Figures 12 and 13 show the mean polar fraction data for both percent of total TOC and Cl/C_{100}. A change from chlorine to chlorine dioxide use results in a decreased (EO) stage Cl/C_{100} for the fraction. The presence of oxygen bleaching before ClO_2 treatment results in an increased D/C stage Cl/C_{100} but a decrease in the percentage of the total TOC within the D/C stage polar fraction. A decreased (EO) stage Cl/C_{100} is also seen when O_2 bleaching precedes ClO_2 treatment.

Hydrophilic Fraction

Table IX presents the entire data set for the hydrophilic fraction or the non-extractable material. The hydrophilic fraction contains 3.4-13.4 kg/t TOC (68-86% of the total TOC) and 0.07-1.4 kg/t AOX (49-85% of the total AOX).

Figures 14 and 15 show the hydrophilic TOC as a percent of the total TOC, and the hydrophilic fraction Cl/C_{100} for the bleaching sequences. The Cl/C_{100} values for this fraction are similar to those found for "high molecular weight" effluent material in other studies (28, 49, 51, 52). Although there may appear to be differences between the sequences in Figure 14, the percentage of total TOC does not differ significantly. This again is due to scatter in the replicate data. The use of chlorine dioxide in place of chlorine causes a reduced Cl/C_{100} for both stages, and the presence of oxygen bleaching before chlorine dioxide treatment reduces the Cl/C_{100} for both stages as well.

Volatile Fraction

The data set for the volatile fraction is shown in Table X. About 0.3-1.1 kg/t TOC or 4-16% of the total TOC, and 0.005-0.3 kg/t or 1.5-18% of the total AOX is volatile material. Figures 16 and 17 show the mean data for the percent of total TOC and Cl/C_{100}. There are no statistically significant differences, due to scatter in the replicate data.

Yield Implications of Whole Effluent TOC

A summary of the TOC removed in both the D/C and (EO) stages, the CE kappa numbers, the kappa change brought about by the bleaching sequence, and the ratio of TOC to the change in kappa number is shown for each bleaching sequence in Table I. Analysis of variance on the ratio of TOC to kappa change showed that the effluents from pulp chlorination contained significantly more TOC per unit of kappa number reduction than either chlorine dioxide case.

The increased amount of TOC in the effluent per unit of kappa loss implies greater carbohydrate loss, or reduced pulp yield with 100% chlorine as compared to 100% chlorine dioxide. In a review of pulp yield data at different levels of ClO_2 substitution, increased yield was seen in 40°C stages at increased ClO_2 substitution, while no such yield increases were seen at lower temperatures (53). This work, in which D/C stages were done at 45°C, is consistent with those results.

Another possible explanation for the decreased TOC per unit kappa number decrease seen with chlorine dioxide bleaching, is formation of carbonate species during bleaching. Such species are evolved as CO_2, and not measured as TOC.

EXPERIMENTAL METHODS

Pulp Bleaching

Two pulp samples were used in these experiments: a 26.0 kappa unbleached southern softwood and a 14.1 kappa O_2 delignified southern softwood. Both pulps were produced at the same mill. The unbleached pulp was collected just before the O_2 stage, and the O_2 delignified pulp was collected just after the O_2 stage. Each pulp was well washed before bleaching.

D/C Stages.

All D/C stages were done in a 20L batch reactor, designed to rapidly add bleaching chemicals. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH in all cases was adjusted to 2 by the addition of sulfuric acid solution.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 X TAC, the O_2 charge was 0.5% on pulp, and 4.1% of the total D/C stage filtrate was included as carryover. The slurry was mixed at 15 Hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D/C stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%.

This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess Na_2SO_3, and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction, the NaOH soluble material is the phenolic fraction, and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done on a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done on a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (54). In this case samples were shaken for 4 hours rather one, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

Figures 18 and 19 summarize the total D/C + (EO) stage TOC and AOX for the bleaching sequences. The size of each graph is proportional to the TOC or AOX (in kg/t) produced in the corresponding bleaching sequence. Figure 18 shows that D(EO) bleaching produces the most effluent TOC, as expected based on the higher kappa number of the pulp. The OC(EO) sequence produces more effluent TOC than OD(EO) because of both the greater delignification effectiveness of chlorine and possible increased carbohydrate loss. As shown in Figure 19, the OD(EO) sequence results in only a small fraction of the total AOX produced by the OC(EO) sequence. The AOX in the effluent fractions is also smaller by a corresponding amount. As expected, the D(EO) sequence produces about twice the AOX as the OD(EO) sequence.

Certain significant conclusions regarding the nature of bleaching effluents produced by both chlorine and chlorine dioxide bleaching can be based on this research. For the whole effluents, chlorine bleaching gives a higher Cl/C_{100} than ClO_2 bleaching of the same pulp. The same trend is seen for effluent fractions which are environmentally significant. In the case of the ether soluble fraction and the phenolic fraction, not only is the Cl/C_{100} greater for Cl_2 bleaching, but a greater percentage of the total TOC partitions into the ether soluble and phenolic fractions as well. The phenolic and neutral fractions for both the D/C and (EO) stages have lower Cl/C_{100} values when oxygen bleaching precedes chlorine dioxide treatment.

The results of this research provide some new evidence in support of the use of chlorine dioxide and O_2 delignification as a means of environmental improvement. By using ClO_2 in place of Cl_2, not only is the amount of chlorine substitution on organic compounds greatly reduced, but the percentage of material within certain environmentally important fractions is also reduced. Oxygen bleaching, in addition to the expected benefit of reducing in half the total effluent load, provides a decreased level of chlorine substitution of organic compounds in the phenolic and neutral fractions of both D/C and (EO) stage effluents. Therefore, both chlorine dioxide substitution and oxygen bleaching may be more environmentally beneficial than the overall AOX reduction suggests.

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. 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.

LITERATURE CITED

1. Reeve, D. W., Earl, P. F., *Pulp and Paper Canada*, "Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part 1: Environmental Impact and Regulation of Effluents," 90(4):T128 (1989).

2. Sjoblom, K., *1990 Tappi Pulping Conference Proceedings*, "Pulp Mill Emissions and Environmental Regulations," pp. 161-172.

3. Germgard, U., Karlsson, R., Kringstad, K., de Sousa, F., Stromberg, L., *Svensk Papperstidning*, "Oxygen Bleaching and It's Impact On Some Environmental Parameters," 88(12):R113 (1985).

4. Blomberg, L., Jarvinen, R., Talka, E., Valttila, O., *1990 Tappi Pulping Conference Proceedings*, "Organic Carry-over in Kraft Pulp and Bleaching Discharges," pp. 217-226.

5. Blomback, S., *1990 Tappi Pulping Conference Proceedings*, "ASSI Karlsborgs Way To Reduce the Formation and Discharge of TOCl," pp. 905-914.

6. Shin, N., Sundaram, M., Jameel, H., Chang, H., *1990 Tappi Pulping Conference Proceedings*, "Bleaching of Softwood RDH Pulps With Low/No Chlorine Bleaching Sequences," pp. 817-828.

7. Dillner, B., Larsson, L., Tibbling, P., *Tappi*, "Non-Chlorine Bleaching of Pulp Produced By the Modified Continuous Cooking Process," 73(8): 167 (1990).

8. Sjoblom, K., Hartler, N., Mjoberg, J., Sjodin, L., *Tappi*, "A New Technique For Pulping To Low Kappa Numbers in Batch Pulping: Results of Mill Trials," 66(9):97 (1983).

9. Liebergott, N., Van Lierop, B., Nolin, A., Faubert, M., Laflamme, J., *1990 CPPA Technical Section Annual Meeting Proceedings*, "Modifying the Bleaching Process to Decrease AOX Formation," pp. B229-B238.

10. Arhippainen, B., Malinen, R., *1987 International Oxygen Delignification Conference Proceedings*, "Cost Competitiveness of Oxygen Bleaching," pp. 23-27.

11. Basta, J., Holtinger, L., Hook, J., Lundgren, P., *Tappi*, "Reducing Levels of Adsorbable Organic Halogens (AOX)," 73(4):155 (1990).

12. Munro, F., Chandrasekaran, S., Cook, C., Pryke, D., *Tappi*, "Impact of High Chlorine Dioxide Substitution on Oxygen Delignified Pulp," 73(5):123 (1990).

13. Liebergott, N., Van Lierop, B., Kovacs, T., Nolin, A., *Tappi*, "A Comparison of the Order of Addition of Chlorine and Chlorine Dioxide in the Chlorination Stage," 73(9):207 (1990).

14. Brunsvik, J., Grundelius, R., Kordes, R., Swan, B., *1989 Tappi Pulping Conference Proceedings*, "Environmental Compatible Bleaching of Chemical Pulp," pp. 411-414.

15. Earl, P., Reeve, D., *1989 Tappi Environmental Conference Proceedings*, "Chlorinated Organic Matter In Bleached Chemical Pulp Production: Part III: The Effect of Chlorintaion Stage Variables on Chlorinated Organic Matter In Effluent," pp. 385-391.

16. Axegard, P., *Tappi*, "Substituting Chlorine Dioxide For Elemental Chlorine Makes the Bleach Plant Effluent Less Toxic," 69(10):54 (1986).

17. Hong, Q., Shin, N., Chang, H., *1988 Tappi Pulping Conference Proceedings*, "Effects of Oxygen Extraction on Organic Chlorine Content in Bleach Plant Effluents," pp. 63-69.

18. Klein, R., Meng, T., Jameel, H., Sundaram, V., *1990 Tappi Pulping Conference Proceedings,* "Hydrogen Peroxide Reinforced Extraction Lowers Chlorinated Organics and Color in Bleach Plant Effluent," pp. 829-835.

19. Reid, D., Billmark, G., Sutton, C., *1990 International Oxygen Delignification Symposium Proceedings,* "Peroxide Bleaching Reduces Dioxin Formation in a Generator Limited Mill," pp. 85-89.

20. NCASI Special Report No. 90-07, "An Examination of the Relationship Between the Adsorbable Organic Halide (AOX) Content of Paper Industry Wastewaters and Potential Aquatic Biological Effects: First Progress Report," July 1990.

21. O' Connor, B. I., Kovacs, T. G., Voss, R. H., Martel, P. H., *1992 CPPA Technical Section Annual Meeting Proceedings,* "A Study of the Relationship Between Laboratory Bioassay Response and AOX Content For Pulp Mill Effluents," pp. A223-A233.

22. Earl, P., Reeve, D., *1989 Tappi Pulping Conference Proceedings,* "Chlorinated Organic Matter In Bleached Chemical Pulp Production: Part VI: Chlorinated Compounds In Effluents," pp. 31-37.

23. Axegard, P., *1988 International Pulp Bleaching Conference Proceedings,* "Improvement of Bleach Plant Effluent By Cutting Back On Cl_2," pp. 69-76.

24. Voss, R. H., Wearing, J. T., Mortimer, R. D., Kovacs, T., Wong, A., *Paperi ja Puu,* "Chlorinated Organics In Kraft Bleaching Effluents," 12(1980):809.

25. Berry, R. M., Luthe, C. E., Voss, R. H., Wrist, P. E., Axegard, P., Gellerstedt, G., Linblad, P. O., Popke, I., *Pulp and Paper Canada,* "The Effects of Recent Changes in Bleached Softwood Kraft Mill Technology on Organochlorine Emissions: An International Perspective," 92(6):T155 (1991).

26. Lindstrom, K., Nordin, J., *Journal of Chromatography,* "Gas Chromatography-Mass Spectrometry of Chlorophenols in Spent Bleach Liquors," 128(1976):13.

27. Gergov, M., Priha, M., Talka, E., Valltila, O., *1988 Tappi Environmental Conference Proceedings,* "Chlorinated Organic Compounds in Effluent Treatment at Kraft Mills," pp. 443-455.

28. O' Connor, B. I., Kovacs, T. G., Voss, R. H., Martel, P. H., van Lierop, B., *EUCEPA International Environmental Symposium Proceedings,* "A Laboratory Assessment of the Environmental Quality of Alternative Pulp Bleaching Effluents," April 1993.

29. Berry, R. M., Fleming, B. I., Voss, R. H., Luthe, C. E., Wrist, P. E., *Pulp and Paper Canada,* "Toward Preventing the Formation of Dioxins During Chemical Pulp Bleaching," 98(8):T279 (1989).

30. Kringstad, K. P., Ljungquist, P. O., de Sousa, F., Stromberg, L. M., *Environmental Science and Technology,* "Identification and Mutagenic Properties of Some Chlorinated Aliphatic Compounds in the Spent Liquor From Kraft Pulp Chlorination," 15(5):562 (1981).

31. Lindstrom, K., Nordin, J., *Svensk Papperstidning,* "Identification of Some Neutral Chlorinated Organic Compounds in Spent Bleach Liquors," 82(2):55 (1978).

32. Lindstrom, K., Osterberg, F., *Environmental Science and Technology,* "Chlorinated Carboxylic Acids in Softwood Kraft Pulp Spent Bleach Liquors," 20(2):133 (1986).

33. Dallons, V. J., Crawford, R. J., *1990 Tappi Pulping Conference Proceedings*, "Chloroform Formation in Bleaching," pp. 195-201.

34. Sameshima, K., Simson, B., Dence, C., *Svensk Papperstidning,* "The Fractionation and Characterization of Toxic Materials in Kraft Spent Bleaching Liquors," 83(6):162 (1979).

35. Jokela, J. K., Salkinoja-Salonen, M., *Environmental Science and Technology,* "Molecular Weight Distributions of Organic Halogens in Bleached Kraft Pulp Mill Effluents," 26(6):1190 (1992).

36. Bryant, C., Amy, G., *1988 Tappi Environmental Conference Proceedings*, "Organic Halide in Kraft Mill Wastewaters: Factors Affecting In-mill Formation and Removal by Biological Treatment," pp. 435-438.

37. Kringstad, K., de Sousa, F., Stromberg, L., *Environmental Science and Technology*, "Evaluation of Lipophilic Properties of Mutagens Present in the Spent Chlorination Liquor From Pulp Bleaching," 18(3):200 (1984).

38. Rannug, U., Jenssen, D., Ramel, C., Ericksson, K., Kringstad, K., *Journal of Toxicology and Environmental Health*, "Mutagenic Effects of Effluents From Chlorine Bleaching of Pulp," 1981(7):33.

39. Salkinoja-Salonen, M., Saxelin, M., Pere, J., Jaakkola, T., Saarikowski, J., Hakulinen, R., Koistinen, O., In: *Advances in the Identification and Analysis of Organic Pollutants in Water. Ch. 56*, "Analysis of Toxicity and Biodegradability of Organochlorine Compounds Released Into the Environment in Bleaching Effluents of Kraft Pulping," L. H. Keith ed., Ann Arbor Science, 1981, pp. 1131-1164.

40. Kringstad, K., Stockman, L., Stromberg, L., *Journal of Wood Chemistry and Technology*, "The Nature and Significance of Spent Bleach Liquor Toxicants: Present State of Knowledge," 4(3):389 (1984).

41. Ander, P., Eriksson, K. E., Kringstad, K., Rannug, U., Ramel, C., *Svensk Papperstidning*, "Studies On the Mutagenic Properties of Bleaching Effluents," 81(14):454 (1977).

42. Lindstrom, K., Nordin, J., Osterberg, F., In: *Advances in the Identification and Analysis of Organic Pollutants in Water. Ch. 52*, "Chlorinated Organic of Low and High Relative Molecular Mass in Pulp Mill Bleachery Effluents," L. H. Keith ed., Ann Arbor Science, 1981, pp. 1039-1059.

43. Harter, H. L., *Biometrics*, "Critical Values For Duncan's New Multiple Range Test," 16(4):671 (1960).

44. Gierer, J., *Holzforschung*, "The Chemistry of Delignification, Part II: Reactions of Lignins During Bleaching," 36(2):55 (1982).

45. Gierer, J., *Holzforschung*, "Basic Principles of Bleaching, Part 1: Cationic and Radical Processes," 44(5):387 (1990).

46. Kolar, J. J., Lindgren, B. O., Pettersson, B., *Wood Science and Technology*, "Chemical Reactions in Chlorine Dioxide Stages of Pulp Bleaching," 17(1983):117.

47. Singh, A., *1988 International Pulp Bleaching Conference Proceedings*, "Mechanisms of Reactions of Chlorine, Chlorine Dioxide and Nitrogen Dioxide," pp. 85-90.

48. Ni, Y., Kubes, G. J., Van Heiningen, A. R. P., *1991 International Pulp Bleaching Conference Proceedings*, "Rate Processes of AOX Formation and Chlorine Species Distribution During ClO_2 Prebleaching of Kraft Pulp," pp. 195-218.

49. Gellerstedt, G., Lindfors, E. L., Pettersson, M., Sjoholm, E., Robert, D., *Appita 6th International Symposium on Wood and Pulping Chemistry Proceedings*, "Chemical Aspects On Chlorine Dioxide as a Bleaching Agent For Chemical Pulps," pp. 331-336 (1991).

50. McFarlane, P. N., Allison, R. W., Clark, T. A., Mackie, K. L., *Water Science and Technology*, "The Effect of Chlorination Conditions On the AOX and Chlorinated Phenol Content of Kraft Bleach Plant Wastewaters," 24(3/4):55 (1991).

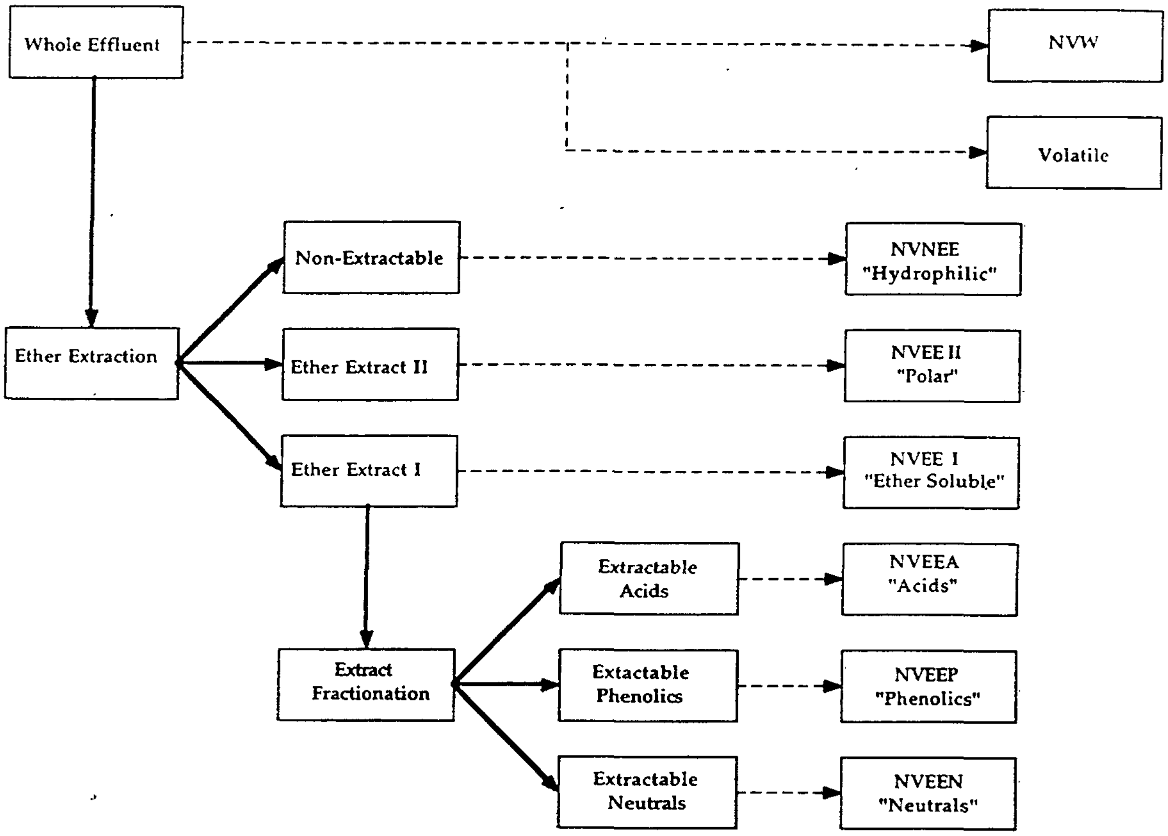
51. Osterberg, F., Lindstrom, K., *Holzforschung*, "Characterization of the High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL), Part II Acidic SBL," 39(3):149 (1985).

52. Lindstrom, K., Osterberg, F., *Holzforschung*, "Characterization of the High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL), Part I Alkaline SBL," 38(4):201 (1984).

53. Mc Donough, T. J., In: *Chlorine Dioxide in the Chlorination Stage: A Survey of Existing Published Information*, "Effect of Chlorine Dioxide Substitution on Yield," T. J. Mc Donough, ed., CPPA Technical Section, April 1985, pp. 28-31.

54. Scandinavian Pulp, Paper, and Board Testing Committee, "Effluents From Pulp Mills, Organically Bound Chlorine By the AOX Method," SCAN-W 9:89.

Figure 1. Effluent Fractionation.



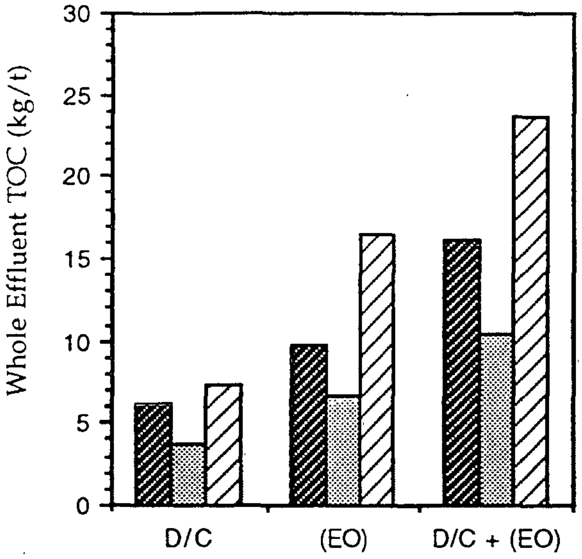


Figure 2. Whole Effluent TOC.

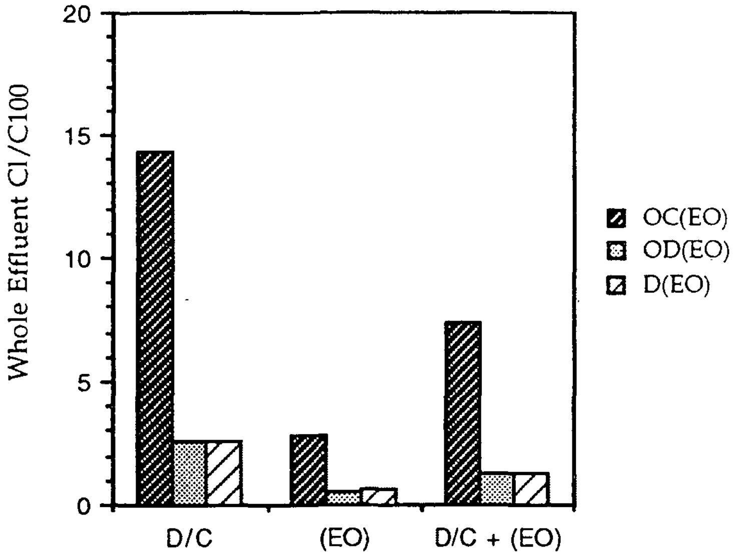


Figure 3. Whole Effluent Cl/C100.

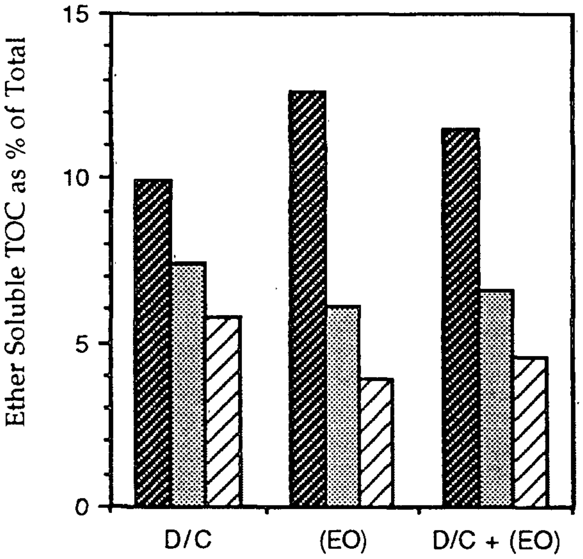


Figure 4. Ether Soluble TOC as % of Total.

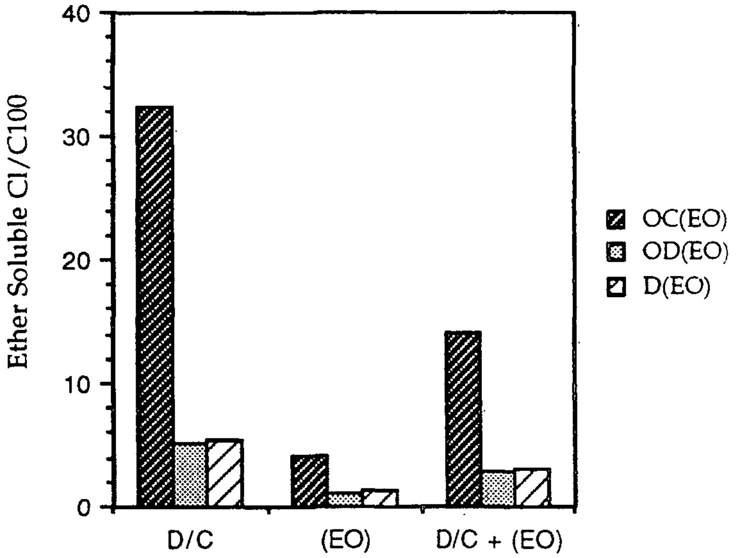


Figure 5. Ether Soluble Cl/C100.

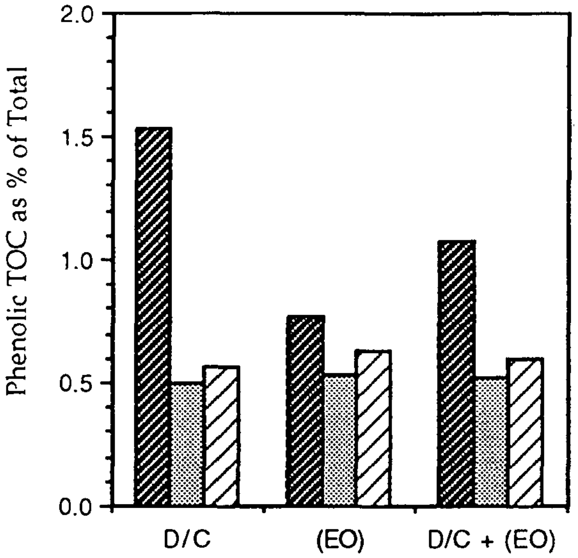


Figure 6. Phenolic TOC as % of Total.

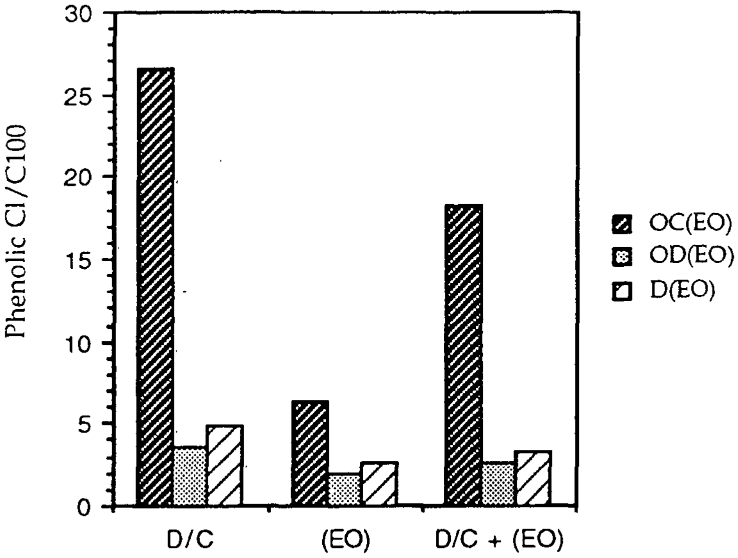


Figure 7. Phenolic Cl/C100.

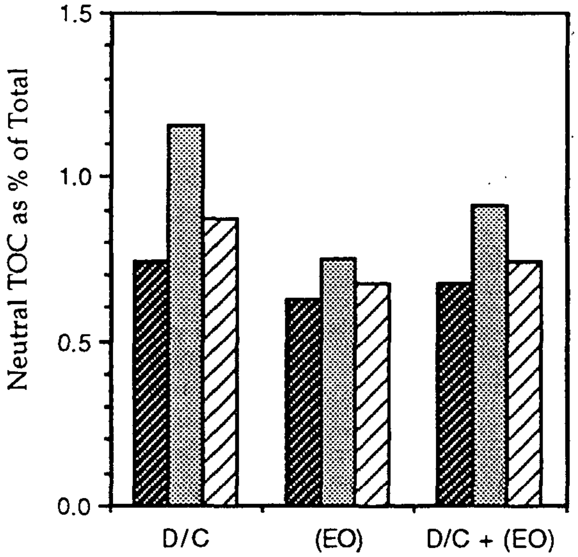


Figure 8. Neutral TOC as % of Total.

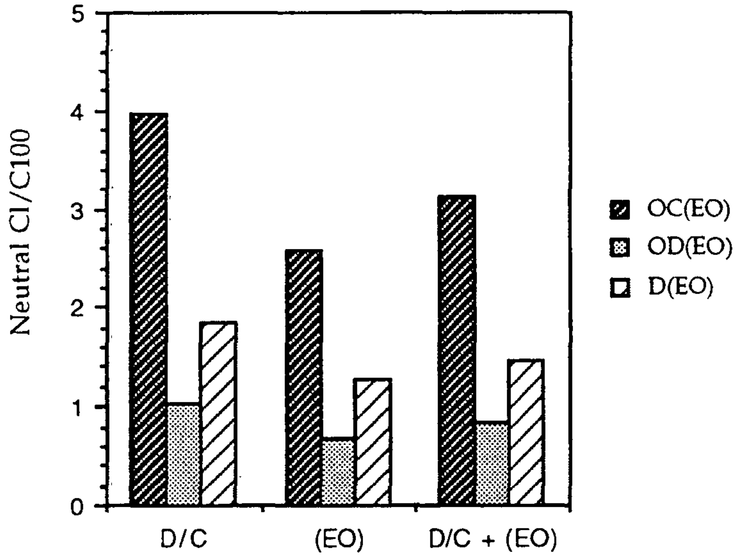


Figure 9. Neutral Cl/C100.

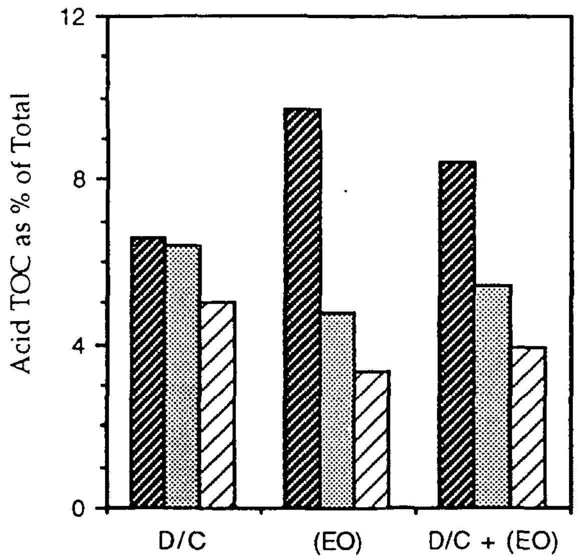


Figure 10. Acid TOC as % of Total.

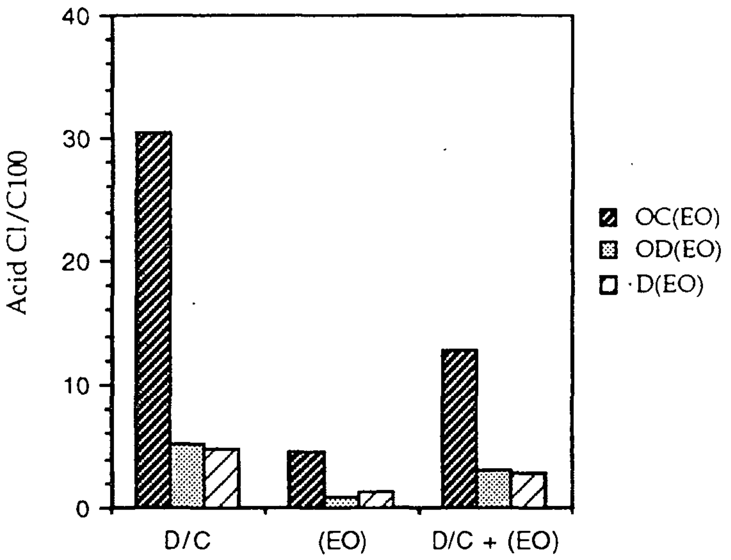


Figure 11. Acid Cl/C100.

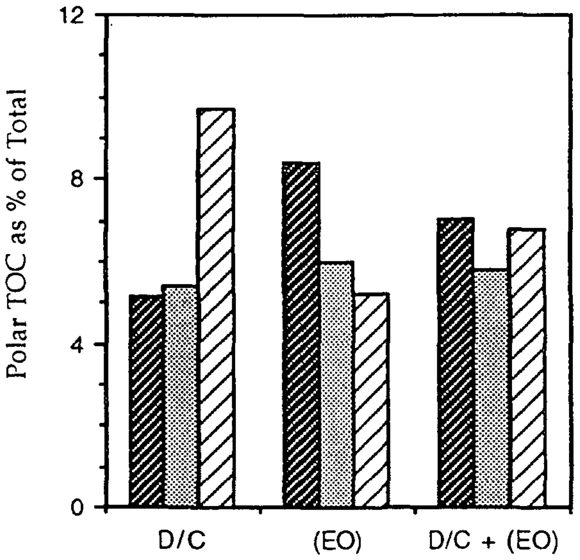


Figure 12. Polar TOC as % of Total.

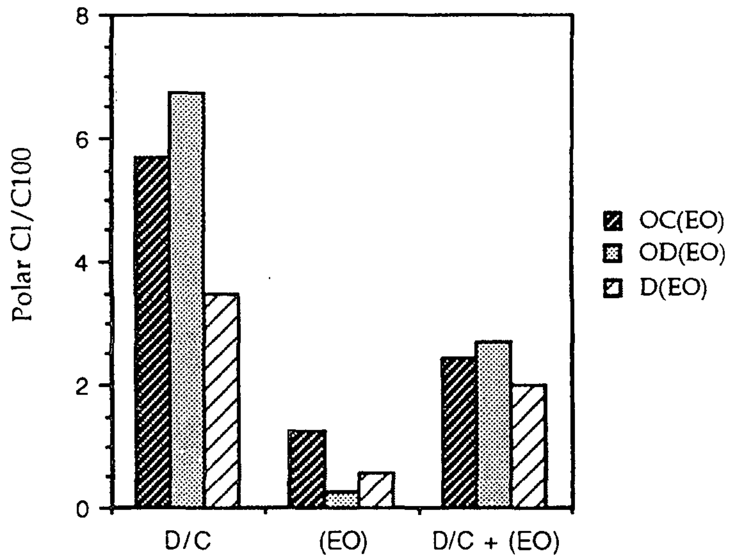


Figure 13. Polar Cl/C100.

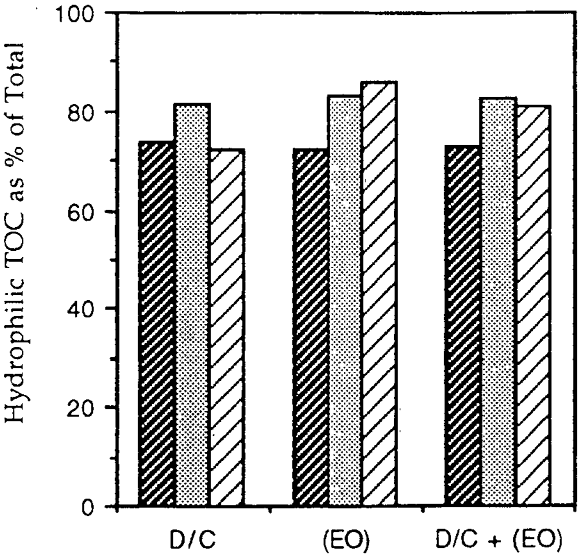


Figure 14. Hydrophilic TOC as % of Total.

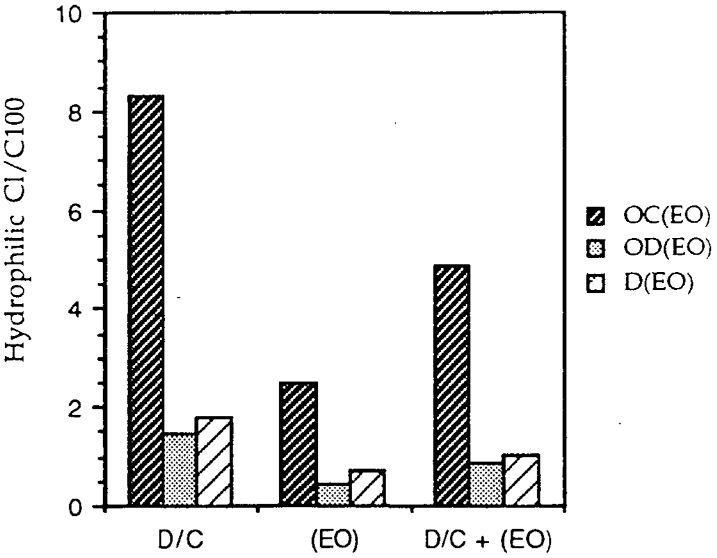


Figure 15. Hydrophilic Cl/C100.

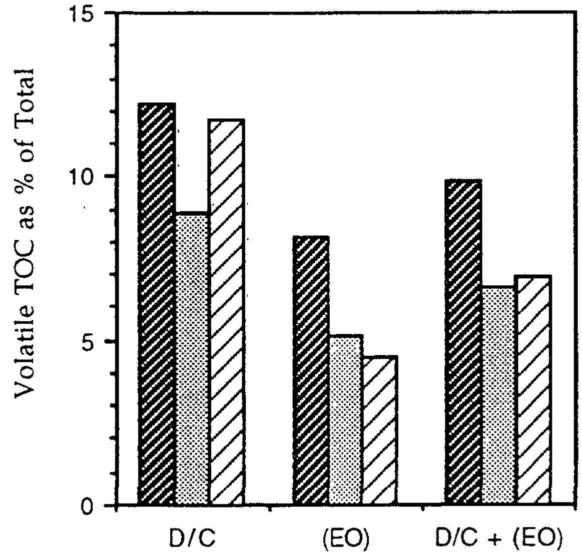


Figure 16. Volatile TOC as % of Total.

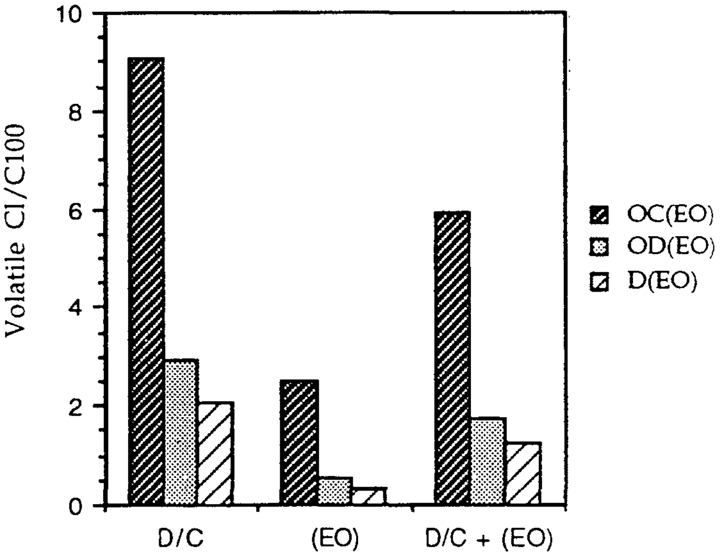


Figure 17. Volatile Cl/C100.

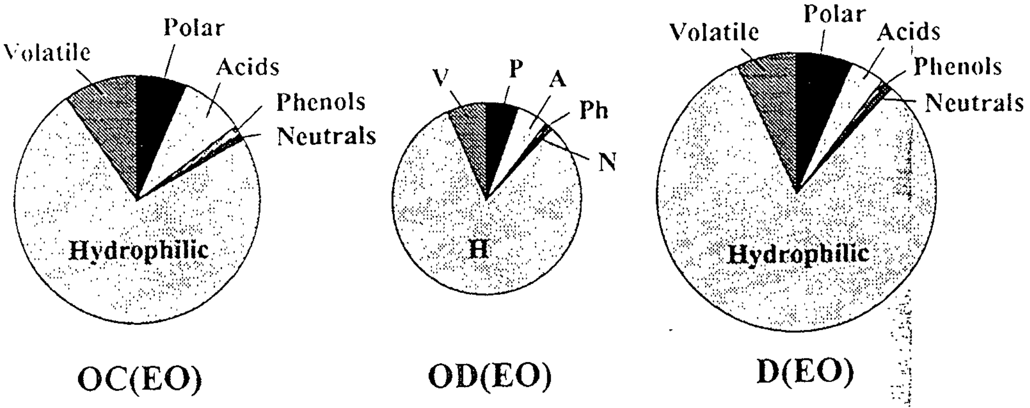


Figure 18. TOC Summary Graphs.

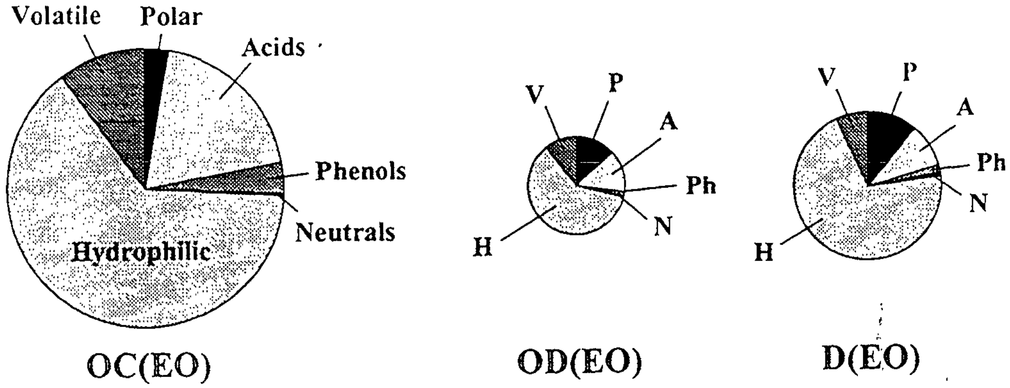


Figure 19. AOX Summary Graphs.

Table I. D/C + (EO) TOC and CE Kappa Number Data.

Sequence	D/C + (EO) TOC (kg/t)	CE kappa	Δ kappa	TOC/Δ kappa
OC(EO)	16.6	2.10	12.0	1.38
OC(EO)	15.5	1.74	12.4	1.26
OD(EO)	10.6	4.23	9.87	1.08
OD(EO)	10.4	4.44	9.66	1.08
D(EO)	24.4	5.27	20.7	1.18
D(EO)	22.9	4.83	21.2	1.08

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, not extracted with ether ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	6.15	6.36	3.85	3.80	7.33	7.23
Total TOC, kg/t	7.03	8.17	4.43	4.29	7.87	8.02
AOX, kg/t	2.75	2.56	0.299	0.294	0.552	0.594
Total AOX, kg/t	2.26	2.13	0.297	0.264	0.447	0.551
Cl/C_{100}	15.1	13.6	2.63	2.61	2.54	2.78

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	9.37	10.2	6.79	6.60	17.1	15.7
Total TOC, kg/t	9.83	11.6	6.70	6.52	15.6	14.9
AOX, kg/t	0.793	0.858	0.101	0.102	0.341	0.309
Total AOX, kg/t	0.738	0.887	0.0938	0.0930	0.324	0.306
Cl/C_{100}	2.86	2.86	0.50	0.52	0.68	0.67

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	15.5	16.6	10.6	10.4	24.4	22.9
Total TOC, kg/t	16.9	19.8	11.1	10.8	23.5	22.9
AOX, kg/t	3.54	3.42	0.400	0.396	0.893	0.903
Total AOX, kg/t	3.00	3.02	0.391	0.357	0.771	0.857
Cl/C_{100}	7.71	6.98	1.27	1.29	1.24	1.33

Table IV. Ether Soluble Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.681	0.832	0.383	0.267	0.501	0.418
% of Total TOC	9.69	10.2	8.65	6.22	6.37	5.21
AOX, kg/t	0.790	0.632	0.0547	0.0439	0.0751	0.0725
% of Total AOX	35.0	29.7	18.4	16.6	16.8	13.2
Cl/C_{100}	39.2	25.6	4.83	5.56	5.05	5.88

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.32	1.36	0.406	0.399	0.663	0.542
% of Total TOC	13.4	11.7	6.06	6.12	4.25	3.64
AOX, kg/t	0.173	0.154	0.0127	0.0125	0.0273	0.0220
% of Total AOX	23.4	17.4	13.5	13.4	8.43	7.19
Cl/C_{100}	4.44	3.83	1.06	1.06	1.39	1.37

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	2.00	2.19	0.789	0.666	1.16	0.960
% of Total TOC	11.9	11.1	7.09	6.16	4.94	4.19
AOX, kg/t	0.963	0.786	0.0674	0.0564	0.102	0.0945
% of Total AOX	32.1	26.0	17.2	15.8	13.2	11.0
Cl/C_{100}	16.3	12.1	2.89	2.86	2.97	3.33

Table V. Phenolic Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.108	0.123	0.0239	0.0198	0.0462	0.0434
% of Total TOC	1.54	1.51	0.54	0.46	0.59	0.54
AOX, kg/t	0.0935	0.0869	0.00255	0.00201	0.00683	0.00602
% of Total AOX	4.14	4.08	0.86	0.76	1.53	1.09
Cl/C_{100}	29.2	23.8	3.60	3.45	5.00	4.69

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0884	0.0725	0.0364	0.0341	0.0820	0.107
% of Total TOC	0.90	0.63	0.54	0.52	0.53	0.72
AOX, kg/t	0.0221	0.00924	0.00243	0.00180	0.00697	0.00730
% of Total AOX	2.99	1.04	2.59	1.94	2.15	2.39
Cl/C_{100}	8.47	4.31	2.26	1.79	2.87	2.31

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.196	0.196	0.0603	0.0539	0.128	0.150
% of Total TOC	1.16	0.99	0.54	0.50	0.55	0.65
AOX, kg/t	0.116	0.0961	0.00498	0.00381	0.0138	0.0133
% of Total AOX	3.87	3.18	1.27	1.07	1.79	1.55
Cl/C_{100}	20.0	16.6	2.79	2.39	3.64	3.00

Table VI. Neutral Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0393	0.0750	0.0551	0.0457	0.0784	0.0583
% of Total TOC	0.56	0.92	1.24	1.07	1.00	0.73
AOX, kg/t	0.00591	0.00629	0.00153	0.00148	0.00342	0.00387
% of Total AOX	0.26	0.30	0.52	0.56	0.77	0.70
Cl/C_{100}	5.08	2.83	0.94	1.09	1.48	2.24

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0671	0.0676	0.0511	0.0480	0.0685	0.137
% of Total TOC	0.68	0.58	0.76	0.74	0.44	0.92
AOX, kg/t	0.00520	0.00513	0.00129	0.000701	0.00275	0.00495
% of Total AOX	0.71	0.58	1.38	0.75	0.85	1.62
Cl/C_{100}	2.62	2.56	0.85	0.49	1.36	1.22

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.106	0.143	0.106	0.0937	0.147	0.195
% of Total TOC	0.63	0.72	0.95	0.87	0.63	0.85
AOX, kg/t	0.0111	0.0114	0.00282	0.00218	0.00617	0.00882
% of Total AOX	0.37	0.38	0.72	0.61	0.80	1.03
Cl/C_{100}	3.54	2.69	0.90	0.79	1.42	1.53

Table VII. Acid Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.450	0.548	0.316	0.242	0.432	0.361
% of Total TOC	6.40	6.71	7.13	5.64	5.49	4.50
AOX, kg/t	0.456	0.430	0.0511	0.0369	0.0561	0.0535
% of Total AOX	20.2	20.2	17.2	14.0	12.6	9.71
Cl/C_{100}	34.2	26.5	5.46	5.15	4.39	5.00

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.02	1.05	0.304	0.321	0.526	0.491
% of Total TOC	10.4	9.05	4.54	4.92	3.37	3.30
AOX, kg/t	0.140	0.135	0.00856	0.00827	0.0192	0.0214
% of Total AOX	19.0	15.2	9.13	8.89	5.93	6.99
Cl/C_{100}	4.67	4.37	0.95	0.87	1.24	1.47

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.47	1.60	0.620	0.563	0.958	0.852
% of Total TOC	8.72	8.09	5.57	5.21	4.08	3.72
AOX, kg/t	0.596	0.565	0.0597	0.0452	0.0753	0.0749
% of Total AOX	19.9	18.7	15.3	12.7	9.77	8.74
Cl/C_{100}	13.7	11.9	3.25	2.71	2.66	2.97

Table VIII. Polar Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.533	0.220	0.226	0.248	0.829	0.719
% of Total TOC	7.58	2.69	5.10	5.78	10.5	8.97
AOX, kg/t	0.0632	0.0479	0.0445	0.0502	0.0882	0.0705
% of Total AOX	2.80	2.25	15.0	19.0	19.7	12.8
Cl/C_{100}	4.00	7.35	6.67	6.85	3.60	3.31

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.05	0.711	0.399	0.395	0.858	0.739
% of Total TOC	10.7	6.13	5.96	6.06	5.50	4.96
AOX, kg/t	0.0288	0.0325	0.00333	0.00280	0.0124	0.0136
% of Total AOX	3.90	3.66	3.55	3.01	3.83	4.44
Cl/C_{100}	0.93	1.55	0.28	0.24	0.49	0.62

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.58	0.931	0.625	0.643	1.69	1.46
% of Total TOC	9.39	4.71	5.62	5.95	7.19	6.36
AOX, kg/t	0.0920	0.0804	0.0478	0.0530	0.101	0.0841
% of Total AOX	3.07	2.66	12.2	14.8	13.1	9.81
Cl/C_{100}	1.97	2.92	2.59	2.79	2.02	1.95

Table IX. Hydrophilic Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	4.80	6.50	3.43	3.69	5.41	6.05
% of Total TOC	68.3	79.6	77.4	86.0	68.7	75.4
AOX, kg/t	1.34	1.37	0.144	0.160	0.278	0.333
% of Total AOX	59.3	64.3	48.5	60.6	62.2	60.4
Cl/C_{100}	9.52	7.09	1.42	1.47	1.74	1.86

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	6.67	8.88	5.50	5.45	13.4	12.7
% of Total TOC	67.9	76.6	82.1	83.6	85.9	85.2
AOX, kg/t	0.531	0.594	0.0728	0.0745	0.276	0.252
% of Total AOX	72.0	67.0	77.6	80.1	85.2	82.4
Cl/C_{100}	2.69	2.26	0.45	0.46	0.69	0.67

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	11.5	15.4	8.93	9.14	18.8	18.8
% of Total TOC	68.0	77.8	80.2	84.6	80.1	81.8
AOX, kg/t	1.87	1.96	0.217	0.235	0.554	0.585
% of Total AOX	62.3	64.9	55.5	65.8	71.9	68.3
Cl/C_{100}	5.51	4.31	0.82	0.87	1.00	1.05

Table X. Volatile Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.11	0.700	0.380	0.396	1.07	0.785
% of Total TOC	15.8	8.57	8.58	9.23	13.6	9.79
AOX, kg/t	0.301	0.186	0.0533	0.0136	0.0141	0.0846
% of Total AOX	13.3	8.73	17.9	5.15	3.15	15.4
Cl/C_{100}	9.17	8.93	4.74	1.16	0.45	3.65

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.935	0.797	0.405	0.271	0.653	0.706
% of Total TOC	9.51	6.87	6.04	4.16	4.19	4.74
AOX, kg/t	0.0108	0.110	0.00539	0.00490	0.00661	0.00637
% of Total AOX	1.46	12.4	5.75	5.27	2.04	2.08
Cl/C_{100}	0.39	4.65	0.45	0.61	0.34	0.30

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	2.05	1.50	0.785	0.667	1.72	1.49
% of Total TOC	12.2	7.59	7.05	6.17	7.33	6.50
AOX, kg/t	0.312	0.296	0.0587	0.0185	0.0207	0.0910
% of Total AOX	10.4	9.80	15.0	5.18	2.68	10.6
Cl/C_{100}	5.14	6.67	2.53	0.94	0.41	2.06

THE EFFECT OF D STAGE PH ON EFFLUENT QUALITY: CHARACTERIZATION OF EFFLUENT FRACTIONS FROM OD(EO) BLEACHING OF SOFTWOOD KRAFT PULP

T. A. Schwantes
Graduate Student
Institute of Paper Science and Technology
Atlanta, GA

T. J. McDonough
Professor of Engineering
Institute of Paper Science and Technology
Atlanta, GA

ABSTRACT

Effluents from OD(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions. The effluents from the sequence with the D stage begun at pH 2 (D-2 bleaching) were compared to the same sequence with the D stage begun at pH 4 (D-4 bleaching). Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from both stages. Each fraction was characterized in terms of its ratio of chlorine to carbon (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of the proportion of total TOC within each fraction. The Cl/C_{100} is a likely predictor of environmental effects caused by certain effluent fractions.

The D-4 bleaching resulted in a reduced kappa number in the extracted pulp compared to the D-2 case. This is consistent with the whole effluent TOC data, in which D-4 bleaching produced more D stage TOC than the D-2. The (EO) stage TOC remained constant. The chlorine-to-carbon ratio decreased for each effluent type when D-4 bleaching was done.

The ether extractable material and the phenolic fraction, which both contain compounds of environmental interest, exhibited reduced Cl/C_{100} values when D-4 bleaching was done. Since the percentage of total TOC within these fractions increased, overall AOX levels were nearly constant, however. Because of the greater delignification at D-4 conditions, environmental and economic benefits may be realized by a reduction of the applied ClO_2 charge.

INTRODUCTION

It is generally accepted that bleaching at a pH of 2 or less results in greater delignification effectiveness for chlorine bleaching (1), for mixtures of chlorine and chlorine dioxide (2), and for chlorine dioxide alone (2, 3, 4, 5). However, an initial pH above 2 may be more effective in some cases (2, 3, 6).

The pH of a chlorination stage also has an effect on the quality of the effluent produced in the stage. The rates of formation of both chlorinated dioxins (7, 8) and chlorinated phenolic compounds (9, 10) are reduced by increased C stage pH. Total AOX is reduced at increased pH for both chlorine and chlorine dioxide bleaching (2).

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (11-15) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (9, 10, 15-21), chlorinated dioxins (7, 8, 18), chlorinated neutral compounds (21-23), chlorinated carboxylic acids (21, 24), and chloroform (17, 25).

Because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of their likely environmental effects. An alternative is summative analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents produced by D(EO), OD(EO), and OC(EO) sequences (26). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental standpoint are found in the extracts. Chlorine-to-carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may predict environmental behavior, were determined for the fractions. The same fractionation and characterization methods were used for the present study of the effects of D stage initial pH in OD(EO) bleaching of softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by an OD(EO) sequence in the laboratory. Only the first two stages of bleaching were done, since most of the delignification and most of the effluent load production occurs in these stages. The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. The pH of the pulp slurry was adjusted to an initial level of 2 or 4 by the addition of sulfuric acid solution. Kappa numbers after bleaching are given in Table I.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction, and the ether extractable material was further separated into acidic, phenolic, and neutral fractions. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction and two ether extractable fractions. The first ether fraction is material readily extracted, and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The D-2 and D-4 bleaching sequences were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. The data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme, and were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

The data for individual fractions were interpreted principally in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between pH levels and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between pH levels, a least significant difference was determined using Duncan's multiple range test (27).

RESULTS AND DISCUSSION

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-7.0 kg/t TOC and 0.1-0.4 kg/t AOX, depending on the stage and initial D stage pH.

Figure 2 compares mean effluent TOC from OD(EO) bleaching with the D stage begun at pH 4 (D-4 bleaching) and from the same sequence with the D stage begun at pH 2 (D-2 bleaching). In the D stage, and overall, the D-4 case results in the production of more effluent TOC. There is no increased TOC production in the (EO) stage following D-4 bleaching. A reduced kappa number is observed for the pulp from D-4 bleaching and could correspond to the higher level of TOC in the D stage effluent. The delignification of the pulp is discussed later in more detail.

Figure 3 presents a comparison of mean Cl/C_{100} for the whole effluents. Both the D and (EO) stage effluents individually have a greater Cl/C_{100} when D-2 bleaching is done. No overall difference is seen, however.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-0.7 kg/t TOC, representing 6-12% of the total TOC, and 0.01-0.08 kg/t AOX, representing 14-23% of the total AOX.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for both pH levels. The mean TOC produced by D-4 bleaching is greater for each stage. Although the difference is not great enough to be statistically significant when all data are used, when the calculated value (see Table IV) is not included in the analysis, the difference is significant. This calculated value was eliminated from analysis because it is likely to contain greater error than measured values. It was determined from several measured values, each with individual errors.

Figure 5 similarly compares both pH levels with respect to Cl/C_{100}. The ether soluble fraction is chlorinated to a larger extent in both the D and (EO) stages when D-2 bleaching is done.

The reduced level of substitution by chlorine on organic material could be the result of a shift in chlorine containing species at pH 4 versus pH 2. Kolar and co-workers (28) reported that the sum of Cl_2 and HOCl during ClO_2 bleaching at pH 4.5 was reduced compared with similar bleaching at pH 2.5. Since Cl_2 and HOCl are responsible for chlorine substitution reactions (29, 30), an overall reduction in the level of these species would result in less substitution by chlorine atoms on organics in the effluent.

In addition to a reduction in the sum of Cl_2 and HOCl concentrations, a change in their ratio will occur. The $Cl_2/HOCl$ equilibrium is such that HOCl is more favored as pH increases.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

As acidity decreases, the equilibrium shifts to the right and to HOCl. Therefore, at pH 4 a greater proportion of the total chlorine exists as HOCl than at pH 2. Since HOCl is a less reactive chlorinating species (31), a reduced degree of chlorine substitution is expected at pH 4.

It is reasonable that a change in substitution behavior with pH will be more clearly seen in the ether soluble fractions. Chlorine substitutes to a greater extent on ether extractable material than on whole effluents (26). Therefore, these fractions are probably more sensitive to changes in substitution behavior than the whole effluents.

Since there is more ether soluble material formed by D-4 bleaching and that material is chlorinated to a reduced extent, the overall AOX remains essentially constant under both sets of conditions. This trend is repeated in other ether extractable fractions as well. This is consistent with the decreased tendency of ClO_2 to be involved in substitution of chlorine atoms at pH 4 and with the increased lignin fragmentation seen at pH 4, as indicated by the reduced kappa number achieved at constant chemical charge. Increased lignin fragmentation could be responsible for a greater proportion of material in the ether soluble fractions.

Phenolic Fraction

Detailed results of the analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.05 kg/t TOC or 0.5-0.7% of the total TOC, and 0.002-0.003 kg/t AOX or 0.8-2.6% of the total AOX.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the two pH levels. In both the D and (EO) effluents, the phenolic fraction represents a higher percentage of the total TOC when the D stage is conducted at pH 4. Figure 7 shows the effect of pH on Cl/C_{100}. A decreased phenolic Cl/C_{100} is seen in the D-4 case.

Other Fractions

Data from the other effluent fractions displayed no statistically significant pH effects. This was generally due to small differences in means and scatter in the replicate data. Data and graphs for these fractions are provided so that the characterization is complete, and so that trends in the data may be observed. Replicate data for the neutral, acid, polar, hydrophilic, and the volatile fractions are provided in Tables VI-X. The corresponding graphs of the mean data are given in Figures 8-17.

It is interesting to note, that despite the lack of statistical significance, the other ether soluble fractions often maintain the trend observed with the ether soluble and phenolic fractions. On the average, the neutral, acid, and polar fractions all appear to contain a larger proportion of the total TOC when bleaching is conducted at pH 4, while the overall mean Cl/C_{100} is lower under D-4 conditions for the acid and polar fractions. Since a larger percentage of the material is extracted from effluents produced with D-4 bleaching, it is expected that the mean proportion of non-extractable TOC should be lower under D-4 conditions (Figure 14), as is the case.

Degree of Delignification

The D stage effluent contains more TOC when the D stage is conducted at an initial pH of 4. The kappa number of the extracted pulp is reduced to 3.7 under D-4 conditions compared with 4.3 under D-2 conditions. The D+(EO) stage TOC, the kappa numbers, the change in pulp kappa number, and the ratio of TOC to kappa change are all given in Table I for the two pH levels. In an earlier study (26), it was stated that increased TOC per unit kappa loss may imply greater carbohydrate loss. Although the D stage begun at pH 4 appears to give slightly increased TOC per unit kappa loss, the apparent difference is not statistically significant.

In D-4 bleaching more delignification or kappa reduction can be done because less of the oxidizing power of ClO_2 may be wasted on other reaction types such as chlorine substitution reactions and chlorate (ClO_3^-) formation. A reaction byproduct of the oxidation of lignin by ClO_2 is chlorite ion (ClO_2^-) which may form chlorate or chlorine dioxide, depending on conditions, by the following reaction scheme (32, 33):

$$Cl_2 + ClO_2^- \longrightarrow Cl^- + [Cl_2O_2] \quad (1)$$

$$HOCl + ClO_2^- \longrightarrow OH^- + [Cl_2O_2] \quad (2)$$

$$[Cl_2O_2] \longrightarrow Cl^- + ClO_3^- \quad (3)$$

$$2[Cl_2O_2] \longrightarrow Cl_2 + 2ClO_2 \quad (4)$$

A high concentration of the reactive intermediate $[Cl_2O_2]$ favors the formation of ClO_2 by reaction 4 (second order in $[Cl_2O_2]$). Since chlorite ion is present in higher concentrations during pulp bleaching at pH 4 compared to pH 2 (28), reactions 1 and 2 (both first order in ClO_2^-) will produce increased levels of $[Cl_2O_2]$ at pH 4 and therefore more ClO_2 will be produced by reaction 4.

EXPERIMENTAL METHODS

Pulp Bleaching

A mill-produced, 14.1 kappa O_2-delignified southern softwood kraft pulp was used in this study. The pulp was collected just after the O_2 stage and was well washed before bleaching.

D Stages.

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH was adjusted to 2 or 4 by the addition of sulfuric acid solution.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and 4.1% of the total D stage filtrate was included as carryover. The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess sodium sulfite, and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts were collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M

NaOH, and these extracts were also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction; and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (34). In this case samples were shaken for 4 hours rather 1 hour, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

An oxygen-bleached softwood kraft pulp was delignified to a greater extent by the OD(EO) sequence when the D stage was run at an initial pH of 4 compared to an initial pH of 2. D-4 bleaching resulted in a greater percentage of the total TOC within the environmentally significant ether soluble and phenolic fractions. However, the material within these fractions was substituted by chlorine atoms to a reduced extent under D-4 conditions. The net result was similar amounts of AOX at both pH levels.

Since D-4 bleaching causes increased D stage delignification, an equivalent amount of delignification can be done with less applied chemical, and an economic gain achieved. A reduced ClO_2 charge will result in less effluent AOX. Reducing the charge may also reduce the extent of lignin fragmentation and may reduce the proportion of material within the ether soluble fractions. If this proportion were reduced, the lower Cl/C_{100} values observed under D-4 conditions would represent a clear environmental advantage.

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. 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.

LITERATURE CITED

1. Russell, N. A., *Tappi*, "The Initial Phase of the Aqueous Chlorination of Kraft Pulp Meals," 49(9): 418 (1966).

2. Bradbury, J. E., Master's Thesis, "Identification and Optimization of Process Variables in the Chlorination Stage," North Carolina State University, Raleigh, 1990.

3. Waartiovaara, I., *Paperi ja Puu*, "The Influence of pH on the D Stages of DE and ODE Bleaching Sequences," 1982(10): 581.

4. Reeve, D. W., Weishar, K. M., *1990 TAPPI Pulping Conference Proceedings*, "Chlorine Dioxide Delignification - Process Variables," pp. 837-841.

5. Liebergott, N., CPPA Bleaching Committee Meeting, "The Effect of the Process Variables in D_{100} Delignification," Columbus, MS, March 1991.

6. Allison, R. W., Wrathall, S. H., *Appita*, "Chlorine Dioxide Prebleaching of Radiata Pine Kraft-Oxygen Pulp," 45(5): 336 (1992).

7. Hise, R. G., *1990 TAPPI Environmental Conference Proceedings*, "Split Addition of Chlorine/pH Control for Reducing Formation of Dioxins," pp. 395-401.

8. Berry, R. M., Fleming, B. I., Voss, R. H., Luthe, C. E., Wrist, P. E., *Pulp and Paper Canada*, "Toward Preventing the Formation of Dioxins

During Chemical Pulp Bleaching," 90(8): T279 (1989).

9. Voss, R. H., Wearing, J. T., Mortimer, R. D., Kovacs, T., Wong, A., *Paperi ja Puu*, "Chlorinated Organics in Kraft Bleaching Effluents," 12(1980): 809.

10. Voss, R. H., Wearing, J. T., Wong, A., *Pulp and Paper Canada*, "The Effect of Softwood Chlorination Conditions on the Formation of Toxic Chlorinated Compounds," 82(2): T65 (1981).

11. Germgard, U., Karlsson, R., Kringstad, K., de Sousa, F., Stromberg, L., *Svensk Papperstidning*, "Oxygen Bleaching and Its Impact on Some Environmental Parameters," 88(12): R113 (1985).

12. Sjoblom, K., Hartler, N., Mjoberg, J., Sjodin, L., *Tappi*, "A New Technique for Pulping to Low Kappa Numbers in Batch Pulping: Results of Mill Trials," 66(9): 97 (1983).

13. Liebergott, N., Van Lierop, B., Nolin, A., Faubert, M., Laflamme, J., *1990 CPPA Technical Section Annual Meeting Proceedings*, "Modifying the Bleaching Process to Decrease AOX Formation," pp. B229-B238.

14. Earl, P., Reeve, D., *1989 TAPPI Environmental Conference Proceedings*, "Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part III: The Effect of Chlorintaion Stage Variables on Chlorinated Organic Matter in Effluent," pp. 385-391.

15. Axegard, P., *Tappi*, "Substituting Chlorine Dioxide for Elemental Chlorine Makes the Bleach Plant Effluent Less Toxic," 69(10): 54 (1986).

16. Earl, P., Reeve, D., *1989 TAPPI Pulping Conference Proceedings*, "Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part VI: Chlorinated Compounds in Effluents," pp. 31-37.

17. Axegard, P., *1988 International Pulp Bleaching Conference Proceedings*, "Improvement of Bleach Plant Effluent by Cutting Back on Cl_2," pp. 69-76.

18. Berry, R. M., Luthe, C. E., Voss, R. H., Wrist, P. E., Axegard, P., Gellerstedt, G., Linblad, P. O., Popke, I., *Pulp and Paper Canada*, "The Effects of Recent Changes in Bleached Softwood Kraft Mill Technology on Organochlorine Emissions: An International Perspective," 92(6): T155 (1991).

19. Lindstrom, K., Nordin, J., *Journal of Chromatography*, "Gas Chromatography-Mass Spectrometry of Chlorophenols in Spent Bleach Liquors," 128(1976): 13.

20. Gergov, M., Priha, M., Talka, E., Valltila, O., *1988 TAPPI Environmental Conference Proceedings*, "Chlorinated Organic Compounds in Effluent Treatment at Kraft Mills," pp. 443-455.

21. O' Connor, B. I., Kovacs, T. G., Voss, R. H., Martel, P. H., van Lierop, B., *EUCEPA International Environmental Symposium Proceedings*, "A Laboratory Assessment of the Environmental Quality of Alternative Pulp Bleaching Effluents," April 1993.

22. Kringstad, K. P., Ljungquist, P. O., de Sousa, F., Stromberg, L. M., *Environmental Science and Technology*, "Identification and Mutagenic Properties of Some Chlorinated Aliphatic Compounds in the Spent Liquor From Kraft Pulp Chlorination," 15(5): 562 (1981).

23. Lindstrom, K., Nordin, J., *Svensk Papperstidning*, "Identification of Some Neutral Chlorinated Organic Compounds in Spent Bleach Liquors," 82(2): 55 (1978).

24. Lindstrom, K., Osterberg, F., *Environmental Science and Technology*, "Chlorinated Carboxylic Acids in Softwood Kraft Pulp Spent Bleach Liquors," 20(2): 133 (1986).

25. Dallons, V. J., Crawford, R. J., *1990 TAPPI Pulping Conference Proceedings*, "Chloroform Formation in Bleaching," pp. 195-201.

26. Schwantes, T. A., McDonough, T. J., *1993 TAPPI Pulping Conference Proceedings*, "Characterization of Effluent Fractions From ClO_2 and Cl_2 Bleaching of Unbleached and O_2 Bleached Softwood Kraft Pulps."

27. Harter, H. L., *Biometrics*, "Critical Values for Duncan's New Multiple Range Test," 16(4): 671 (1960).

28. Kolar, J. J., Lindgren, B. O., Pettersson, B., *Wood Science and Technology*, "Chemical Reactions in Chlorine Dioxide Stages of Pulp Bleaching," 17(1983): 117.

29. Gierer, J., *Holzforschung*, "The Chemistry of Delignification, Part II: Reactions of Lignins During Bleaching," 36(2): 55 (1982).

30. Gierer, J., *Holzforschung*, "Basic Principles of Bleaching, Part 1: Cationic and Radical Processes," 44(5): 387 (1990).

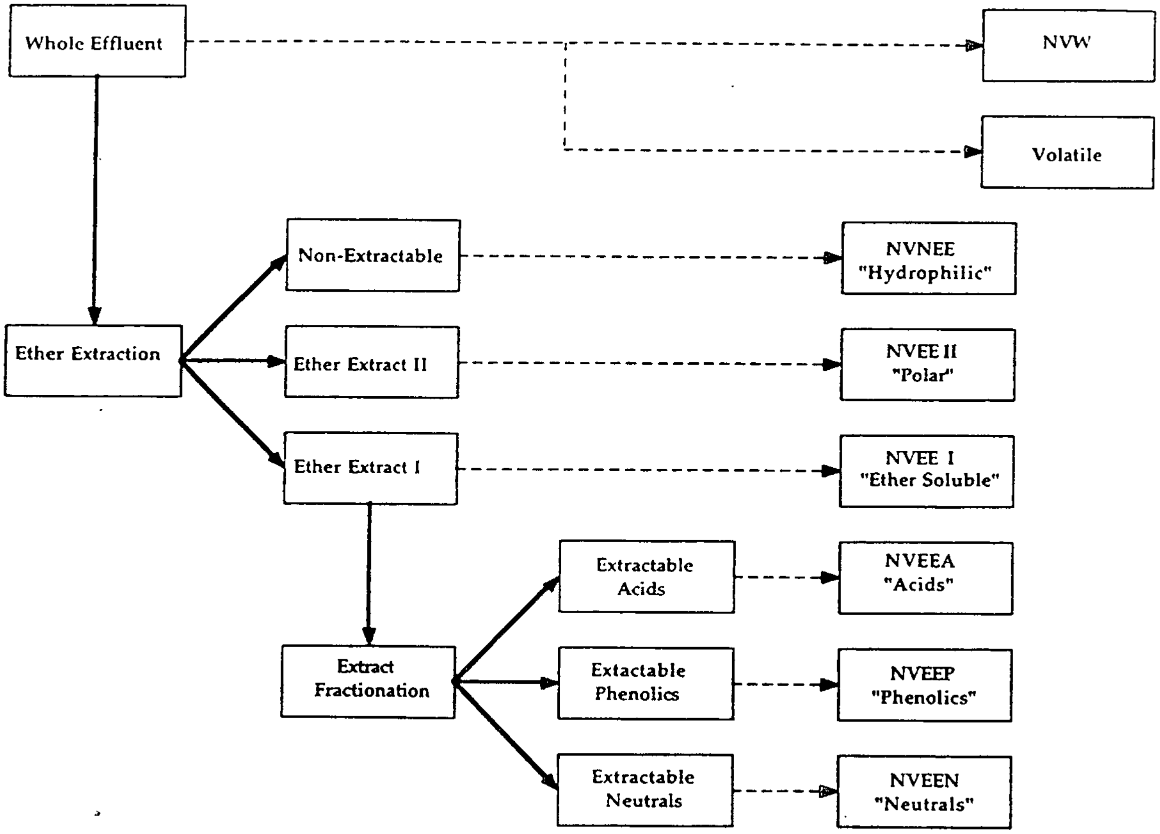
31. Swain, C. G., Crist, D. R., *Journal of the American Chemical Society*, "Mechanisms of Chlorination by Hypochlorous Acid. The Last of the Chloronium Ion, Cl^{+1}," 94(9): 3195 (1972).

32. Emmenegger, F., Gordon, G., *Inorganic Chemistry*, "The Rapid Interaction Between Sodium Chlorite and Dissolved Chlorine," 6(3): 633 (1967).

33. Ni, Y., Van Heiningen, A. R. P., *1992 CPPA Technical Section Annual Meeting Proceedings*, "Mechanism of Chlorate Formation During Bleaching of Kraft Pulp With Chlorine Dioxide," pp. A403-A409.

34. Scandinavian Pulp, Paper, and Board Testing Committee, "Effluents From Pulp Mills, Organically Bound Chlorine by the AOX Method," SCAN-W 9:89.

Figure 1. Effluent Fractionation.



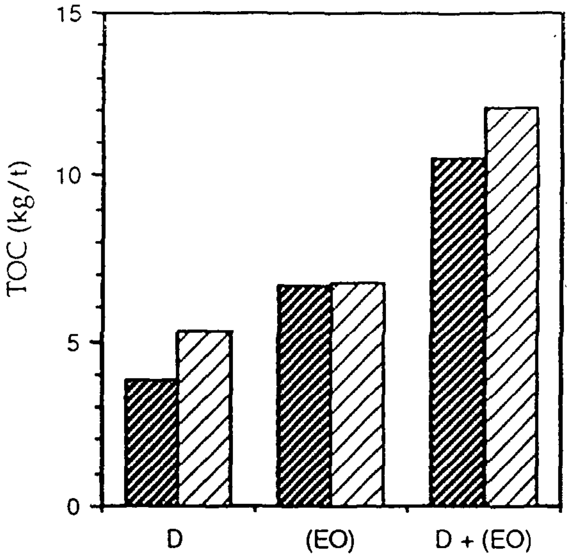


Figure 2. Whole effluent TOC.

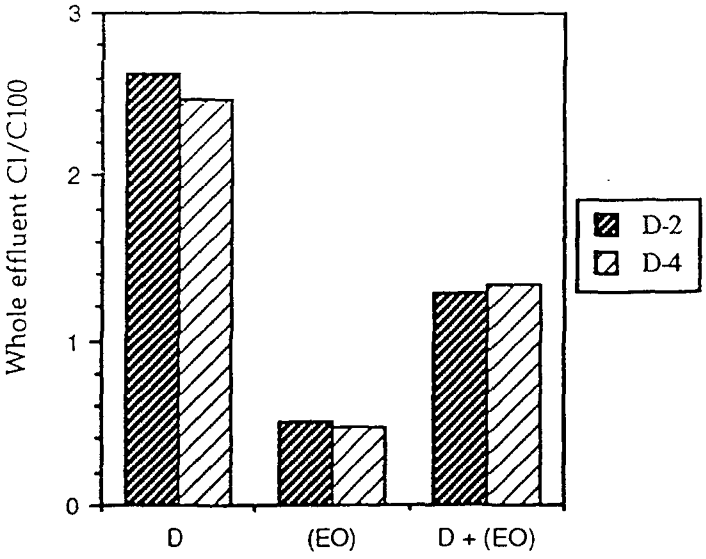


Figure 3. Whole effluent Cl/C100.

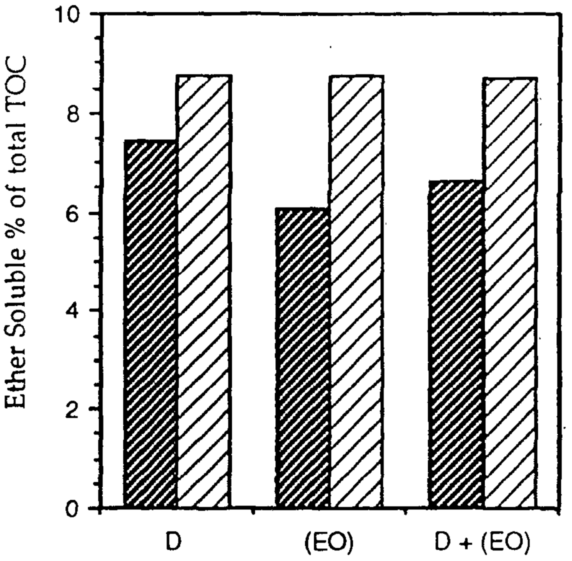


Figure 4. Ether Soluble % of total TOC.

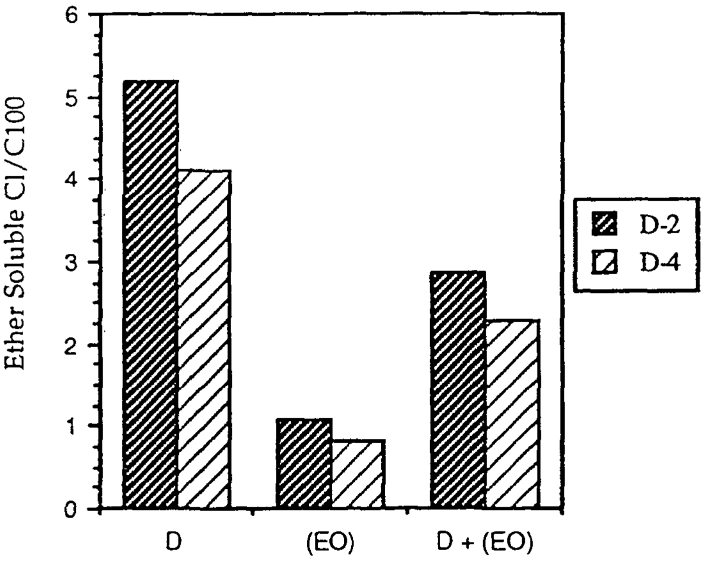


Figure 5. Ether Soluble Cl/C100.

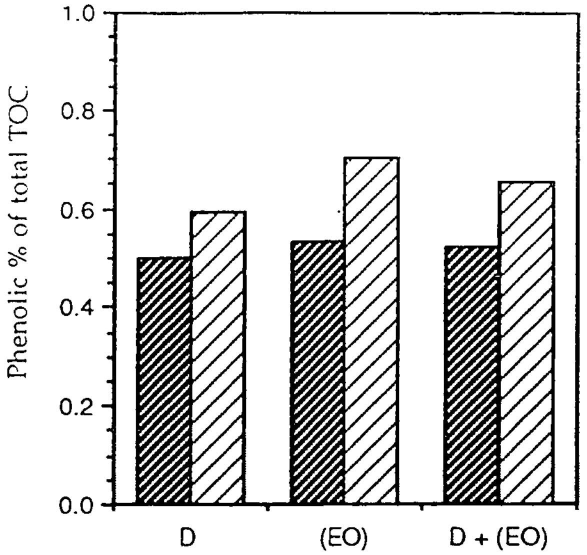


Figure 6. Phenolic % of total TOC.

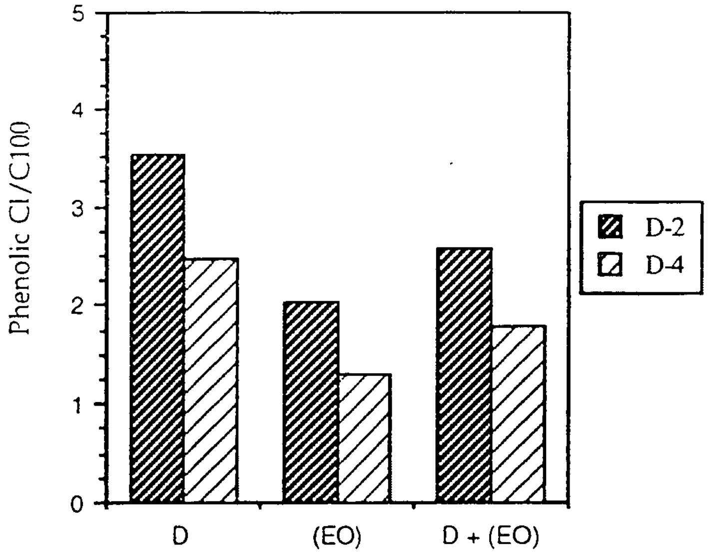


Figure 7. Phenolic Cl/C100.

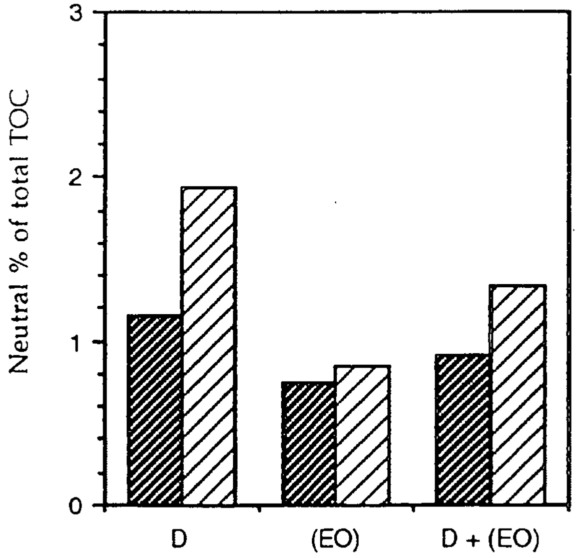


Figure 8. Neutral % of total TOC.

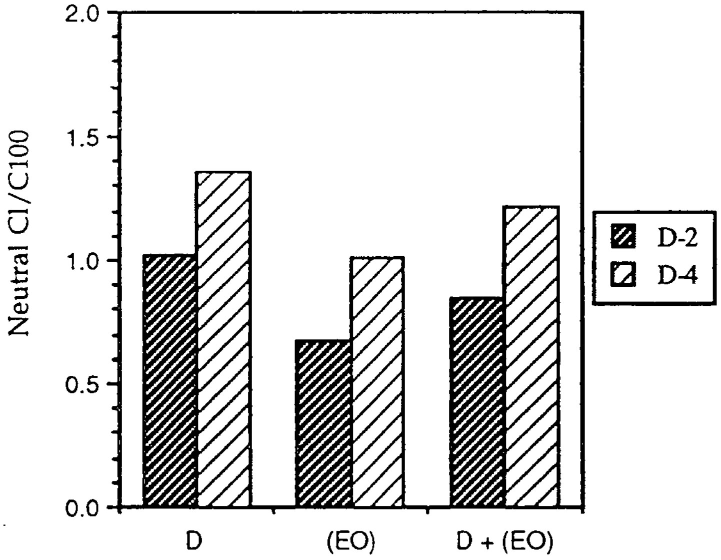


Figure 9. Neutral Cl/C100.

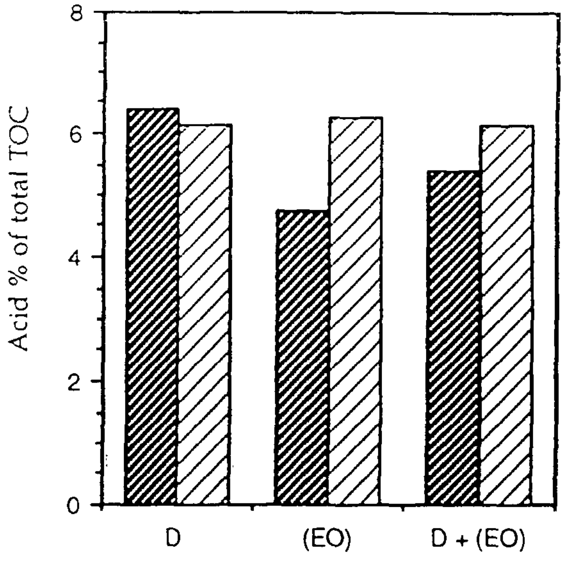


Figure 10. Acid % of total TOC.

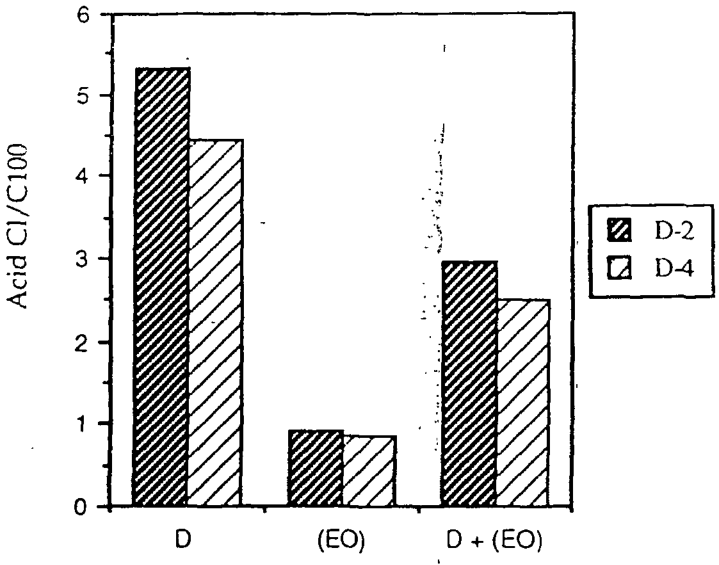


Figure 11. Acid Cl/C100.

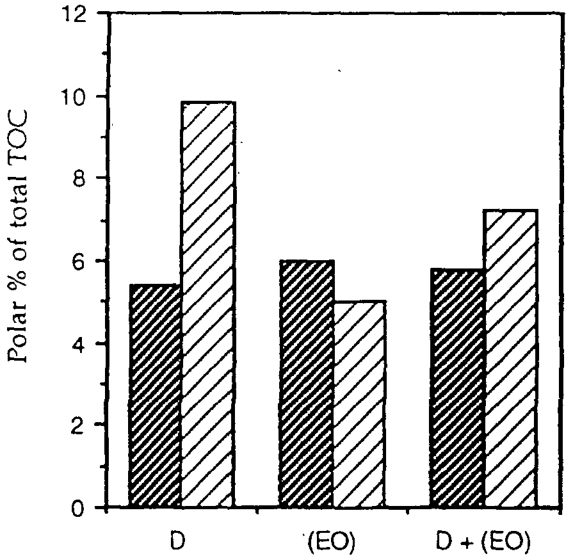


Figure 12. Polar % of total TOC.

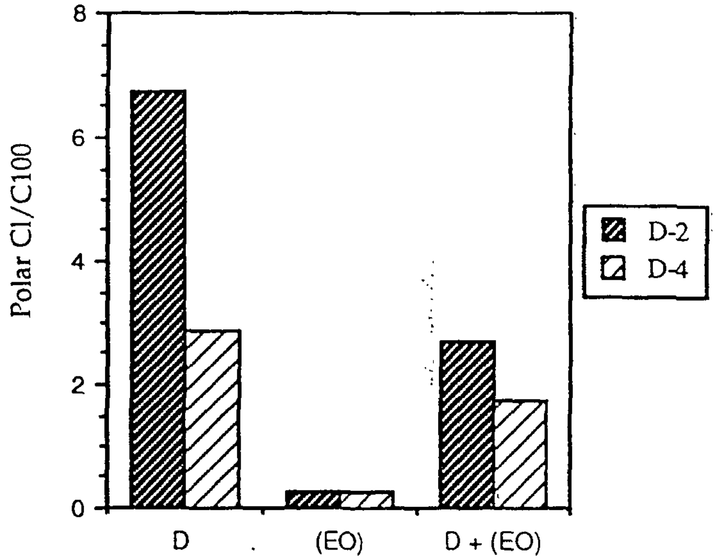


Figure 13. Polar Cl/C100.

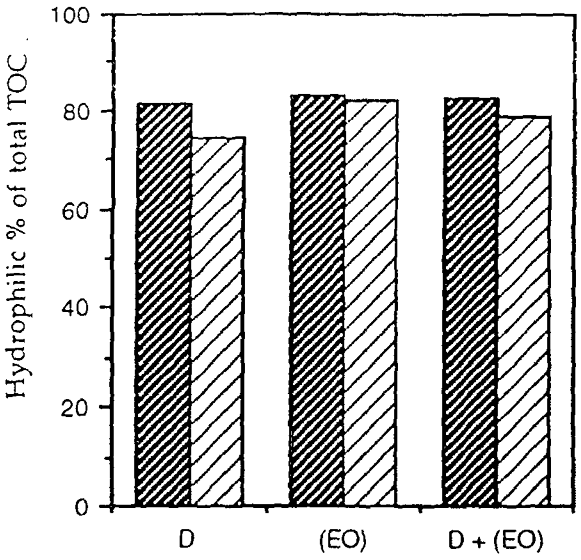


Figure 14. Hydrophilic % of total TOC.

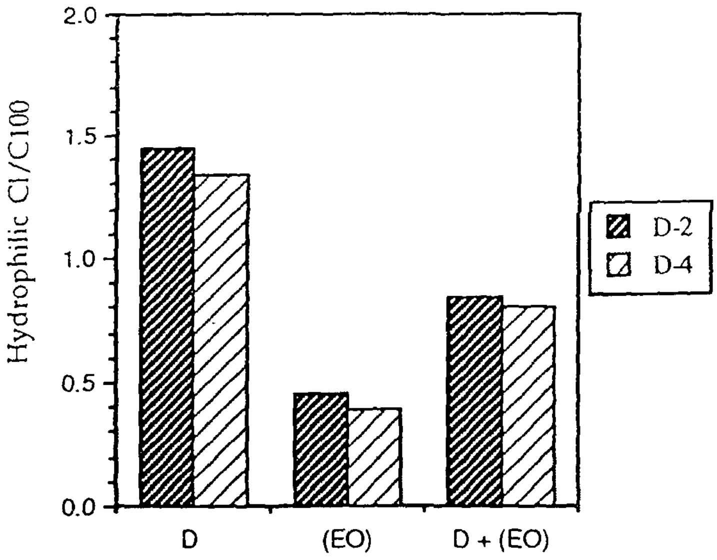


Figure 15. Hydrophilic Cl/C100.

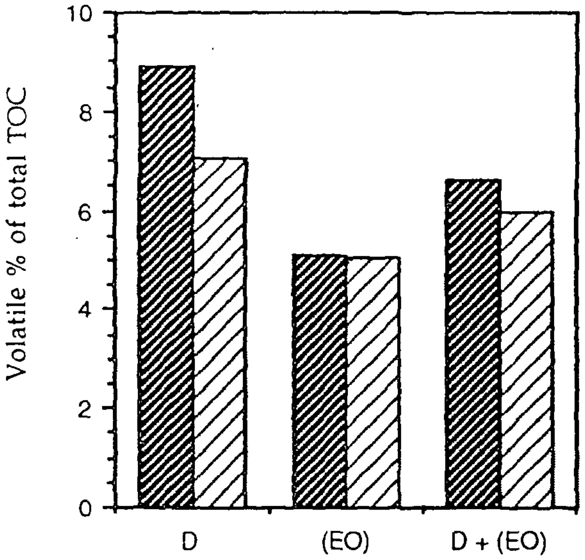


Figure 16. Volatile % of total TOC.

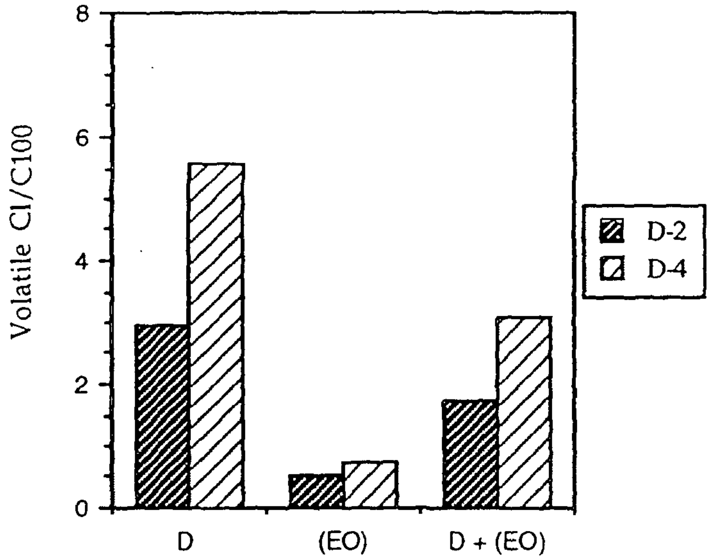


Figure 17. Volatile Cl/C100.

Table I. D+(EO) TOC and Kappa Number Data for OD(EO) Sequence.

D Stage Type	D + (EO) TOC (kg/t)	Kappa Number	Δ kappa	TOC/Δ kappa
D-2	10.6	4.23	9.87	1.07
D-2	10.4	4.44	9.66	1.08
D-4	12.4	3.70	10.40	1.19
D-4	11.7	3.71	10.39	1.13

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	**Description**
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent and Summed Fraction Characteristics.

D Stage	pH 2		pH 4	
TOC, kg/t	3.85	3.80	5.37	5.17
Total TOC[a], kg/t	4.43	4.29	5.55	6.64
AOX, kg/t	0.299	0.294	0.381	0.386
Total AOX[a], kg/t	0.297	0.264	0.337	0.336
Cl/C_{100}	2.63	2.61	2.40	2.53
(EO) Stage				
TOC, kg/t	6.79	6.60	7.01	6.54
Total TOC[a], kg/t	6.70	6.52	6.99	7.60
AOX, kg/t	0.101	0.102	0.0943	0.0929
Total AOX[a], kg/t	0.0938	0.0930	0.0983	0.0877
Cl/C_{100}	0.50	0.52	0.45	0.48
D Stage + (EO) Stage				
TOC, kg/t	10.6	10.4	12.38	11.71
Total TOC[a], kg/t	11.1	10.8	12.54	14.24
AOX, kg/t	0.400	0.396	0.475	0.479
Total AOX[a], kg/t	0.391	0.357	0.435	0.424
Cl/C_{100}	1.27	1.29	1.30	1.38

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[a] Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

Table IV. Ether Soluble Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.383	0.267	0.643	0.388[a]
% of total TOC	8.65	6.22	11.6	5.85[a]
AOX, kg/t	0.0547	0.0439	0.0773	0.0474
% of total AOX	18.4	16.6	22.9	14.1
Cl/C_{100}	4.83	5.56	4.07	4.13[a]
(EO) Stage				
TOC, kg/t	0.406	0.399	0.532	0.748
% of total TOC	6.06	6.12	7.61	9.84
AOX, kg/t	0.0127	0.0125	0.0150	0.0154
% of total AOX	13.5	13.4	15.3	17.6
Cl/C_{100}	1.06	1.06	0.95	0.69
D Stage + (EO) Stage				
TOC, kg/t	0.789	0.666	1.175	1.136[a]
% of total TOC	7.09	6.16	9.37	7.98[a]
AOX, kg/t	0.0674	0.0564	0.0923	0.0628
% of total AOX	17.2	15.8	21.2	14.8
Cl/C_{100}	2.89	2.86	2.66	1.87[a]

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[a] Determined from TOC balances. Sample was contaminated during evaporation.

Table V. Phenolic Fraction.

	pH 2		pH 4	
D Stage				
TOC, kg/t	0.0239	0.0198	0.0325	0.0389
% of total TOC	0.54	0.46	0.59	0.59
AOX, kg/t	0.00255	0.00201	0.00273	0.00239
% of total AOX	0.86	0.76	0.81	0.71
Cl/C_{100}	3.60	3.45	2.84	2.07
(EO) Stage				
TOC, kg/t	0.0364	0.0341	0.0513	0.0502
% of total TOC	0.54	0.52	0.73	0.66
AOX, kg/t	0.00243	0.00180	0.00216	0.00177
% of total AOX	2.59	1.94	2.20	2.02
Cl/C_{100}	2.26	1.79	1.42	1.19
D Stage + (EO) Stage				
TOC, kg/t	0.0603	0.0539	0.0838	0.0891
% of total TOC	0.54	0.50	0.67	0.63
AOX, kg/t	0.00498	0.00381	0.00489	0.00416
% of total AOX	1.27	1.07	1.12	0.98
Cl/C_{100}	2.79	2.39	1.97	1.58

Table VI. Neutral Fraction.

	pH 2		pH 4	
D Stage				
TOC, kg/t	0.0551	0.0457	0.175	0.0483
% of total TOC	1.24	1.07	3.15	0.73
AOX, kg/t	0.00153	0.00148	0.00350	0.00290
% of total AOX	0.52	0.56	1.04	0.86
Cl/C_{100}	0.94	1.09	0.68	2.03
(EO) Stage				
TOC, kg/t	0.0511	0.0480	0.0885	0.0313
% of total TOC	0.76	0.74	1.27	0.41
AOX, kg/t	0.00129	0.000701	0.00202	0.00114
% of total AOX	1.38	0.75	2.05	1.30
Cl/C_{100}	0.85	0.49	0.78	1.23
D Stage + (EO) Stage				
TOC, kg/t	0.106	0.0937	0.264	0.0796
% of total TOC	0.95	0.87	2.10	0.56
AOX, kg/t	0.00282	0.00218	0.00552	0.00404
% of total AOX	0.72	0.61	1.27	0.95
Cl/C_{100}	0.90	0.79	0.71	1.72

Table VII. Acid Fraction.

	pH 2		pH 4	
D Stage				
TOC, kg/t	0.316	0.242	0.428	0.301
% of total TOC	7.13	5.64	7.71	4.53
AOX, kg/t	0.0511	0.0369	0.0627	0.0350
% of total AOX	17.2	14.0	18.6	10.4
Cl/C_{100}	5.46	5.15	4.95	3.92
(EO) Stage				
TOC, kg/t	0.304	0.321	0.340	0.578
% of total TOC	4.54	4.92	4.86	7.61
AOX, kg/t	0.00856	0.00827	0.0105	0.0115
% of total AOX	9.13	8.89	10.7	13.1
Cl/C_{100}	0.95	0.87	1.04	0.67
D Stage + (EO) Stage				
TOC, kg/t	0.620	0.563	0.768	0.879
% of total TOC	5.57	5.21	6.12	6.17
AOX, kg/t	0.0597	0.0452	0.0732	0.0465
% of total AOX	15.3	12.7	16.8	11.0
Cl/C_{100}	3.25	2.71	3.22	1.79

Table VIII. Polar Fraction.

	pH 2		pH 4	
D Stage				
TOC, kg/t	0.226	0.248	0.386	0.848
% of total TOC	5.10	5.78	6.95	12.8
AOX, kg/t	0.0445	0.0502	0.0498	0.0336
% of total AOX	15.0	19.0	14.8	10.0
Cl/C_{100}	6.67	6.85	4.37	1.34
(EO) Stage				
TOC, kg/t	0.399	0.395	0.316	0.424
% of total TOC	5.96	6.06	4.52	5.58
AOX, kg/t	0.00333	0.00280	0.00269	0.00226
% of total AOX	3.55	3.01	2.74	2.58
Cl/C_{100}	0.28	0.24	0.29	0.18
D Stage + (EO) Stage				
TOC, kg/t	0.625	0.643	0.702	1.272
% of total TOC	5.62	5.95	5.60	8.93
AOX, kg/t	0.0478	0.0530	0.0525	0.0359
% of total AOX	12.2	14.8	12.1	8.46
Cl/C_{100}	2.59	2.79	2.53	0.95

Table IX. Hydrophilic Fraction.

	pH 2		pH 4	
D Stage				
TOC, kg/t	3.43	3.69	4.25	4.79
% of total TOC	77.4	86.0	76.6	72.1
AOX, kg/t	0.144	0.160	0.152	0.206
% of total AOX	48.5	60.6	45.1	61.3
Cl/C_{100}	1.42	1.47	1.21	1.46
(EO) Stage				
TOC, kg/t	5.50	5.45	5.84	6.13
% of total TOC	82.1	83.6	83.5	80.7
AOX, kg/t	0.0728	0.0745	0.0714	0.0644
% of total AOX	77.6	80.1	72.6	73.4
Cl/C_{100}	0.45	0.46	0.41	0.36
D Stage + (EO) Stage				
TOC, kg/t	8.93	9.14	10.09	10.92
% of total TOC	80.2	84.6	80.5	76.7
AOX, kg/t	0.217	0.235	0.223	0.270
% of total AOX	55.5	65.8	51.4	63.8
Cl/C_{100}	0.82	0.87	0.75	0.84

Table X. Volatile Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.380	0.396	0.276	0.609
% of total TOC	8.58	9.23	4.97	9.17
AOX, kg/t	0.0533	0.0136	0.0658	0.0557
% of total AOX	17.9	5.15	19.5	16.6
Cl/C_{100}	4.74	1.16	8.06	3.09
(EO) Stage				
TOC, kg/t	0.405	0.271	0.352	0.384
% of total TOC	6.04	4.16	5.04	5.05
AOX, kg/t	0.00539	0.00490	0.00956	0.00662
% of total AOX	5.75	5.27	9.73	7.55
Cl/C_{100}	0.45	0.61	0.92	0.58
D Stage + (EO) Stage				
TOC, kg/t	0.785	0.667	0.628	0.993
% of total TOC	7.05	6.17	5.01	6.97
AOX, kg/t	0.0587	0.0185	0.0754	0.0623
% of total AOX	15.0	5.18	17.3	14.7
Cl/C_{100}	2.53	0.94	4.06	2.12

THE EFFECT OF D STAGE REACTION TIME ON THE CHARACTERISTICS OF WHOLE EFFLUENTS AND EFFLUENT FRACTIONS FROM D(EO) BLEACHING OF OXYGEN DELIGNIFIED SOFTWOOD KRAFT PULP

T. A. Schwantes
Graduate Student
Institute of Paper Science and Technology
Atlanta, GA

T. J. McDonough
Professor of Engineering
Institute of Paper Science and Technology
Atlanta, GA

ABSTRACT

The effect of D stage reaction time on the characteristics of effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp is considered in this paper. Effluents from the OD(EO) sequence with D stage reaction times of 3 seconds, 1 minute, 5 minutes, and 30 minutes were fractionated and characterized. The fractionation consisted of ether extraction and separation of the extract into acidic, phenolic, and neutral subfractions. Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from each stage. Each fraction was characterized in terms of its chlorine to carbon ratio (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of the proportions of the total TOC and AOX contained within it.

A D stage of only 3 seconds duration resulted in 67% of the delignification achieved in a 30 minute stage. The 3 second D stage resulted in only 26% as much AOX and 34% of the Cl/C_{100} given by the 30 minute D stage. A one minute D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30 minute stage.

The Cl/C_{100} of all effluent fractions except the neutral fraction was reduced when the D stage was shortened from 30 minutes to 3 seconds. The extent of this reduction was different for the different fractions. In addition to a sharp Cl/C_{100} reduction in the environmentally significant ether soluble fraction, the proportion of ether soluble TOC was reduced at short D stage reaction times, and the proportion of the total AOX found in the environmentally significant ether soluble fraction reached a minimum value at 1 minute of D stage reaction time. These effects are primarily due to the acid subfraction of the ether soluble material. A bleaching sequence with a very short D stage may therefore possess environmental advantages in addition to an overall AOX reduction.

INTRODUCTION

In the area of pulp bleaching, environmental issues continue to gain importance relative to more conventional concerns such as efficiency of delignification and economics. The threat of extremely low AOX limits and consumer demand have already led many mills to substantially reduce their AOX discharge by a variety of methods including improved brownstock washing (1-3), extended Kraft delignification (4-6), oxygen delignification (1, 4, 7, 8), substitution of chlorine dioxide for chlorine (4, 7, 9-14), and oxidative caustic extraction (9, 15-17).

Although these methods reduce AOX, it remains uncertain what effect they have on the environment, because AOX reduction does not necessarily mean the environmental impact is reduced (18, 19). On the other hand, it may be somewhat irrelevant whether AOX reduction actually affects the environment, due to impending regulation.

Levels of AOX in proposed regulations may not be achievable using chlorine containing bleaching agents. However, both chlorine dioxide bleaching and oxygen delignification offer more environmental benefits over conventional chlorine bleaching than the AOX reduction alone suggests (20). Since conversion to totally chlorine free bleaching processes is not yet a viable alternative for most pulp producers, bleaching with chlorine dioxide is worth further study. If such a system can be optimized with respect to certain process variables, perhaps the required AOX reduction may be achieved and the environmental effects of the sequence minimized as well. The effect of D stage pH on the characteristics of whole effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp has been previously investigated (21) using an effluent fractionation based on ether extraction (20).

Another D stage process variable which may be expected to impact the nature of the effluent is reaction time. Removal of lignin and substitution on organic material by chlorine during chlorine dioxide treatment would be expected to have different time dependence, since the two processes occur by different mechanisms (22, 23). A variety of bleaching studies have considered the effect of reaction time on lignin removal in the chlorination of kraft pulps (24-30), in the chlorine dioxide prebleaching of kraft pulps (31), and in the prebleaching of kraft pulps with various combinations of chlorine and chlorine dioxide (32, 33). However, none of these studies has considered the effect of reaction time on the nature of the effluents.

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (34-38) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (34, 39, 40, 41-46), chlorinated dioxins (43, 47, 48), chlorinated neutral compounds (46, 49, 50), chlorinated carboxylic acids (46, 51), and chloroform (42, 52). However because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of their likely environmental effects. A preferable alternative is summative analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents (20, 21). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental standpoint are found in the extracts. Chlorine-to-carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may be expected to correlate with environmental behavior, were determined for the fractions. The same fractionation and characterization methods were used for the present study of the effect of D stage reaction time on D(EO) bleaching of oxygen delignified softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by a D(EO) sequence in the laboratory. D stage reaction times of 3 seconds, 1 minute, 5 minutes, and 30 minutes were considered. The D stages were quenched with excess sodium sulfite after the appropriate bleaching time. Only the first two stages of bleaching were done, since most of the delignification and therefore most of the effluent load production occurs in these stages. The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. Kappa numbers after bleaching are given in Table I.

A schematic diagram of the D stage bleaching reactor used in this study is given in Figure 1. The reactor was specially designed to bleach pulp for short periods of time, to quench the reaction after a given time interval, and to produce sufficient quantities of effluent for analysis. This batch reactor allowed consistencies of 2% and reaction times as short as 3 seconds.

The reactor consists of a thermostatted 20 L cylindrical reaction chamber with chemical injection cylinders on 3 sides of it. During a typical bleaching experiment only 2 of the injection cylinders were used: one for the bleaching agent, one for the quench. During such experiments a pulp slurry of the appropriate consistency, pH, and temperature is put in the mixing chamber. The mixing chamber is initially separated from the injection cylinders by teflon rupture membranes. The cover, equipped with a teflon-coated mixer, is attached and the chemicals added to the cylinders. Once the pulp is mixing at 350 rpm the bleaching agent is injected, through the membrane by an air-driven piston, into the slurry. At this point the consistency is 2%. The injection of chlorine dioxide triggers a timer which automatically injects the quench after the appropriate time.

Based on work by Liebergott and coworkers (27) the mixing rate of 350 rpm should be sufficient to insure uniform bleaching with aqueous bleaching agents. Data showing no effect of mixing on reaction rate (27, 29) suggest that bulk phase diffusion does not limit the reaction rate. During a preliminary mixing study done at only 250 rpm, high speed videotape demonstrated that mixing was complete in about 0.5 seconds.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 2 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions:

a non-extractable fraction and two ether extractable fractions. The first ether fraction is the most non-polar of the extractable material and is readily extracted, while the second is more polar and is removed slowly over an extended period. The first ether fraction was further separated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 2 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The bleaching sequences with different D stage reaction times were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each D stage reaction time. The data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme, and were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

The data for individual fractions were interpreted in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC or AOX. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between D stage reaction times and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect of reaction time, a least significant difference was determined using Duncan's multiple range test (53).

RESULTS AND DISCUSSION

Degree of Delignification

The effect of D stage reaction time on delignification (expressed as DE Kappa number) is shown in Figure 3 and the data are given in Table I. D stage bleaching for only 3 seconds results in a Kappa number decrease from 14.1 to about 7.8, or 67% of the Kappa number reduction that occurs in 30 minutes. One minute of D stage bleaching results in about 84% of the total 30 minute kappa number reduction, or a DE Kappa number of about 6.2. This shows that in conventional bleaching the greater part of the lignin is made soluble after only a very short time, and undergoes further reaction with chlorine containing chemicals for an extended period. This results in increased chlorine substitution on the organics as reaction time increases.

In addition to the kappa number data, Table I shows the sum of the TOC values for the D and (EO) effluents and the TOC per unit of Kappa number decrease, for the different D stage reaction times. Although at 3 seconds the mean TOC/ΔKappa is higher than at the other D stage times, the difference is not large enough to be considered statistically significant.

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 2.2-7.0 kg/t TOC and 0.04-0.40 kg/t AOX, depending on the stage and on the D stage reaction time.

Figure 4 shows the effect of D stage reaction time on effluent TOC content. The D stage TOC and the overall D + (EO) stage TOC increase with increasing reaction time. The (EO) stage TOC remains relatively constant at all reaction times. The D stage effluent TOC formation and the Kappa number reduction are virtual mirror images (Figure 5) indicating that the increased delignification seen at longer reaction times is due to increased D stage delignification, not (EO) stage delignification.

The amount of (EO) stage TOC formed at 3 seconds is almost identical to the amount formed at 30 minutes of D stage reaction time. This indicates that lignin removal in the latter part of the D stage and (EO) stage lignin removal may be parallel reaction sequences operating independently rather than sequential reactions, since after 3 seconds D stage reaction time has little or no effect on (EO) stage delignification.

Figure 6 shows the effect of D stage reaction time on the whole effluent Cl/C_{100}. While 67% of the delignification is seen after 3 seconds in the D stage, the overall Cl/C_{100} in the effluent is only about 34% of that seen after 30 minutes of D stage bleaching. AOX produced with the 3 second D stage is only 26% of that produced using a 30 minute D stage. Similarly a one minute D stage achieves 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30 minute stage. Short reaction times favor lignin removal over substitution of chlorine atoms onto organic material. The whole effluent Cl/C_{100} approaches an asymptotic level as D stage reaction time increases.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. It contains 0.2-0.9 kg/t TOC, representing 7-20% of the total TOC, and 0.01-0.10 kg/t AOX, representing 14-36% of the total AOX.

The mean ether soluble TOC, expressed as a percentage of the total TOC, is shown in Figure 7 for all D stage reaction times. For both the D and (EO) stage effluents, a greater proportion of the TOC is ether soluble when the D stage is 30 minutes long than when it is of short duration. Increased reaction time may allow further fragmentation of already solublized lignin, resulting in a lower molecular weight material and more ether soluble TOC. Although the D stage effluent appears to have a maximum proportion of ether soluble TOC at 1 minute of reaction time and the (EO) stage effluent a minimum, the overall D + (EO) proportion of ether soluble TOC increases to an asymptotic level with increased D stage reaction time.

Figure 8 shows the ether soluble Cl/C_{100} for the different D stage reaction times. Increased D stage reaction time generally results in increased Cl/C_{100} in the ether soluble fraction for both stages. Increased levels of chlorine substitution and associated decreases in water solubility may be responsible, in part, for the increase in the size of the ether soluble fraction at longer D stage reaction times. After 3 seconds of D stage bleaching, the overall D + (EO) Cl/C_{100} value is only about 38% of it's value at 30 minutes, although about two-thirds of the delignification occurs. A one minute D stage results in only 29% of the ether soluble AOX and 43% of the Cl/C_{100} of the 30 minute D stage, yet 84 % of the delignification is done.

The proportion of ether soluble AOX present in the effluents produced by the various D stage reaction times is shown in Figure 9. A minimum proportion of ether soluble AOX (presumed to be "bad" AOX) occurs in effluents produced using the 1 minute D stage. A similar trend is evident in both the D and (EO) stage effluents.

Within the ether soluble fraction, a reduced D stage reaction time may have several benefits of an environmental nature: a substantially reduced Cl/C_{100} for the ether soluble material, a reduced proportion of ether soluble TOC, and a minimum proportion of ether soluble AOX. Based on these results the potential environmental effects of the OD(EO) sequence may be minimized by running the D stage for 1 minute or less.

Polar Fraction

Detailed results for the polar fraction, or that material which is extracted slowly by ether, are shown in Table V. The phenolic fraction contains 0.1-0.8 kg/t TOC or 4-12% of the total TOC, and 0.002-0.04 kg/t AOX or 3-15% of the total AOX.

Although no increase in the proportion of polar TOC is seen as D stage reaction time increases, the Cl/C_{100} increases at longer reaction times, as shown in Figure 10. At 3 seconds, the overall D + (EO) polar Cl/C_{100} is only about 19% of that which occurs at 30 minutes.

Hydrophilic Fraction

Complete data on the hydrophilic fraction are given in Table VI. The fraction contains 2-5 kg/t TOC (70-85% of the total TOC) and 0.03-0.16 kg/t AOX (41-77% of the total AOX).

No trend in the proportion of TOC within this fraction is seen with increasing D stage reaction time. However, the Cl/C_{100} increases at longer D stage reaction times, as shown in Figure 11. The overall D + (EO) hydrophilic Cl/C_{100} is only 36% of it's 30 minute value after 3 seconds of D stage reaction time.

It is interesting to note that both the polar and hydrophilic fraction D stage Cl/C_{100} values exhibit relative maximums at 1 minute of D stage reaction time, corresponding to the apparent minimum seen within the D stage ether soluble Cl/C_{100}. This is consistent with the steadily increasing whole D stage effluent Cl/C_{100} and lends additional credibility to the data.

Acid Fraction

Table VII presents the detailed results for the acid subfraction of the ether soluble material. About 0.15-1.2 kg/t TOC, representing 6-18 % of the total TOC and 0.006-0.10 kg/t AOX, representing 12-31% of the total AOX, is contained within this fraction.

Increased D stage reaction time generally results in an increased proportion of acidic ether soluble TOC, as shown in Figure 12. The increased proportion of ether soluble TOC (shown previously) is accounted for by the acid fraction, since the proportions of phenolic and neutral TOC do not change with D stage reaction time.

The acid fraction Cl/C_{100} increases to an asymptotic level with D stage reaction time, as shown in Figure 13. The overall Cl/C_{100} at 3 seconds is only 30% of that at 30 minutes. The minimum in the proportion of ether soluble AOX is also likely to be due to the acid fraction's contribution to the ether soluble material. Figure 14 shows an apparent minimum proportion of acid fraction AOX at 1 minute of D stage reaction time, as was seen for the ether soluble fraction.

A reduction in D stage reaction time appears to have several benefits within the acid fraction: a substantially reduced Cl/C_{100}, a reduced proportion of acid fraction TOC, and a minimum proportion of acid fraction AOX. Although the acid fraction is not considered the most potentially harmful subfraction of the ether soluble material since it is the most polar portion, it is nevertheless the largest component of the environmentally significant ether soluble fraction, and improvements within this fraction are therefore of environmental interest.

Phenolic Fraction

Complete data for the phenolic fraction are shown in Table VIII. The fraction contains 0.02-0.06 kg/t TOC or 0.6-1.0% of the total TOC, and 0.001-0.003 kg/t AOX or 0.9-2.3% of the total AOX.

The duration of the D stage does not affect the proportion of phenolic TOC. On the other hand, the Cl/C_{100} of this fraction increases with D stage reaction time as shown by Figure 15. The effect appears to be smaller in the phenolic fraction than in the other fractions (for example the acid fraction) since the phenolic Cl/C_{100} reaches an asymptotic level at a shorter D stage reaction time. The overall reduction in the extent of the Cl/C_{100} from 30 minutes to 3 seconds (49%) is less in this case, but still an important reduction since this is an environmentally significant fraction.

Neutral Fraction

Table IX presents the entire data set for the neutral fraction of the ether soluble material. This fraction contains 0.02-0.06 kg/t TOC (0.4-4.8% of the total TOC) and 0.0006-0.0030 kg/t AOX (0.8-2.4% of the total AOX).

The proportion of neutral fraction TOC is not affected by D stage reaction time. As shown by Figure 16, there is no clear reduction in neutral fraction Cl/C_{100} with reduced D stage reaction time as occurred in other fractions. However the Cl/C_{100} at 1 minute is significantly reduced versus that at 5 minutes. Although these data have considerable scatter, it is very interesting that both the D and (EO) stage curves are nearly identical. The reproducibility of these graphs lends some credibility to the data within them.

Volatile Fraction

There are no significant time related effects observed in the volatile fraction data, due to scatter and incomplete data. The data set is included here (Table X) for the purposes of a complete analysis, however.

Practical Implications

A major practical consideration of this work is that a sequence with a very limited D stage (3 seconds long) removes two-thirds of the material removed by a sequence with a 30 minute D stage, while reducing the D + (EO) stage AOX to only 26% of that formed by a sequence with a 30 minute D stage. Similarly a one minute D stage results in 84% of the lignin removal with only 51% of the AOX production. Since (EO) stage lignin removal is unaffected by the extent of the D stage, limiting the D stage, either in time or perhaps in level of charge, may allow compliance with AOX regulation if the remaining lignin can be removed by other means. Possible methods of removal may be additional oxidative enhancement of the caustic extraction stages or a second, very limited chlorine dioxide delignification stage prior to brightening. A second delignification stage would have minimal impact on the effluent since most lignin is already removed, and a small ClO_2 charge would be applied.

A second practical consideration of this work is that such a limited D stage would require no bleach tower, simply a static mixer and a length of pipe for retention. Since towers are not needed, an additional chlorine dioxide delignification stage could be installed at a much lower capital cost than a conventional stage.

EXPERIMENTAL METHODS

Pulp Bleaching

A mill-produced, 14.1 kappa O_2-delignified southern softwood kraft pulp was used in this study. The pulp was collected just after the O_2 stage and was well washed before bleaching.

D Stages.

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH was adjusted to 2 by the addition of sulfuric acid solution. A 13 g/L solution of sodium sulfite was used for D stage quenching. After quenching with 1.5 L of the sulfite solution, the D stage slurry was at about 1.8% consistency.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and no carryover was added since it contained sodium sulfite . The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 1.8% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 1.8%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts were collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts were also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction; and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation on a rotary evaporator. A vacuum pump was applied to the evaporator containing the samples for a minimum of 3 hours. The samples were then acidified and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a modification of method SCAN-W 9:89 (54). After the initial adsorption on carbon, the filtrate was treated with a second batch of carbon to minimize "breakthrough". All samples were shaken for an hour, the carbon filtered, the filtrate collected, and more carbon added to this filtrate. This filtrate was treated identically to the first AOX batch.

SUMMARY AND CONCLUSIONS

A 3 second D stage in the OD(EO) bleaching of a softwood kraft pulp, resulted in 67% of the delignification that occurred with the same sequence utilizing a 30 minute D stage. At the same time the overall whole effluent Cl/C_{100} was reduced to 34% of it's 30 minute value while the overall D + (EO) stage AOX was reduced to 26% of the 30 minute AOX. A one minute D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30 minute stage. Additional reaction time provided limited delignification benefits, while increasing quite significantly the level of chlorine substitution on dissolved organics. Based on effluent TOC measurements, the (EO) stage delignification remained constant for all D stage reaction times.

With the exception of the neutral fraction, the Cl/C_{100} of all effluent fractions were reduced to varying degrees as the D stage reaction time is shortened. In the environmentally significant ether soluble fraction, in addition to a sharp reduction in the Cl/C_{100}, the proportion of ether soluble material was reduced for short D stage reaction times and the proportion of ether soluble AOX (assumed to be "bad" AOX) reached a minimum under the 1 minute D stage conditions. These effects are likely to be caused primarily by the acidic fraction of the ether soluble material. In addition to reducing the overall effluent AOX, a bleaching sequence with a limited D stage may therefore represent environmental benefits in addition to the obvious reduction in total AOX.

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. 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.

LITERATURE CITED

1. Germgard, U., Karlsson, R., Kringstad, K., de Sousa, F., Stromberg, L., *Svensk Papperstidning*, "Oxygen Bleaching and It's Impact On Some Environmental Parameters," 88(12):R113 (1985).
2. Blomberg, L., Jarvinen, R., Talka, E., Valttila, O., *1990 TAPPI Pulping Conference Proceedings*, "Organic Carry-over in Kraft Pulp and Bleaching Discharges," pp. 217-226.
3. Blomback, S., *1990 TAPPI Pulping Conference Proceedings*, "ASSI Karlsborgs Way To Reduce the Formation and Discharge of TOCl," pp. 905-914.
4. Shin, N., Sundaram, M., Jameel, H., Chang, H., *1990 TAPPI Pulping Conference Proceedings*, "Bleaching of Softwood RDH Pulps With Low/No Chlorine Bleaching Sequences," pp. 817-828.
5. Dillner, B., Larsson, L., Tibbling, P., *Tappi*, "Non-Chlorine Bleaching of Pulp Produced By the Modified Continuous Cooking Process," 73(8): 167 (1990).
6. Sjoblom, K., Hartler, N., Mjoberg, J., Sjodin, L., *Tappi*, "A New Technique For Pulping To Low Kappa Numbers in Batch Pulping: Results of Mill Trials," 66(9):97 (1983).
7. Liebergott, N., Van Lierop, B., Nolin, A., Faubert, M., Laflamme, J., *1990 CPPA Technical Section Annual Meeting Proceedings*, "Modifying the Bleaching Process to Decrease AOX Formation," pp. B229-B238.
8. Arhippainen, B., Malinen, R., *1987 International Oxygen Delignification Conference Proceedings*, "Cost Competitiveness of Oxygen Bleaching," pp. 23-27.
9. Basta, J., Holtinger, L., Hook, J., Lundgren, P., *Tappi*, "Reducing Levels of Adsorbable Organic Halogens (AOX)," 73(4):155 (1990).
10. Munro, F., Chandrasekaran, S., Cook, C., Pryke, D., *Tappi*, "Impact of High Chlorine Dioxide Substitution on Oxygen Delignified Pulp," 73(5):123 (1990).
11. Liebergott, N., Van Lierop, B., Kovacs, T., Nolin, A., *Tappi*, "A Comparison of the Order of Addition of Chlorine and Chlorine Dioxide in the Chlorination Stage," 73(9):207 (1990).
12. Brunsvik, J., Grundelius, R., Kordes, R., Swan, B., *1989 TAPPI Pulping Conference Proceedings*, "Environmental Compatible Bleaching of Chemical Pulp," pp. 411-414.
13. Earl, P., Reeve, D., *1989 TAPPI Environmental Conference Proceedings*, "Chlorinated Organic Matter In Bleached Chemical Pulp Production: Part III: The Effect of Chlorintaion Stage

Variables on Chlorinated Organic Matter In Effluent," pp. 385-391.

14. Axegard, P., *Tappi,* "Substituting Chlorine Dioxide For Elemental Chlorine Makes the Bleach Plant Effluent Less Toxic," 69(10):54 (1986).

15. Hong, Q., Shin, N., Chang, H., *1988 TAPPI Pulping Conference Proceedings,* "Effects of Oxygen Extraction on Organic Chlorine Content in Bleach Plant Effluents," pp. 63-69.

16. Klein, R., Meng, T., Jameel, H., Sundaram, V., *1990 TAPPI Pulping Conference Proceedings,* "Hydrogen Peroxide Reinforced Extraction Lowers Chlorinated Organics and Color in Bleach Plant Effluent," pp. 829-835.

17. Reid, D., Billmark, G., Sutton, C., *1990 International Oxygen Delignification Symposium Proceedings,* "Peroxide Bleaching Reduces Dioxin Formation in a Generator Limited Mill," pp. 85-89.

18. NCASI Special Report No. 90-07, "An Examination of the Relationship Between the Adsorbable Organic Halide (AOX) Content of Paper Industry Wastewaters and Potential Aquatic Biological Effects: First Progress Report," July 1990.

19. O' Connor, B. I., Kovacs, T. G., Voss, R. H., Martel, P. H., *1992 CPPA Technical Section Annual Meeting Proceedings,* "A Study of the Relationship Between Laboratory Bioassay Response and AOX Content For Pulp Mill Effluents," pp. A223-A233.

20. Schwantes, T. A., McDonough, T. J., *1993 TAPPI Pulping Conference Proceedings,* "Characterization of Effluent Fractions From ClO_2 and Cl_2 Bleaching of Unbleached and O_2 Bleached Softwood Kraft Pulps," pp.17-41.

21. Schwantes, T. A., McDonough, T. J., *1994 CPPA Technical Section Annual Meeting Proceedings,* "The Effect of D Stage pH on Effluent Quality: Characterization of Effluent Fractions From OD(EO) Bleaching of Softwood Kraft Pulp," pp. A95-A108.

22. Gierer, J., *Holzforschung,* "The Chemistry of Delignification, Part II: Reactions of Lignins During Bleaching," 36(2): 55 (1982).

23. Gierer, J., *Holzforschung,* "Basic Principles of Bleaching, Part 1: Cationic and Radical Processes," 44(5): 387 (1990).

24. Russell, N. A., *Tappi,* "The Initial Phase of the Aqueous Chlorination of Kraft Pulp Meals," 49(9): 418 (1966).

25. Karter, E. M., Bobalek, E. G., *Tappi,* "The Role of Physico-Chemical Rate Phenomena in Wolld Pulp Chlorination," 54(11): 1882 (1971).

26. du Manoir, J. R., *1979 International Pulp Bleaching Conference Proceedings,* "Chlorination In Closed Bleach Plants - A Laboratory Investigation," pp. 281-288.

27. Liebergott, N., Trinh, D. T., Poirier, N., Crotogino, R. H., *1984 TAPPI Pulping Conference Proceedings,* "Chlorination of Pulp - The Effect of Mixing Intensity, Chlorine Concentration and Reaction Temperature. Part 1: Chlorine Water - Pulp System," pp. 359-368.

28. Berry, R. M., Fleming, B. I., *1985 International Symposium on Wood and Pulping Chemistry,* "Why Does Chlorination and Extraction Fail to Delignify Kraft Pulp Completely?" pp. 71-78.

29. Pugliese, S. C. III, McDonough, T. J., *Tappi,* "Kraft Pulp Chlorination: A New Mechanistic Description," 72(3): 159 (1989).

30. Ni, Y., Kubes, G. J., Van Heiningen, A. R. P., *Journal of Pulp and Paper Science,* "A New Mechanism for Pulp Delignification During Chlorination," 16(1): J13 (1990).

31. Germgard, U., Teder, A., *Transactions of the CPPA Technical Section,* "Kinetics of Chlorine Dioxide Prebleaching," 6(2): TR31 (1980).

32. Germgard, U., *Paperi ja Puu,* "Kinetics of Prebleaching Softwood Kraft Pulp with Chlorine Dioxide and Small Fractions of Chlorine," 1982(2): 76.

33. Germgard, U., Teder, A., Tormund, D., *Paperi ja Puu,* "The Three Phases in the Sequential Pre-

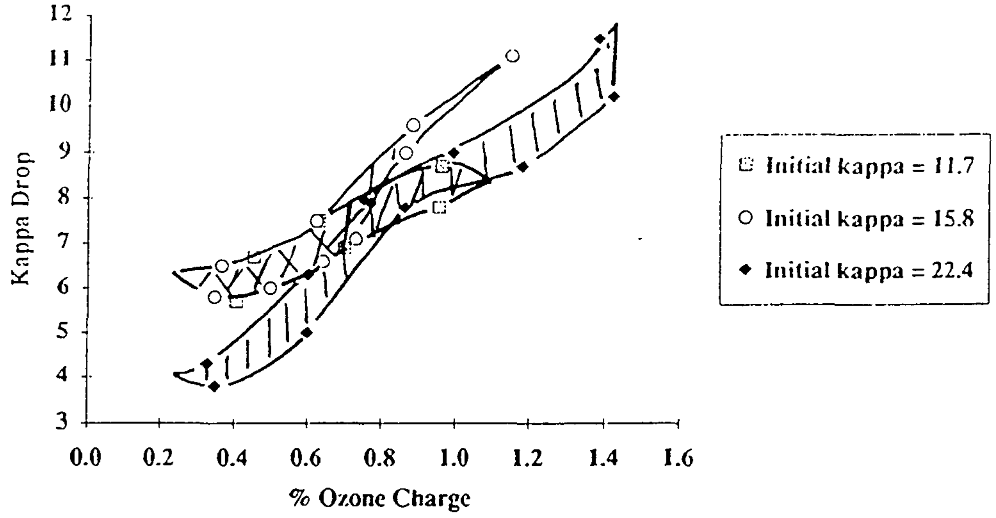


Figure 7. Delignification from Ozonation of Kraft and Oxygen Delignified Pulps.

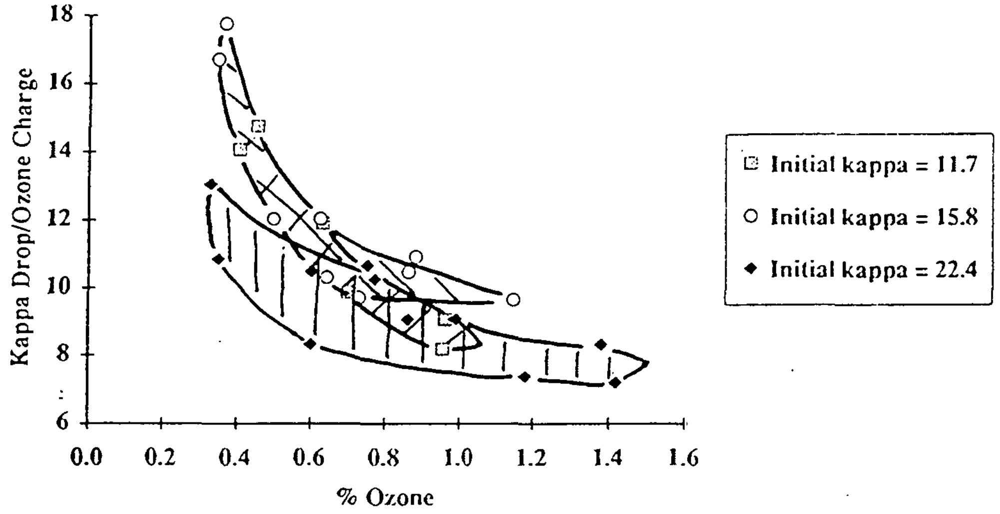


Figure 8. Delignification per Unit Ozone Consumed in Kraft and Oxygen Delignified Pulps.

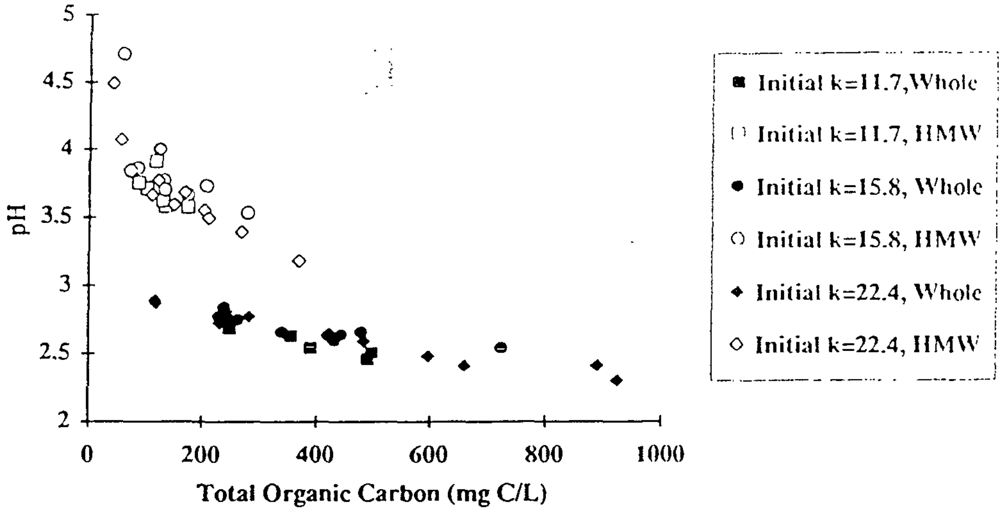


Figure 9. pH and Total Organic Carbon in Ozonation Filtrates.

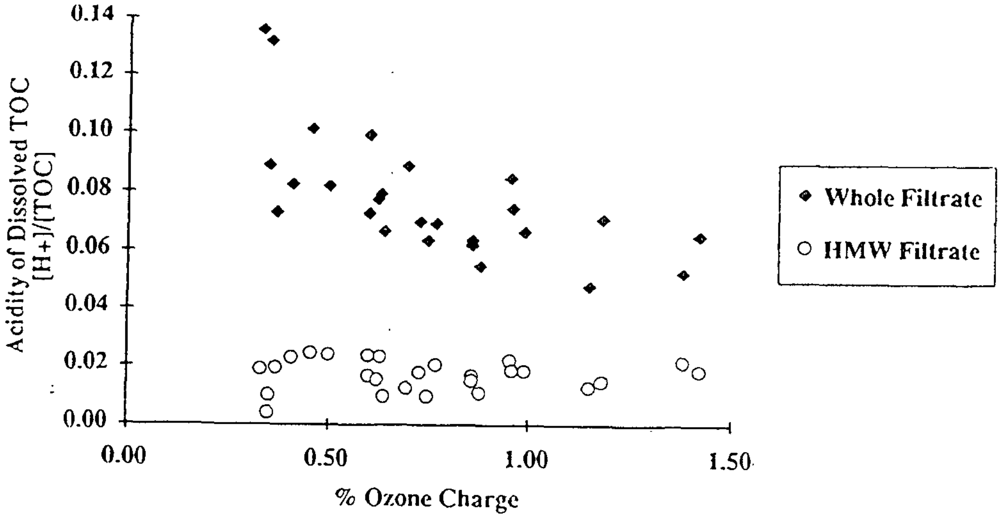


Figure 10. Relative Acidity of Organic Carbon in Ozonation Filtrates.

Table 1. Functional Groups on Ozonated Kraft and Oxygen Delignified Pulps

% O_3 Charge	Final kappa number	meq COOH/ 100 g pulp	meq lig.[1] COOH/ 100 g pulp	meq carb.[2] COOH/ 100 g pulp	meq[3] COOH/ g lignin	meq OCH_3/ 100 g pulp	meq PhOH/ 100 g pulp	meq[3] PhOH/g lignin	PhOH/ OCH_3 meq/meq	lignin COOH/ OCH_3 meq/meq
Kraft Pulp	k = 22.4									
0	22.4	6.5	0.2	6.3	0.1	15	8.4	2.5	0.56	0.01
0.33	18.1	7.0	1.4	5.6	0.5	18	6.6	2.4	0.37	0.08
0.35	18.6	6.7	1.0	5.7	0.4	16	-	-	-	0.06
0.60	17.4	5.8	nd[4]	5.8	nd	13	6.3	2.4	0.48	nd
0.60	16.1	6.3	-	-	-	14	-	-	-	-
0.86	13.5	5.7	-	-	-	11	-	-	-	-
1.38	11.2	5.0	-	-	-	8	4.7	2.9	0.59	-
1.42	10.9	5.2	0.8	4.4	0.4	8	-	-	-	0.10
O_2 Delig.	k = 15.8									
0	15.8	5.3	0.6	4.7	0.3	11	5.3	2.2	0.48	0.06
0.35	10.0	6.0	1.9	4.2	1.2	8	-	-	-	0.23
0.37	9.3	5.8	0.9	4.9	0.6	8	2.9	2.1	0.36	0.11
0.62	8.3	5.3	-	-	-	11	4.1	5	0.37	-
0.64	9.2	5.3	-	-	-	10	-	-	-	-
0.86	6.8	4.9	-	-	-	8	-	-	-	-
0.88	6.2	4.7	-	-	-	7	-	-	-	-
1.15	4.7	4.5	0.3	4.2	5	7	2.1	5	0.30	0.04
O_2 Delig.	k = 11.7									
0	11.7	5.9	1.4	4.5	0.8	7	2.8	1.6	0.40	0.50
0.41	6.0	4.3	0.2	4.1	5	8	-	-	-	0.03
0.45	5.0	4.4	-	-	-	8	1.7	5	0.21	-
0.70	4.8	4.4	0.7	3.7	5	4	-	-	-	-
0.95	3.9	4.1	-	-	-	4	1.4	5	0.35	-
0.96	3.0	4.0	nd	4.0	5	4	-	-	-	nd

[1] Milliequivalents of COOH associated with the lignin per gram of pulp (calculated).
[2] Millequivalents of COOH associated with the carbohydrates per gram of pulp.
[3] Lignin estimates based on kappa number (% lignin by weight = 0.15 x kappa number)
[4] nd = nondetectable levels
[5] Lignin estimates from kappa numbers below 10 are invalid.

Bleaching Kraft Pulps with In-Situ Generated Dioxiranes

I. Introduction

Bleaching kraft pulps is undergoing profound technical changes as environmental and market forces have combined to substantially alter this process (Browner, 1993; Cockram, 1991). Current kraft bleaching operations have considerably improved waste management practices and research efforts are continuing to improve the environmental performance of these operations (Hise, R.G., 1992). To address future needs, researchers have examined a variety of oxidative bleaching technologies including molecular oxygen (Tench and Harper, 1987), hydrogen peroxide (Lachapellen et al., 1992), peracids (Hill et al., 1992; Muurinen and Sohlo, 1991) and ozone (Liebergott, 1992). To date, only ozone and oxygen delignification have developed sufficiently so as to allow for commercial applications. Nonetheless, a need to continue exploring alternative bleaching technologies which complement the bleaching capabilities of ozone is generally acknowledged.

Recently, several research institutions (Lee et al., 1993a, 1993b; Ragauskas, 1993) have begun to investigate the bleaching capabilities of dimethyldioxirane (DMD). This cyclic three member peroxide structure, illustrated in Figure 1, has shown much promise as an efficient, selective, bleaching agent for kraft pulps. Based upon numerous fundamental research investigations (Adam, 1989; Murray, 1989), it is well established that dimethyldioxirane is an effective oxidizing agent which can be can be generated from acetone and peroxymonosulfate (see Fig. 1). The resulting dioxirane can be isolated, or as in the case with kraft pulps, generated and employed in-situ. Upon oxidation of a substrate with DMD, oxygen is transferred to the substrate and acetone is re-generated (see Fig 1). In this manner, acetone acts as a true catalyst and therefore can be employed in relatively small amounts and recovered upon completion of the reaction. Investigative studies by Ragauskas (1993) and Lee et al. (1993) have shown that DMD is a very effective reagent for the deligification of kraft pulps. Preliminary investigative studies demonstrated that a freshly prepared solution of DMD in acetone was very effective at removing lignin from kraft pulps. Employing a 5% charge of a DMD/acetone solution, Ragauskas demonstrated that 66% of the lignin present in a softwood kraft pulp could be removed. This level of delignification had previously only been observed with ozone (Liebergott, 1992). Studies by Lee and Ragauskas have both demonstrated that these results can also be achieved employing in-situ generated DMD. In-situ generation of DMD is an attractive technology for bleaching kraft pulps since it avoids the need to isolate this reactive peroxide and takes full advantage of the catalytic properties of acetone and peroxymonosulfate.

Although the bleaching properties of DMD hold much promise, many technical challenges need to be resolved prior to full commercial application, including bleaching sequence studies, design of a DMD bleaching reactor, and further improvements in our fundamental knowledge of dioxirane bleaching chemistry. Research efforts by Lee (1992), Qui (1993), and McDonough (1994) have begun to examine bleaching sequence studies with DMD. Studies directed by Lee are examining the technical issues surrounding commercial applications of DMD, including on-site generation of peroxymonosulfate and recovery of acetone. Our own studies have recently focused on the sensitivity of DMD to metals present in kraft pulps and the potential application of alternative dioxirane structures for bleaching kraft pulps. In this report we wish to describe the results of our studies directed at bleaching kraft pulp from in-situ generated substituted dioxiranes.

2. Experimental

All reagents were commercially purchased and used without further purification. Oxone™, a triple salt of K_2SO_4•$KHSO_4$•$KHOSO_4$ was employed as a source of peroxymonosulfate. The softwood kraft pulp was prepared from commercial wood chips in a laboratory digester.

All bleaching experiments were executed following standard laboratory conditions for handling peroxides (National Academy Press, 1981). The standard bleaching procedure consisted of adding a softwood kraft pulp (63 g fiber, oven dry weight) and $NaHCO_3$ to water (2.50 l) and then adding the ketone solvent (2.45 mol) to an open beaker in a well ventilated fume hood. This mixture was then vigorously stirred and the peroxymonosulfate was added over the duration of 10 min. After vigorously stirring this mixture for 1 h the pulp slurry was filtered, washed and analyzed for lignin content, viscosity, and Tappi brightness values following standard testing methods (TAPPI, 1992). The pulp was then extracted with an aqueous 0.04 N solution of NaOH (1000 ml alkaline solution/30 g of fiber). After stirring for 1 h at RT, the mixture was filtered and washed. The resulting pulp was analyzed for lignin content, viscosity, and Tappi brightness values as described above.

3. Results and Discussion

To date, only dimethyldioxirane has been reported to be an effective dioxirane bleaching agent for kraft pulps (Murray and Jeyaraman, 1985). Nonetheless, a variety of dioxirane structures have been prepared and employed for general oxidative chemistry purposes. Indeed, a review of the chemical literature indicates that acetone may be one of the least effective dioxiranes generated from peroxymonosulfate. Early studies by Montgomery (1974) demonstrated that cyclohexanone and N,N-dimethyl-4-oxo-piperidium nitrate were substantially more effective at catalyzing peroxymonosulfate reactions than acetone. Studies since this paper have shown that trifluoroacetone is another effective ketone precursor for the generation of substituted dioxiranes (Adam et al., 1992). Although practical considerations preclude the application of many of these types of structures for bleaching kraft pulps, the incorporation of a ketone recovery system after dioxirane bleaching (Forber, 1992) and the possibility of developing a more effective bleaching agent for kraft pulp heightened our interest in this research area. To explore the reactivity of alternative dioxiranes towards kraft pulp, we initially examined the use of 2-butanone, 3-pentanone, and cyclopentanone as ketone precursors for in-situ generation of substituted dioxiranes. The bleaching properties of these systems was evaluated by preparing an aqueous suspension of softwood kraft pulp and ketone. We added to this mixture sodium bicarbonate and peroxymonosulfate in the form of $K_2SO_4 \cdot KHSO_4 \cdot KHOSO_4$. The resulting pulp slurry was stirred for 1 h at RT, filtered, washed, and extracted with caustic solution. Since preliminary experiments had suggested that some of the keto-solvents were not effective catalysts for peroxymonosulfate, we elected to employ excessively large charges of the oxidant so as to be able to rank the bleaching efficiency of all ketones examined. The results of our initial studies are summarized in Table 1. Several interesting trends are apparent from these experiments. First, at very high charges, peroxymonosulfate can itself effectively delignify kraft pulps. Of greater practical interest is the observation that the softwood kraft pulp was further delignified and brightened when the bleaching solvent contained either acetone, 2-butanone, or 3-pentanone. These differences were apparent not only after the bleaching experiments but also after each caustic extraction procedure. Interestingly, the improved performance of the ketone catalyzed bleaching properties of peroxymonosulfate become readily apparent even at the relatively high charge of 85% peroxymonosulfate.

Although the enhanced bleaching properties of peroxymonosulfate in the presence of acetone have been reported (Lee, 1993; Ragauskas, 1993), this paper now extends these properties to 2-butanone and 3-pentanone. Presumably, use of these latter two reagents also results in the in-situ formation of substituted dioxiranes which are more effective at removing lignin from kraft pulp than peroxymonosulfate itself. The enhanced delignification of the kraft pulps with either acetone, 2-butanone or 3-pentanone is also accompanied by increased oxidative degradation of cellulose as observed by the viscosity values for the mixed solvent bleaching systems.

In contrast to these results, the use of cyclopentanone appeared to retard the bleaching properties of caroic acid at either of the two high charges employed. As summarized in Table 1, kraft pulps treated with peroxymonosulfate and cyclopentanone were delignified to a lesser extent than pulps treated only with peroxymonosulfate and water. Although we are uncertain as to the exact factors contributing to this divergence in bleaching properties, it may well be due in part to the differences in the water solubility of the in-situ generated dioxiranes and/or starting keto-reagents. Clearly, if the water solubility of the substituted dioxirane is low, then a portion of the dioxirane would remain in the organic phase and secondary dioxirane decomposition reactions (Fig. 1, pathway B) could reduce bleaching efficiency.

To explore the overall relationship between water solubility of the keto-catalyst and bleaching efficiency of peroxymonosulfate reactions, we repeated the above bleaching reactions with cyclohexanone and tetrahydro-4H-pyran-4-one. Presumably, if water solubility of the starting ketone and/or dioxirane was a principle factor influencing the bleaching properties of cyclopentanone and peroxymonosulfate, then cyclohexanone should yield similar bleaching results since the water solubility of these two ketones is comparable. In contrast, tetrahydro-4H-pyran-4-one is substantially more water soluble and should act as a better bleaching catalyst for peroxymonosulfate.

As summarized in Table 1 the catalytic bleaching properties of cyclohexanone were substantially more effective than those observed for cyclopentanone. This result suggests that water solubility is not the principal factor contributing to the poor bleaching capabilities of cyclopentanone. In contrast to these results, tetrahydro-4H-pyran-4-one was shown to be a very effective bleaching catalyst for peroxymonosulfate. Although several factors may be contributing to the bleaching efficiency of this reagent, presumably its improved water solubility contributes to the enhanced bleaching properties.

To explore the potential application of more reactive dioxiranes for bleaching kraft pulps, we examined the bleaching capabilities of trifluoroacetone/caro's acid as a bleaching system. Following our standard bleaching procedure, a softwood pulp was treated with peroxymonosulfate employing a 57:1 molar ratio of water to 1,1,1-trifluoroacetone. After oxidative bleaching and caustic extraction, the pulp was analyzed for lignin content and brightness values. This data, summarized in Table 1, indicates that 1,1,1-trifluoroacetone improves the bleaching properties of peroxymonosulfate both in terms of extent of delignification and brightness gains. Nonetheless, comparison of these results against the values obtained from acetone clearly indicates that acetone/water provides a more efficient reagent for catalyzing the bleaching properties of peroxymonosulfate. This result suggests that in-situ generation of a very reactive dioxirane is counter productive for bleaching proposes.

Following these preliminary studies, it was apparent that tetrahydro-4H-pyran-4-one, 1,1,1-trifluoracetone, acetone, 2-butanone and 3-pentanone could catalyze the bleaching reactions of peroxymonosulfate, although for practical proposes only the latter three ketones were of interest. To determine if these catalytic properties occurred under conditions which are closer to practical applications, we repeated the bleaching reactions employing a 10% charge of peroxymonosulfate. The results of these bleaching studies are summarized in Table 2. Under these conditions the trends that started to become apparent in Table 1 are further amplified. Our experiments suggest that acetone is one of the most effective bleaching catalyst for peroxymonosulfate treatment of softwood kraft pulp followed by 2-butanone and 3-pentanone.

4. Conclusions

It has been shown that several keto-compounds can act as catalysts for bleaching reactions with peroxymonosulfate. The use of keto-compounds, such as 1,1,1-trifluoracetone which have been reported to yield more reactive dioxiranes than DMD, failed to enhance the overall bleaching process. These results suggest that the effectiveness of a given ketone to enhance bleaching reactions appears to be influenced by its water solubility properties and its intrinsic reactivity. Presumably, the reactivity and water solubility of dimethyldioxirane and acetone correspond well to the requirements for bleaching kraft pulps with dioxirane reagents.

Literature Cited

1. Adam, W.; Curci, R.; Edwards, J.O. Dioxiranes: A New Class of Powerful Oxidants. *Acc. Chem. Res.*, **1989**, *22*, 205.
2. Adam, W.; Hadjirapoglou, L.P.; Curci, R.; Mello, R. Dioxiranes, Three-Membered Ring Cyclic Peroxides, *Organic Peroxides*, Ando, W., Ed., John Wiley & Sons Ltd., NY, **1992**, *4*, 194.
3. Browner C. Pulp, Paper and EPA: Linking the Environment and the Economy. *Paperage*, **1993**, *July*, 41.
4. Cockram, R. The Chlorine Issue: Marketing Implications in Europe. *Proceedings of Market Pulp One: Looking for the Next Recovery*, Montreal, Canada, *October*, **1991**, 1.
5. Forber, C.L. Chlorine and Chlorine Dioxide Replacements in Kraft Pulp Bleaching: Emerging Technologies or Laboratory Curiosities, *Proceedings of the 1992 TAPPI Pulping Conference,* Boston, MA, November, **1992**, *3*, 1209.
6. Hill, R.T.; Walsh, P.B.; Hollie, J.A. Part 1: An Effective Alternative for Chlorine Compound Free Delignification of Kraft Pulp. *Proceedings of the 1992 TAPPI Pulping Conference*, Boston, MA, November, **1992**, *3*, 1219.
7. Hise, R.G. Process Changes to Lower the Formation of Dioxins and Chlorinated Organics During Chemical Pulp Bleaching. *Proceedings of 1992 TAPPI Bleach Plant Operations Short Course*, **1992**, *8-1*, 201.
8. Lachapellen R.C.; Strunk, W.G.; Klein, R.J. Using Hydrogen Peroxide in 100% Chlorine Dioxide Bleaching Sequences. *TAPPI J.*, **1992**, *75*, 181.
9. Lee, C.L.; Hunt, K.; Murray, R.W. A Novel Non-Chlorine Agent for Chemical Pulp Bleaching, *1992 TAPPI Pulping Proceedings*, Boston, MA, November, **1992**, *3*, 1237.
10. Lee, C.L.; Hunt, K.; Murray, R.W. Dimethyldioxirane as a nonchlorine agent for chemical pulp bleaching. *Tappi, J.*, **1993a**, *76*(11), 137.
11. Lee, C.L.; Hunt, K.; Murray, R.W. Activated Oxygen, A Selective Bleaching Agent for Chemical Pulps, *Proceedings from the 7th International Symposium on Wood Pulping and Chemistry*, Beiijing, China, **1993b**, *1*, 188.

12. Liebergott, N.; Lierop, B.v.; Skothos, T. A Survey of the Use of Ozone in Bleaching Pulps, Part 2. *TAPPI J.*, **1992**, *75*(2), 117.

13. McDonough, T.J.; Marquis, A.; Ragauskas, A.J. "Totally Chlorine Free Bleaching with Dimethyldioxirane", paper accepted for 1994 International Pulp Bleaching Conference, Vancouver Canada.

14. Montgomery, R.E. Catalysis of Peroxymonosulfate Reactions by Ketones. *J. Am. Chem. Soc.*, **1974**, *96*, 7820.

15. Murray, R.W., Dioxiranes. *Chem. Rev.*, **1989**, *89*, 1187.

16. Muray, R.W.; Jeyaraman, R. Dioxiranes: Synthesis and Reactions of Methyldioxiranes. *J. Org. Chem.*, **1985**, *50*, 2847.

17. Muurinen, E.; Sohlo J. Recovery of Chemical from Peroxyformic Acid Pulping. *The 6th International Symposium on Wood and Pulping Chemistry*, Melbourne, April, **1991**, 169.

18. National Academy Press, Committee on Hazardous Substances in the Laboratory, Assembly of Mathematical and Physical Sciences, *Prudent Practices for Handling Chemicals in the Laboratories*, Washington, DC, **1981**.

19. Nutt, W.E.; Griggs, B.F.; Eachus, S.W.; Pikulin, M.A. Developing an ozone bleaching process. *TAPPI J.*, **1993**, *76*, 115.

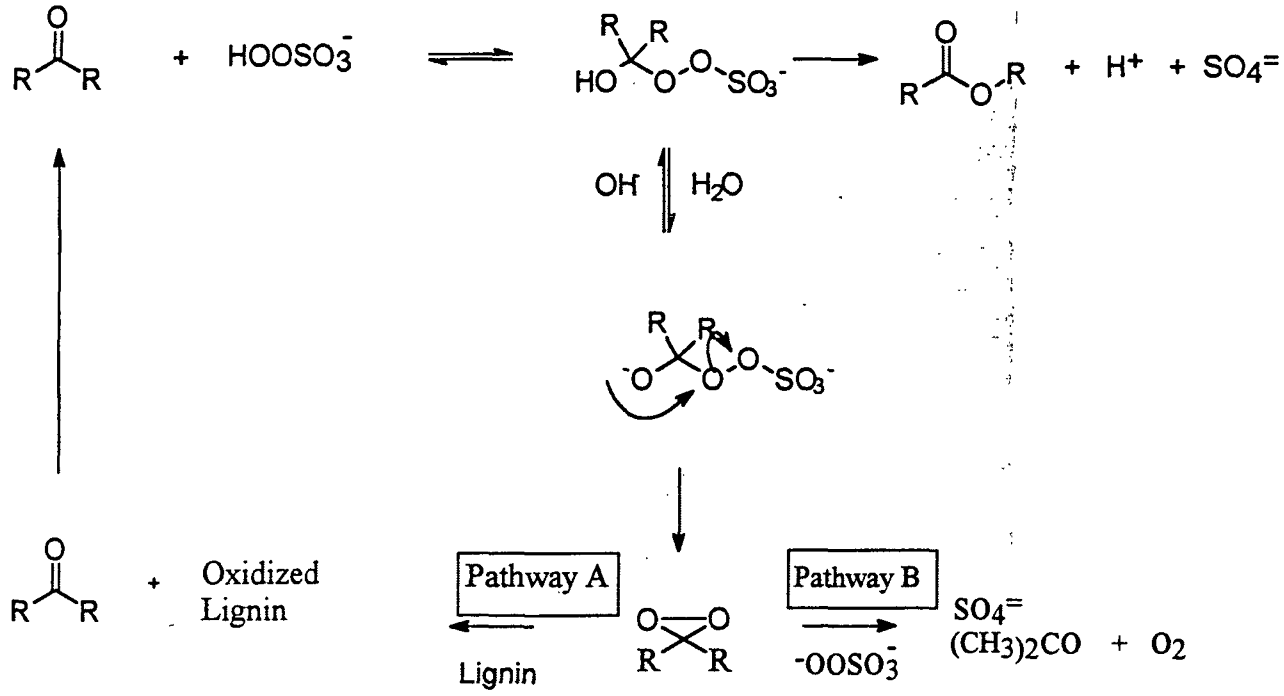
20. Qui, C.; Senior, D.J.; Rodriguez, A.; Ragauskas, A.J. Fundamental Studies of Dimethyldioxirane as a Bleaching Reagent for Kraft Pulps. *Proceedings from the 1993 Non-chlorine Bleaching Conference*, Hilton Head, SC, **1993**, 41.

21. Ragauskas, A.J. Investigation of Dimethyldioxirane as a Bleaching Reagent for Kraft Pulp. *Tappi J.*, **1993**, *76*(11), 87.

22. TAPPI Test Methods, TAPPI PRESS, Atlanta **1991**.

23. Tench, L.; Harper, S. Oxygen Bleaching Practices and Benefits: An Overview. *TAPPI J.*, **1987**, *70*(11), 55.

Figure 1: Overview of DMD Generation and Oxidation Chemistry.



DMD: R= CH3

Table 1. Bleaching softwood kraft pulp with *in-situ* generated dioxiranes[a].

Ketone	Chemical Charge of Peroxymonosulfate[b]	Fiber Properties of the Bleached/Extracted Pulps		
		Kappa #	Brightness	Viscosity/cp
-	0%	26.3	23.2	41.9
-	250%	7.3/4.4	49.8/54.1	34.3/23.6
-	85%	15.1/14.5	32.5/34.2	34.2/26.8
Acetone	250%	2.7/1.8	60.3/64.8	22.3/17.1
	85%	5.2/3.4	50.2/53.7	27.7/25.7
2-Butanone	250%	2.4/2.2	61.8/66.1	---/17.8
	85%	5.3/4.0	50.5/53.2	31.6/30.3
3-Pentanone	250%	2.8/1.7	66.7/69.4	16.5/15.1
	85%	6.9/5.6	45.9/50.2	30.7/30.9
Cyclopentanone	250%	16.4/12.2	32.8/34.7	23.0/20.7
	85%	19.4/19.0	26.7/28.3	34.4/33.2
Cyclohexanone	85%	10.6/10.0	34.0/33.8	----
Tetrahydro-4H-pyran-4-one	85%	---/2.4	---/55.2	---/20.5
Trifluoracetone	85%	---/5.1	---/50.4	----

[a]the first value given in each column was determined after bleaching, the second value was determined after bleaching and caustic extraction; [b]charge is based on the weight of peroxymonosulfate employed/weight of pulp, oven dry.

Table 2. Bleaching softwood kraft pulp[a] with a 10% charge of peroxymonosulfate and water/ketone solvent mixtures.

Ketone	Fiber Properties of the Bleached/Extracted Pulps	
	Kappa #	Brightness
Acetone	12.5.6/10.1	35.0/36.9
2-Butanone	14.6/12.2	32.4/34.1
3-Pentanone	18.0/16.6	29.8/29.8

[a] see Table 1 for a complete description of the softwood kraft pulp; the first value given in each column was determined after bleaching, the second value was determined after bleaching and caustic extraction.

Application of Biobleaching Technology for Improved Oxygen-Based Bleaching Technology

1. Introduction

Over the last decade worldwide concern has developed over the impact that industrial processes, including pulp and paper operations, have on the environment.[1] In response to these concerns, kraft pulp bleaching operations have begun to modify their processes to improve their environmental performance.[2] Research efforts are also ongoing to develop oxygen-based bleaching agents as replacements for chlorine. Although many potential chemical agents have been examined, only a selected few appear to possess attractive bleaching properties. Currently, the most promising oxygen-based bleaching chemicals are molecular oxygen,[3] ozone,[4] hydrogen peroxide,[5] and dimethyldioxirane (DMD).[6]

Fortuitously, developments in nonchlorine bleaching have been paralleled by advances in biobleaching technology.[7] Preliminary research studies by Viikari et al. in 1986 demonstrated that the pretreatment of kraft pulps with xylanase (X) was effective at reducing the amount of chlorine needed to achieve a target brightness.[8] In addition to the reduced chemical costs, the enzyme pretreatment procedure was shown to lower the chloro-organics present in the pulp and in the effluent.[9] From these initial studies, significant resources have been directed toward transferring this technology from the laboratory to the paper mill.[10] Numerous laboratory[11] and mill studies[12] have made it apparent that pretreatment of kraft pulps with xylanase significantly enhances the bleachability of these pulps for chlorine-based bleaching sequences such as (DC)EDED or DEDED.[13] Typical savings for active chlorine average about 25%, and reductions in AOX range from 15 to 25%.

The development of oxygen-based bleaching agents for kraft pulps opens an alternative avenue of research for biobleaching technology. Based upon the synergism observed between xylanase and chlorine/chlorine dioxide bleaching procedures we had anticipated that biobleaching technologies could improve the bleaching efficiency, pulp properties, and chemical costs associated with oxygen-based bleaching technologies. Indeed, recent research studies in our laboratory and others have demonstrated that xylanase can substantially improve the bleaching performance of several oxygen-based bleaching agents. Figures 1 and 2 summarize some of the bio-bleaching benefits that we have previously observed when treating kraft pulp with either ozone or DMD.[14] To explore the potential value of biobleaching kraft pulps to high brightness values, we elected to examine the synergistic interactions for xylanase treated softwood kraft pulps bleached with ozone, DMD, hydrogen peroxide and chlorine dioxide.

2. Experimental

The EMCC oxygen-delignified softwood kraft pulp employed for the experiments summarized in Table 1 was acquired from a commercial source. An alternative commercial source of EMCC softwood kraft pulp was utilized for the remaining experiments. A standard oxygen delignification procedure was applied to the latter pulp.[15] The X, W and Z stages were preformed following previously established bleaching protocols developed in the authors laboratories.[14]

Chlorine-dioxide, free of elemental chlorine was employed for the ECF bleaching experiments. The bleaching solution was prepared by calculating the amount of free chlorine in the solution and adding stoichiometrically equivalent amount of sodium chlorite. All D stages were carried out in glass Mason jars.

The P stages were preformed at 70° C employing 3% hydrogen peroxide at 12% consistency for 2 h.

The (EO) stages were preformed at 10% consistency, 1% caustic and 60 psi for 1 1/2 h. The E stages were preformed at RT using 1.5% caustic and at 3% consistency.

3. Results and Discussion

<u>**Xylanase/Ozone:**</u> Although our earlier studies had identified xylanase pretreatment

as a promising method of improving the bleaching efficiency of ozone, these preliminary studies did not determine if these benefits had an impact on the final stages of bleaching.[14] Furthermore, since oxygen-delignification is commonly employed prior to ozone bleaching, the need to examine the biobleaching effects on these types of pulps was readily apparent.[15] Although it has been speculated that xylanase will not enhance the bleaching properties of oxygen delignified kraft pulps, recent laboratory studies and mill trials have shown clear benefits for employing xylanase on an oxygen-delignified kraft pulp prior to either bleaching with chlorine and/or chlorine dioxide.[16] A recent report by Eriksson has extended these biobleaching studies to oxygen delignified eucalyptus kraft pulp which was subsequently bleached with ozone and hydrogen peroxide.[17]

As a preliminary investigation of the biobleaching effects of xylanase, we treated a commercial oxygen delignified softwood kraft pulp with xylanase and then ozonated and extracted these pulps. As a control we repeated the xylanase stage with a control wash (W-stage) which replicates the biobleaching treatment in all experimental features except that the enzyme is omitted. This latter pulp was then bleached with ozone and extracted under the same conditions employed for the enzyme treated pulp. The results from these experiments are summarized in Table 1. A review of this data indicates that the incorporation of an oxygen stage prior to xylanase has a detrimental effect on the performance of the biobleaching process. After the enzyme treatment we were unable to observe any substantial changes in the nature of the control and enzyme treated pulps. Furthermore, when these two pulps were treated with a 0.5% charge of ozone, the xylanase treated pulps do not exhibit substantial improvements in the delignification or brightness. The results after caustic extraction failed to show any improved performance for the enzyme treated pulps. These results are in contrast to our previous studies which had shown clear benefits of pretreating a conventional kraft pulp (i.e., not oxygen delignified) with xylanase prior to ozone bleaching. Presumably the inclusion of an O-stage alters the nature of the residual lignin and hemicellulose present in the pulp and these two factors contribute to reducing the efficiency of xylanase treatment.

As a follow through to these preliminary results we repeated the studies on a large scale with an EMCC, oxygen delignified southern softwood kraft. Following our standard experimental procedures, xylanase treated and control pulps (W-stage) were prepared and characterized according to brightness, viscosity and lignin content. These results, summarized in Table 2, indicate that the xylanase procedure did result in the removal of additional lignin as exhibited by a difference of 0.4 kappa units between the OX and OW pulps. The drop in lignin content for the OX pulp also resulted in a 5% brightness gain for the enzyme treated pulp. Unfortunately, the usually observed gain in viscosity for the xylanase treated pulp was not apparent and the enzyme treated pulp exhibited a 4% drop in viscosity in comparison to the starting O_2 brownstock. Although it is difficult to fully explain the differences observed between these two sets of experimental results, undoubtedly part of the answer is due to the different pulping conditions employed in preparing the brownstock and perhaps changes in the types of softwood furnish. Studies directed at further understanding these factors are currently ongoing.

To evaluate the impact of xylanase on the latter stages of bleaching, we treated the biobleached and control pulps with a 0.6% charge of ozone at high consistency and then washed and extracted the pulps with an oxygen reinforced caustic extraction (1%, 60 psi). Analysis of these pulps indicated that the differences in lignin content between the OXZ and OWZ were diminished while differences in brightness and viscosity remained approximately the same. Nonetheless, since the full effects of xylanase pretreatment are frequently observed only after the final bleaching stage we elected to investigate these effects by treating the pulps with either DMD, hydrogen peroxide, or chlorine dioxide.

Xylanase/ECF: The OXZ(EO) and OWZ(EO) pulps were treated with three different charges of chlorine dioxide and changes in brightness between the two pulps were determined. These results and selected viscosity values are summarized in Table 3. Examination of the ECF bleaching results clearly demonstrates that the xylanase treated pulps responded more effectively to chlorine dioxide than the control pulps as determined by the final brightness values for the fully bleached pulps. Also of interest is the observation that the lower the charge of chlorine dioxide employed the more beneficial the biobleaching effect becomes. Presumably this response pattern is due to diminishing gains in delignification at the higher chlorine dioxide charges. The changes in brightness are also accompanied by changes in the viscosity values. Viscosity determinations for the pulps bleached with 1.2% charge of chlorine dioxide indicate that the loss in viscosity between the (EO) stage and the D stage are reduced for the xylanase treated pulp and as a result the differences in viscosity for the OW(EO)D and OX(EO)D pulps are diminished.

Xylanase/TCF: A review of the literature indicates that TCF bleaching of softwood kraft pulps to high brightness values is one of the most difficult challenges that the industry may encounter in the near future.[18] Although ozone will undoubtedly be employed for the production of TCF pulps, the need for an additional brightening agent in manufacturing high brightness TCF pulps is of substantial interest. Based upon these concerns, we examined the use of hydrogen peroxide or DMD as a last stage in bleaching the OZ(EO) pulps. These results are summarized in Tables 4 and 5, respectively. Two stages of hydrogen peroxide were employed. The first stage employed a 3% hydrogen peroxide charge and the caustic charge was varied from 0.8% to 1.8%. The second P-stage utilized a 3% charge of hydrogen peroxide and a 1.4% charge of caustic. An examination of the brightness values indicates that the enzyme treated pulps clearly responded more favorably to the hydrogen peroxide treatment than the control pulps. Furthermore, the control pulps do not reach the brightness values of the xylanase treated pulps regardless of the exact experimental conditions employed. A comparison of these results with the previous results observed for the ECF bleaching experiments clearly indicate that chlorine dioxide provides substantially higher brightness pulps at lower chemical charges. These differences are undoubtedly due to the diminished oxidative bleaching capabilities of hydrogen peroxide.

Examination of the viscosity values for the fully bleached TCF pulps indicates that the enzyme treated pulps are of lower viscosity than the control pulps. A comparison of the viscosity values before and after the two P-stages also indicates that the enzyme treated pulps exhibit greater viscosity losses than the control pulps. Nonetheless, the viscosity differences between the pulps after the (EO) stage and the fully bleached pulps has narrowed. These latter results are comparable to the ECF bleaching results.

Finally, we also examined the use of DMD as a TCF brightening agent. Employing a 50% charge of peroxymonosulfate, the OXZ(EO) and OWZ(EO) pulps were treated with an aqueous acetone solution under conditions previously shown to favor the in-situ generation of DMD. The results of these studies are summarized in Table 5. Although the enzyme treated pulps responded more favorably to DMD than the control pulps, a comparison of these results with the hydrogen peroxide bleaching experiments clearly suggests that hydrogen peroxide is a more efficient brightening agent than DMD. Recent studies by McDonough et al. have shown comparable results indicating the use of DMD is preferred in the early stages of bleaching.[19]

4. Conclusions

The results of these investigations illustrate several important features of the biobleaching phenomena as it applies to oxygen-based bleaching technologies. First, the application of oxygen-delignification prior to a xylanase-stage appears to diminish the biobleaching effect on ozone. This undoubtedly occurs in part due to the removal of hemicelluloses during oxygen bleaching. Nonetheless, a xylanase stage after oxygen delignification does provide beneficial results for subsequent bleaching stages although these results become apparent only in the final bleaching stage. Given the recent interest in developing high brightness TCF bleaching sequences for softwood kraft pulps, these results support a continuing role for biobleaching technology in the development of oxygen-based bleaching procedures.

Future developments in biobleaching will include the production and use of alternative hemicellulases, enzymatic delignification procedures and a refined understanding of the fundamental mechanisms contributing to biobleaching. These advances promise to accelerate the incorporation of these bioassisted bleaching technologies into the kraft mill of the future.

Acknowledgements: The author wishes to thank the member companies of IPST and ICI Canada for support of the studies described in this report.

Figure 1: Biobleaching Effect For Ozone Treatment of Softwood Kraft Pulp

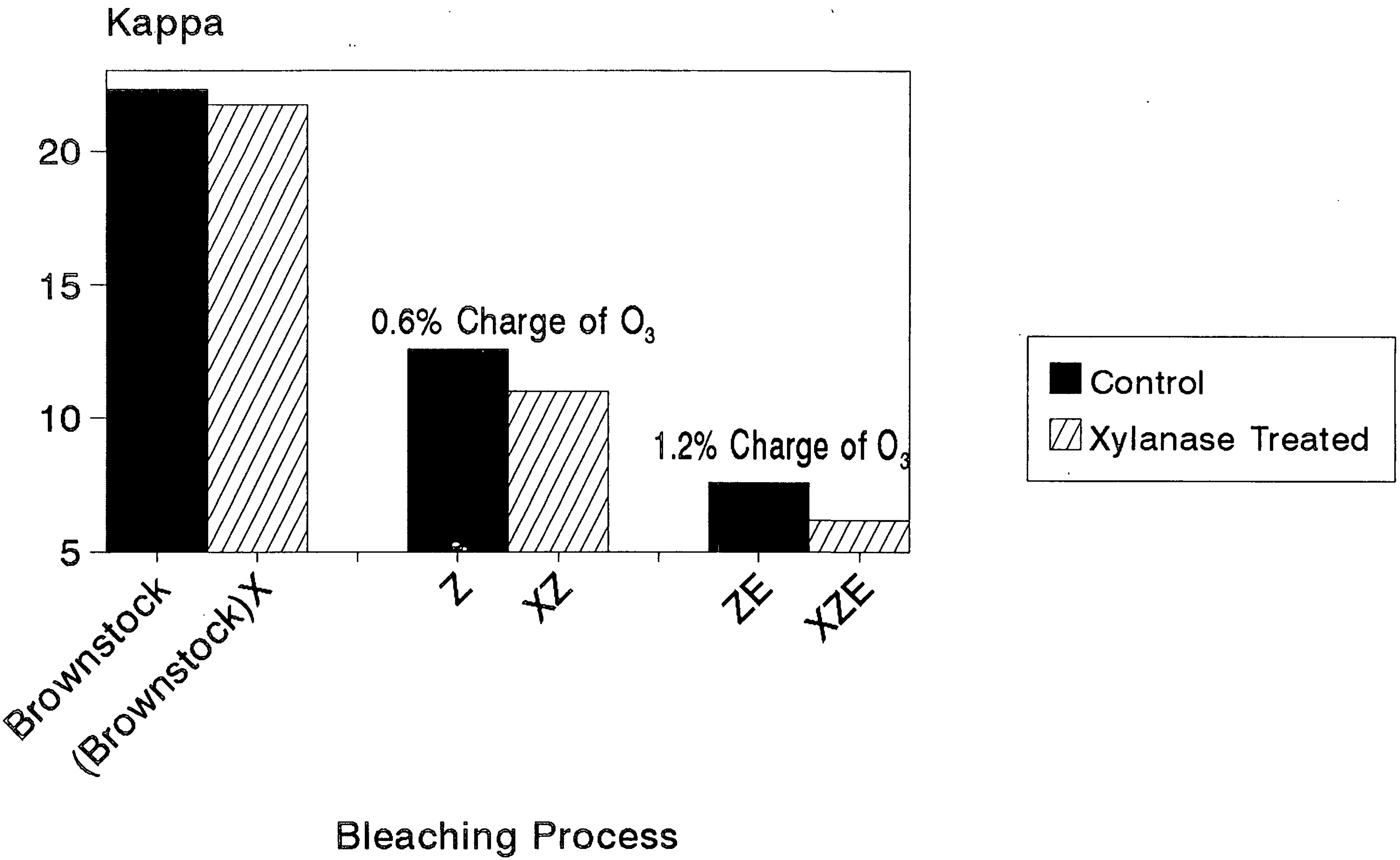


Figure 2: Biobleaching Effects on DMD Bleaching of Kraft Hardwood

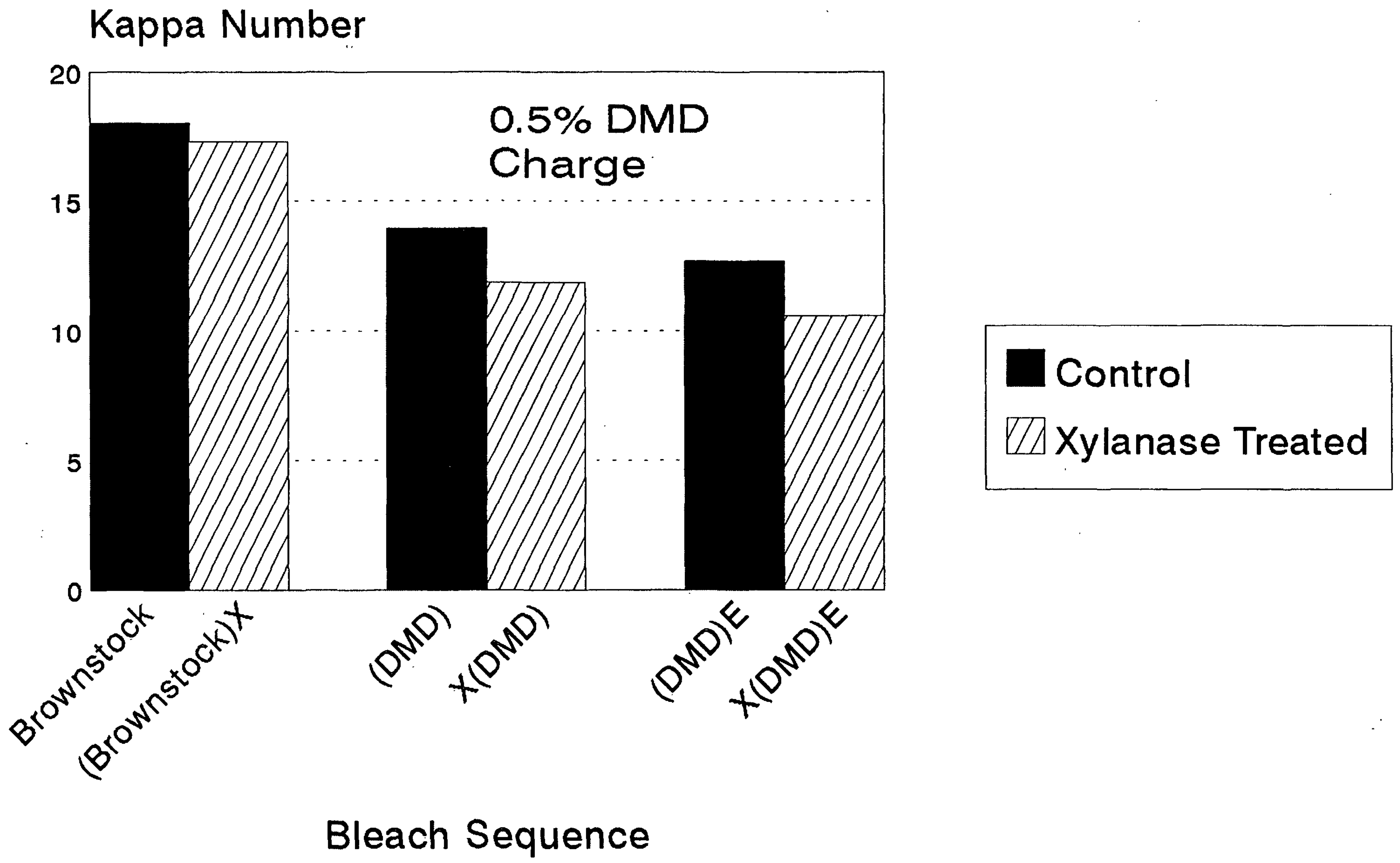


Table 1: Evaluation of Xylanase Pretreatment of O2-Delignified Softwood Kraft Pulp For Ozone Bleaching.

	Pulp Properties	
Sequence[a]	Kappa #	Tappi Brightness
O_2 Brownstock		
OX	10.0	39.8
OW	9.9	40.3
OXZ	5.6	53.8
OWZ	5.8	53.2
OWZE	3.7	58.5
OXZE	3.8	57.6

[a] see experimental for general experimental conditions; ozone bleaching reactions employed a 0.5% charge of ozone.

Table 2: Evaluation of Xylanase Pretreatment of O2-Delignified EMCC Softwood Kraft Pulp For Ozone Bleaching.

		Pulp Properties	
Sequence[a]	Kappa #	ISO Brightness	Viscosity/mPa.s
Brownstock	19.3	26.5	32.3
O_2 Brownstock	9.6	36.2	19.8
OX	8.9	39.5	18.9
OW	9.3	37.6	20.1
OXZ	3.6	56.9	12.4
OWZ	3.8	55.6	13.2
OXZ(EO)	2.2	63.5	10.6
OWZ(EO)	2.1	62.3	11.5

[a] see experimental for general experimental conditions; ozone bleaching reactions employed a 0.6% charge of ozone.

Table 3: Chlorine Dioxide Bleaching Results for OXZ(EO) and OWZ(EO) Treated Softwood EMCC Kraft Pulps.

		Pulp Properties		
Pulp	% D Charge[a]	Residual %D	ISO Brightness	Viscosity/mPa.s
OXZ(EO)	0.4	0.03	86.3	--
	0.8	0.15	88.6	--
	1.2	0.32	89.1	10.8
OWZ(EO)	0.4	0.02	84.6	--
	0.8	0.13	87.6	--
	1.2	0.32	88.3	10.5

[a]see experimental section for further experimental details.

Table 4: Hydrogen Peroxide Bleaching Results for OXZ(EO) and OWZ(EO) Treated Softwood EMCC Kraft Pulps.

			Pulp Properties After 2nd P-Stage[a]	
Pulp	Charge for 1st P	ISO Brightness	ISO Brightness	Viscosity/mPa.s
OXZ(EO)				
	3% P/0.8% NaOH	82.8	86.4	---
	3% P/1.4% NaOH	83.0	86.6	5.8
	3% P/1.8% NaOH	82.4	86.6	5.8
OWZ(EO)				
	3% P/0.8% NaOH	81.8	85.3	---
	3% P/1.4% NaOH	82.0	85.7	---
	3% P/1.8% NaOH	81.8	86.0	6.2

[a]3% charge of hydrogen peroxide and 1.4% charge of caustic and 0.05% $MgSO_4$.

Table 5: In-Situ DMD Bleaching Results for OXZ(EO) and OWZ(EO) Treated Softwood EMCC Kraft Pulps.

Pulp	ISO Brightness	
	In-Situ DMD[a]	In-Situ DMD/Caustic Extraction
OXZ(EO)	82.8	83.0
OWZ(EO)	82.0	82.2

[a] applied a 50% charge of peroxymonosulfate following previously established methods for in-situ generation of DMD.

Literature Cited

1. Amato, I., Science 261, 152 (1993).
2. Hise, R.G., Proceedings of 1992 TAPPI Bleach Plant Operations Short Course, 8-1, 201 (1992).
3. McDonough, T.J., Tappi 69(6):46 (1986).
4. Byrd, M.V.; Gratzl, J.S.; Singh, R.P., TAPPI J., 75(3), March, 207 (1992).
5. Lierop, B.v.; Liebergott, N.; Faubert, M.G., 79th Annual CPPA Meeting, Technical Section, Montreal, B81 (1993).
6. (a) Ragauskas, A.J.; Rodriguez, A.; Senior, D.J.; Qui, C., Proceedings of the Non-Chlorine Bleaching Conference, Hilton Head, South Carolina, 1993.
   (b) Ragauskas, A.J., TAPPI J., 76, July, 87 (1993).
   (c) Murray, R.W.; Hunt, K.; Lee, C.L., 79th Annual CPPA Meeting, Technical Section, B167 (1993).
   (d) Lee C.-L., Bleaching of Lignocellulosic Material with Dioxirane. PCT, International Publication Number, WO 91/12369, Aug. 22, 1991.
7. Trotter. P.C., TAPPI J. 73, April, 198 (1990).
8. Viikari, L.; Ranua, M.; Kantelinen, A.; Linko, M.; Sundquist, J., Proceedings of 1987 International Symposium on Wood and Pulping Chemistry, Paris, 1, 151 (1987).
9. Senior, D.; Hamilton, J., J. Pulp and Paper Science, 18 (5), J165 (1992).
10. Senior, D.J.; Hamilton, Pulp and Paper, September, 111 (1992).
11. a) Manoir, J.R.; Hamilton, J.; Senior, D.J.; Bernier, J.E.; Moser, L.E.; Dubelsten, P,. Proceedings of the 1991 International Pulp Bleaching Conference, Stockholm, 2, 123 (1991).
   (b) Pedersen, L.; Elm, D.D.; Nissen, A.M.; Choma, P.P., Proceedings of the 1991 International Pulp Bleaching Conference, Stockholm, 2, 107 (1991).
   (c) Skerker, P.S.; Farrell, R.L.; Chang, H.-m., Proceedings of the 1991 International Pulp Bleaching Conference, Stockholm, 2, 93 (1991).
12. (a) Turner, J.C.; Skerker, P.S.; Burns, B.J.; Howard, J.C.; Alonso, M.A.; Andres, J.L., TAPPI J. 75, December, 83 (1992).
   (b) Scott, B.P.; Young, F.; Paice, M.G., 79th Annual CPPA Meeting, Technical Section, B167 (1993).

13. a) Lahtinen, T.; Ojapalo, P.; Laukkanen,A.; Senior, D., Spring Conference CPPA, Technical Session, Whistler, BC, May (1993).
    b) Tolan, J.S., CPPA Annual Meeting Preprints, A164 (1992).
14. Ragauskas, A.J.; Poll, K.M.; Cesternino, A.J., Enzyme and Microbial Technology, May 1 (1994).
15. Liebergott, N.; Lierop, B.v.; Skothos, T., TAPPI J., 75, February, 117 (1992).
16. Yang, J.L.; Lou, G.; Eriksson, K.-E., TAPPI J., 75, December, 95 (1992).
17. Yang, J.L.; Sacon, V.M.; Law, S.E.; Eriksson, K.-E. L., TAPPI J., 76, July, 91 (1993).
18. Macas, T.S.; Jiang, J.E.; Becker, E.S.; Greenwood, B.F., 1991 International Pulp Bleaching Conference Proceeding, SPCI,Stockholm, 67 (1991).
19. McDonough, T.J.; Marquis, A.; Ragauskas, A.J., "Totally Chlorine Free Bleaching with Dimethyldioxirane" manuscript accepted for the 1994 Pulp Bleaching Conference.

SULFUR-FREE SELECTIVE PULPING PROCESS
PROJECT 3661

Donald R. Dimmel
Xiaoqi Pan

and the staff at
National Renewable Energy Laboratory
(Golden, CO)

March 23, 1994

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, GA 30318

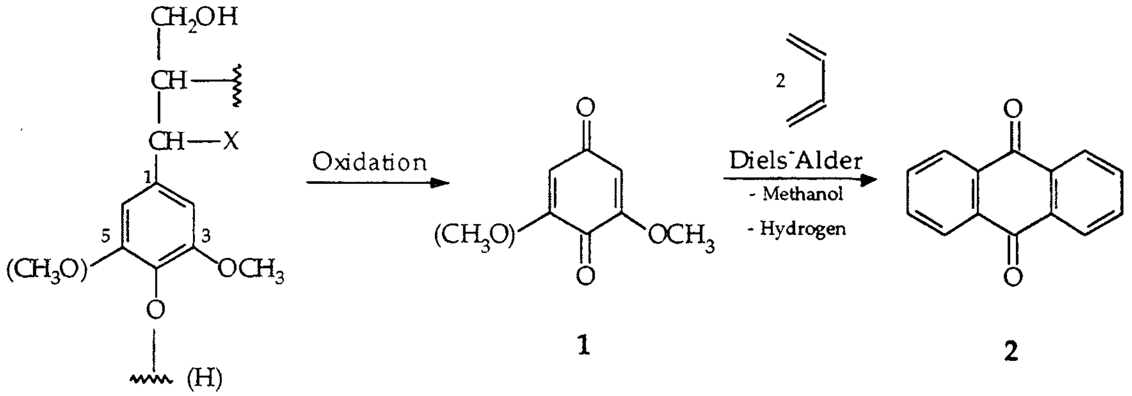
TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE:	SULFUR-FREE SELECTIVE PULPING PROCESS
PROJECT STAFF:	Donald R. Dimmel and Xiaoqi Pan, and staff at the National Renewable Energy Laboratory (Golden, CO)
BUDGET (FY 94-95):	$200,000
REPORTING PERIOD:	March 1993 - February 1994
DIVISION:	Chemical and Biological Sciences
PROJECT NUMBER:	3661
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.
IPST GOAL:	Improved pulping processes

SUMMARY:

A joint research effort between the Institute of Paper Science and Technology and the National Renewable Energy Laboratory is being conducted on ways to produce cost-effective pulping catalysts from lignin. The principal focus of the research has been addressing the most important factor in the cost of the catalysts, namely the overall yield of the synthesis. The synthesis involves treating a low-molecular-weight lignin with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones (Fig. 1, structure **1**), which are converted into nonaromatic anthraquinone (AQ) precursors by treatment with a diene (Diels-Alder reac-

tion). Final conversion of these precursors to AQ derivatives 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.



1

2

Lignin

DMBQ = two OCH3 groups
MMBQ = one OCH3 group

Anthraquinone

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

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%). The yield of benzoquinones from lignin needs to be near 50% to reach our targeted catalyst price of $1.00-1.50/lb. Research with lignin model compounds has indicated that simple NO_2/O_2 oxidization only works well on phenolic, syringyl lignin units. This means that only *terminal* syringyl end units of a *hardwood* lignin polymer will be converted to benzoquinones by simple NO_2/O_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. However, such a step probably would not be practical 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/O_2 oxidation step.

There appears to be two ways to get high (on a relative basis) yields of DMBQ from

NO_2 oxidation of a lignin. One is to lower the molecular weight of a whole lignin with treatments, such as copper oxide, before performing the NO_2/O_2 oxidation. The other is to extract a lignin sample to obtain a low-molecular-weight fraction before NO_2/O_2 oxidation.

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.

BACKGROUND OF PAST PROJECT ACTIVITY

The synthesis of a low-cost anthraquinone catalysts from lignin began in 1985 with the start of John Wozniak's Ph.D. thesis. The thesis research demonstrated the feasibility of converting lignin materials to AQ catalysts and led to three publications, two patents, and the start of a DOE-funded research project between IPST and NREL in the summer of 1988. 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,[1-6] and in the annual reports to DOE.[7-11]

The funding from DOE was continuous from August 1988 to October 1992. A break in funding occurred between October 1992 and February 1994; however, some research funds were stretched into 1993. The project, with a new annual budget of $600,000 (half to IPST), is again in full swing. The majority of the research results of 1993 were presented in our last annual Status Report; therefore, there are no new results to report on at this time. The future activity section that follows is identical to that previously presented.

FUTURE ACTIVITY

The objective of future research will be to move the successful results of the laboratory research to a larger scale. Our primary focus will be to prepare the best possible package to present to the industry for technology transfer. However, the scale up effort needs to be supported by continued research in process improvement to assure that a most cost-effective approach is taken. Each component of the process will be subjected to a technoeconomic evaluation and judged for its overall merit.

Lignin Processing. Regardless of the lignin source, scale up of the extraction is an important step in development of a commercial process. A number of different features must be considered since each has a bearing on the overall economic feasibility of the process. These features include:

- assessment of appropriate sources of lignin, i.e., extraction of an isolated lignin or crude pulping liquors,
- comparison of the yield of low-molecular-weight material obtained on a larger scale process to that of the laboratory scale,
- the physical characteristics of a given low-molecular-weight lignin, such as detailed structure, average molecular weight, etc., both before extraction and after isolation of the low-molecular-weight material,
- the performance of the low-molecular-weight lignin in subsequent chemical processing, and
- the economic feasibility of the proposed extraction, based on the material balance of the extraction process and the efficiency of recovery and reuse of the extraction solvents.

To fully explore the utility of organosolv lignins, NREL intends to design and build an extraction device of suitable size to prepare between one and ten pounds of a low-molecular-weight fraction from a whole organosolv lignin. In addition, we are currently working with a commercial producer of organosolv pulp and lignin to obtain pulping liquor for evaluation as a source of lignin for catalyst synthesis.

Catalyst Production. The results of our research program has shown that each step of the lignin-to-catalyst process is chemically feasible, using low cost reagents and conditions.[7-11] However, several areas still need to be addressed; these include:

improving the yield of the oxidation of lignin to benzoquinones, optimizing the Diels-Alder conditions, completing a set of synthesis steps with moderate amounts of materials, and testing the catalyst mixture for pulping activity.

1) A scaled up experiment will be carried through using the best conditions to date. The results of the experiment will be used as a basis for further process improvements and to update economic evaluations. The steps consist of:

  a) a low-molecular-weight lignin NO_2 oxidation,
  b) without purification, or with minimum purification, the NO_2 oxidation product will be treated with a diene,
  c) the resulting product will be tested for catalytic pulping activity, and
  d) the products from each reaction in sequence will be analyzed as completely as possible by available spectroscopic techniques.

2) Process improvement chemistry will continue in the following areas:

  a) Oxidation technology. Heteropoly anion catalyzed chemistry, both with peroxide and oxygen as cheap and clean oxidizing agents, as well as improvement of the NO_2 technology will be examined. Lignin structures will be correlated to product yields to guide scale up efforts. The dimer models will be used to explore alternative conditions which would cleave the linkages between lignin units as the oxidation reactions proceed. The results of such studies will be applied to more complex lignin structures in order to optimize the overall yield of benzoquinones from the oxidation step of the process.
  b) Byproducts. Examination of byproducts from lignin oxidation procedures will be assessed to determine the need and methodology for recovery of unreacted oxidant and methods to handle spent reagents. This information is important to the process economics.
  c) Diels-Alder reaction. Continue emphasis will be placed on optimizing yields in water as the solvent. New Diels-Alder catalysts, based on titanium and ruthenium, will be synthesized and investigated as a means to improve yields in non aqueous solvents.

3) Other biomass will be investigated in the oxidation technology. The emphasis will remain on pulping byproducts; however, bleach plant byproducts (new waste

minimization technology), wood pyrolysis products and select non-woody materials will be screened.

Some specific technical areas to be assessed include:

- evaluating conditions leading to complete oxidation of a lignin dimer,
- correlating lignin structure with reactivity towards oxidizing agents,
- improving MMBQ yields from softwood lignin oxidation by metal/H_2O_2,
- examining the potential of "early-stage" lignin, organosolv lignin phenolics, and bleach liquors for generating benzoquinones,
- examining reductive lignin fragmentation procedures to develop starting materials for the catalyst synthesis,
- determining the economically feasible of C-5 functionalization of lignin prior to oxidation, and
- developing methods for obtaining consistent high yields of aromatic components from the Diels-Alder reactions.

Catalyst Performance. Pulping with AQ is a well studied process. However, the catalysts from our process will be part of a quinone containing mixture, which may include substituted AQ, AQ precursors, and unreacted low-molecular-weight lignin. The catalysts mixtures, prepared using the best synthetic routes, will first be evaluated for their ability to catalyze pulping on a small scale. Rate efficiencies of the mixtures will be determined. The best catalyst mixtures will then be tested on larger scale so that evaluation of the pulp quality and ease of chemical recovery from these liquors can be determined.

Work will be initiated on the detailed compositional analysis of the catalyst mixture remaining on the pulps. Such analyses may be required for FDA approval of the new process; however, AQ is already an approved pulping catalyst, components in the mixture are closely related to AQ, and most of the catalyst components are burned in the chemical recovery cycle.

The pulps will also be analyzed for normal strength properties, and, importantly, their bleachability. The bleaching tests will be carried out with different bleaching strategies: sequences that have chlorine-containing agents (principally chlorine dioxide) and others which do not. The latter bleaching strategy will lead to substantial environmental benefits by giving both a sulfur-free and chlorine-free pulp.

The spent pulping liquors will be evaluated, initially at a small scale. The recovery of these liquors will be similar to the recovery of a soda liquor; substantial energy and cost savings are expected compared to the conventional kraft process. For example, if a fluidized-bed combustion process can be combined with autocausticizing technology, a major reduction in capital cost of recovery will be obtained.

The technical areas to be assessed in this portion of the research include:

- pulping studies to define appropriate catalyst levels and strength parameters of the resulting pulp,
- bleaching studies to define the amounts and types of bleaching chemicals that are required for these pulps,
- developing chemical recovery technologies that compliment the less complex chemical system and contribute to the cost savings, and
- analyzing pulps for residual catalysts.

At this point, a more complete comparative technoeconomic analysis will be carried out based on these experimental results and performance of the operation at a small scale. These data will substantiate the projected energy and cost savings and provide the industry with the necessary information before investment in a pilot facility. The overall process will then be defined, and will underscore low overall emissions to air or waste water streams.

Catalyst Scale Up. As the program proceeds, the most promising technology for chemical processing of the low-molecular-weight lignin will be scaled to a larger size. The objective is to prepare between 0.5 and 5 lb. of pulping catalyst from low-molecular-weight lignin using this technology and to estimate the cost of producing this level of material as a guide to future scale up costs. The following areas will be considered:

- equipment design for scale up of the lignin isolation and chemical steps,
- the effect of scale up on product yields, quality, and distribution, and
- the economic feasibility of the different technologies.

REFERENCES

1. Wozniak, J. C.; Dimmel, D. R.; and Malcolm, E. W. "The Generation of Quinones from Lignin and Lignin-Related Compounds," J. Wood Chem. Technol., 9, 499 (1989).

2. Wozniak, J. C.; Dimmel, D. R.; and Malcolm, E.W. "Diels-Alder Reactions of Lignin-Derived Quinones," J. Wood Chem. Technol., 9, 513 (1989).

3. Wozniak, J. C.; Dimmel, D. R.; and Malcolm, E. W. "Lignin-Derived Quinones as Pulping Additives," J. Wood Chem. Technol., 9, 535 (1989).

4. Dimmel, D. R.; and Wozniak, J. C. "Preparation of Quinone-Related Substances and Their Use in the Delignification of Lignocellulosic Materials," U. S. Patent 5,002,634, March 1991.

5. Dimmel, D. R.; and Wozniak, J. C. "Lignin Derived Quinone Compound Mixtures Useful for the Delignification of Cellulosic Materials," U. S. Patent 5,049,236, September 1991.

6. Dimmel, D. R.; and Bozell, J. J. "Pulping Catalysts from Lignin," Tappi Journal, 74 (5), 239 (1991).

7. DOE Annual Report on Contract No. AC02-83CH10093, Power, A. J., Bozell, J. J., and Chum, H. L., "Preliminary Feasibility Study of Pulping Catalyst Production from Lignin," November 1989.

8. DOE Annual Report on Contract No. AC02-83CH10093, Bozell, J. J., Hames, B., Chum, H. L., Dimmel, D. R., Van Vreede, P. J., Karim, M. R., and von Oepen, D. G., "Sulfur-free Selective Pulping," August 1990.

9. DOE Annual Report on Contract No. AC02-83CH10093, Power, A. J., Bozell, J. J., and Chum, H. L., "Pulping Catalyst Production from Lignin: A Technoeconomic Appraisal," December 1990.

10. DOE Annual Report on Contract No. AC02-83CH10093, Bozell, J. J., Hames, B., Chum, H. L., Dimmel, D. R., Althen, E., Caldwell, P. L., Daube, A. K., and Kuroda, K.-I.,"Sulfur-free Selective Pulping," March 1992.

11. DOE Annual Report on Contract No. DE-AC02-83CH10093, Bozell, J. J., Hames, B., Chum, H. L., Dimmel, D. R., Kuroda, K.-I., and Pan, X., "Sulfur-free Selective Pulping," Available March 1993.

FUNDAMENTALS OF BRIGHTNESS STABILITY
PROJECT 3524

Arthur J. Ragauskas
Xiaqui Pan

March 23, 1994

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, GA 30318

TECHNICAL PROGRAM REVIEW

FY 1993-94

Project Title:	FUNDAMENTALS OF BRIGHTNESS STABILITY
Project Code:	BRITE
Project Number:	3524
Division:	Chemical and Biological Sciences
Project Staff:	A.J. Ragauskas, X. Pan
FY 93-94 Budget:	$99,980
FY 94-95 Budget:	$100,000

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:

<u>Past Studies</u>: 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 the several UV absorbers, such as substituted hydroxyphenyl 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.

Along with the development of UV absorbers for mechanical pulp, we have also examined the use of several antioxidants to photostabilize mechanical pulps. Research efforts demonstrated that ascorbic acid, although effective at photostabilizing mechanical pulps, actually accelerated thermal reversion properties. Several co-additives were examined as potential methods of halting the thermal discoloration process but these attempts were not successful. Given the commercial interest in developing ascorbic acid as a photostabilizer for mechanical pulps, this study has served as a bench mark demonstrating the importance of evaluating both thermal and brightness reversion properties of any chemically stabilized mechanical pulp.

Research studies have also examined the ability of dithiols derivatives to stabilize mechanical pulps. The results of these investigative studies clearly defined the roles by which mercaptans retard photo-yellowing of mechanical pulps. These studies provide the first experimental results demonstrating that thiols retard reversion by scavenging radicals and removing chromophores from kraft pulp.

1993-94: Our research efforts for the last fiscal year have attempted to build on our previous efforts. Having identified several new and promising di-thiol additives which retarded brightness reversion, we attempted to incorporated this functionality into a polymeric structure. The use of a thiol-polymer to stabilize mechanical pulp was initiated on the assumption that these high-weight materials would not have any malodorous properties. Our initial target was to chemically derivatize cellulose. Although we were successful in preparing a thio-cellulose compound, the resulting material did not act as a photostabilization agent for high-yield pulps. This initial difficulty demonstrated the need to manufacture a flexible-thiol polymer which would effectively interact with mechanical pulp fibers. To this end, we applied di-thiol polyethylene glycols onto mechanical pulp samples and were able to retard the overall photo-yellowing properties of test handsheets. This result validated our hypothesis that polymeric thiols could stabilize mechanical pulps, provided that the additives were not rigid and coated mechanical fibers effectively. Our preliminary studies have also shown that the use of thiol polymers does remove the malodorous properties of thiols.

The development of new polymeric thiol-based additives has been coupled to research efforts directed at determining what types of mercapto compounds are most effective at stabilizing mechanical pulps. Our research efforts have shown that thiol-derivatives do not retain their photo-stabilization abilities during prolonged storage. In contrast, disulfide ethers have been shown to be thermally stabile for extended periods of storage. Unfortunately, these additives are not as effective at photostabilizing mechanical pulps. Preliminary photo-aging with disulfides have suggested that their photostabilization properties can be improved. Future studies will attempt to further develop the effectiveness of these additives.

GOALS FOR FISCAL YEAR 94-95:

Future research studies will examine methods of unifying several photostabilization technologies. We believe that a mixture of a UV absorber/quencher and a radical scavenger will act synergistically when applied onto high-yield pulps and provide a very effective means of photostabilizing mechanical pulps. Research studies will therefore examine the use of thiols and thiol ethers with benzophenones and hexadienoic acid.

Furthermore, our past research efforts have shown that the malodorous properties of thiols can be removed by incorporating these additives into a polymer. We plan to incorporate thiol based compounds into starch and cellulose derivatives, thus developing a new class of antioxidant stabilizers which would be bio-degradable and not retain any offensive properties.

Finally, as these studies advance we will continue to explore the mechanisms by which these new photostabilizing additives interact with mechanical pulps to retard brightness reversion.

Introduction

The manufacturing of high-yield pulps has advanced substantially over the last few decades. Modern mechanical pulping technology provides furnishes with brightness values greater than 85% which can be readily incorporated into a variety of paper products. The principle obstacle for increased use of these grades of pulp is their well known tendency to undergo photoyellowing.[1] The photochemical mechanisms contributing to brightness reversion have been extensively studied.[2] It is generally accepted that the basic mechanism of photoyellowing involves three reaction pathways:

- Direct absorption of UV light by conjugated phenolic groups to form phenoxyl radicals;
- Abstraction of phenolic hydroxyl hydrogen by aromatic carbonyl triplets;
- Cleavage of non-phenolic phenacyl-α-O-arylethers to phenacyl/phenoxyl free radical pairs.

Based on the proposed mechanisms, a potential means of inhibiting brightness reversion is the addition of a radical scavenging agent that may compete with free phenolic units in lignin, thereby preventing the formation of highly reactive phenoxyl radicals. Mercaptans are efficient hydrogen donors and various sulfur-containing compounds act as antioxidants for synthetic polymers.[3] When applied onto a variety of mechanical pulps, sulfur-containing compounds have been found to possess bleaching and/or photostabilization effects.[4] Cole and Sarkanen have proposed that the photostabilization effects may be due to radical scavenging and Michael-type additions to chromophoric compounds.[5]

The objective of this study was to investigate the impact of long term storage on the photostabilization effects of well known mercapto-stabilizers and to determine the role of Michael-type additions of thiols during brightness reversion.

Results and Discussion

Practical considerations require that any additive applied onto mechanical pulps must fulfill several other criteria including thermal stability and the retention of photostabilization effects over certain periods of storage. To date, no studies have been done to examine the photostabilization effects of sulfur containing compounds after prolonged storage on mechanical pulps. Furthermore, it is frequently assumed that any additive that provides effective photostabilization of mechanical pulps will not detrimentally impact upon the thermal discoloration of mechanical pulps. This assumption has been shown to be incorrect for ascorbic acid. Research studies in our laboratory have demonstrated that ascorbic acid promotes thermal discoloration of mechanical pulps.[6]

To evaluate the thermal aging properties of mercapto-stabilized BCTMP pulps, we impregnated a series of handsheets with sulfur additives which have been previously examined in the literature. Table 1 summarizes the types of additives which were applied onto BCTMP handsheets.

Table 1. Additives Applied onto BCTMP Handsheets.

Thiol Additive		Disulfide Additive	
$HSCH_2CO_2H$	(1)	$\text{-}SCH_2CH(OH)CH(OH)CH_2S\text{-}$	(6)
$HSCH_2CH_2CO_2H$	(2)	$S_2(CH_2CH_2CO_2H)_2$	(7)
$(HSCH_2CO_2CH_2\text{-})2$	(3)		
$HS(CH_2)_{11}CH_3$	(4)		
$HO_2CCH_2CH(SH)CO_2H$	(5)		

Photostabilization effects of the additives were then assessed for freshly prepared handsheets and for testsheets stored for a period of three months. The results of these studies, which are summarized in Table 2 and in Figure 1, demonstrate that the photostabilization effects of thiol additives diminishes substantially with time. Several of the thiol additives appear to have lost approximately 50% of their photostabilization capabilities upon storage for three months. Although the mechanism contributing to this diminished photoprotection effect remains uncertain, we have tentatively attributed these observations to autoxidation reactions of the thiol compounds impregnated on mechanical pulp. This study demonstrates for the first time the transient nature of the photoprotection effects of thiol additives.

Of greater practical interest was the observation that the disulfide additives appeared to be inert to the effects of long term storage. Examination of the results in Table 2 indicates that the disulfide treated handsheets retain full photoprotection benefits of mercapto-additive even after three months of storage. Based upon the results of these investigations, we have begun to study several new more effective disulfide photostabilizing additives. The results of these studies are ongoing and will be reported in the near future.

Relationship Between Brightness Stabilization and Sulfur Contents of Impregnated BCTMP Handsheets

It is commonly speculated that thiols brighten and photostabilize mechanical pulps in part through Michael type additions to eliminate chromophores such as α,β-unsaturated carbonyl and quinoid structures [4,5]. However, no direct evidence has been obtained to confirm that mercaptans are chemically bonded to the lignin moiety. In this work, we conceived an idea to attempt to examine the role of the Michael addition. The exhaustive extraction with organic solvents was assumed to remove all thiols absorbed onto handsheets. The detection of sulfurs in the handsheets after such an extraction can be considered to be due to strongly attached and/or chemically bonded mercapto-lignin structures. The amount of sulfurs may reflect the extent of the occurrence of the Michael addition which results in bleaching and photostabilization. To this end, a sulfur-free bleached mechanical pulp was employed. Extraction was conducted successively with methylene chloride, ethyl acetate and chloroform to maximize removal of the sulfurs. The sulfur contents of a series of handsheet samples are reported in Table 3.

The data of Table 3 show that most of the mercaptans impregnated onto the handsheets can be removed by an exhaustive extraction. The removable portion was assumed to be free mercaptans. The rest might be strongly attached and/or chemically bonded to fibres of the handsheets. The mechanisms involved in the attachment are most likely the Michael type addition of thiols to α,β-unsaturated carbonyl structures and quinones present in the lignin. The contents of sulfur in the impregnated/extracted handsheets are quite low in all cases, which is in agreement with the previous finding that the mercaptans employed in this study provided a minor bleaching effect on the BCTMP handsheets.

On the other hand, the photolysis appeared to substantially change the nature of the sulfurs present in the handsheets. As can be seen in Table 3, the impregnated handsheets before (I) and after (I/hv 15) photolysis had comparable amounts of sulfur. However, the photolysis substantially increased the amount of unextractable sulfurs in the handsheets with irradiation time. The occurrence of the Michael addition of the thiols to the lignin during irradiation was the most probable source of the increment in unextractable sulfurs, which led to brightness stabilization of the BCTMP handsheets. In a model compound study, Lee and Sumimoto isolated Michael addition products from 3,4-dimethoxy stilbene-p-quinone irradiated in the presence of thioglycerol [7].

It is interesting to note that the degrees of photostabilization observed for the thiols and the amounts of thiols attached to the handsheets follow the same order, namely:

$$(HSCH_2CO_2CH_2\text{-})_2 > HSCH_2CH_2CO_2H > HSCH_2CO_2H >> CH_3(CH_2)_{11}SH$$

1-dodecanethiol could not sufficiently be attached to fibres of the handsheets upon irradiation, and thus is ineffective in retarding brightness reversion. To our knowledge, this is the first experimental result that correlates the amount of sulfurs present in handsheets to the photostabilization effect in the studies on mercaptans as a brightness stabilizer for mechanical pulps. Our work also supports the speculation that stabilizing mechanical pulps by thiols partially results from the Michael addition mechanism.

Table 2. TAPPI brightness values of hardwood BCTMP sheets before and after addition of various sulfur-containing compounds and after long-term storage and irradiation.

	Addition		After	Irradiation (min)			
	before	after	storage	15	30	60	90
Control	85.9			66.4	59.9	54.0	49.6
$HSCH_2CO_2H$	84.6	85.1		76.1	71.1	63.4	58.7
$HSCH_2CH_2CO_2H$	85.5	86.4		77.8	73.2	66.2	61.7
$(HSCH_2CO_2CH_2\text{-})_2$	85.6	86.2		80.8	76.8	70.1	64.4
$CH_3(CH_2)_{11}SH$	85.5	84.1		65.5	59.7	53.1	49.1
$CH_2(OH)CH(OH)CH_2SH$	84.3	85.3		75.7	70.9	63.6	59.0
$HO_2CCH_2CH(SH)CO_2H$	84.7	84.1		74.8	68.8	61.1	55.1
$SCH_2CH(OH)CH(OH)CH_2S$	84.4	84.9		72.8	66.4	57.6	52.3
$S_2(CH_2CH_2CO_2H)_2$	85.7	85.9		74.1	67.8	61.5	56.7
1 month storage							
Control	86.0		84.9	65.7	60.9	53.7	50.1
$HSCH_2CO_2H$	86.1	86.6	86.2	75.5	69.5	61.1	55.6
$HSCH_2CH_2CO_2H$	85.5	86.1	85.2	76.5	72.6	66.2	61.1
$(HSCH_2CO_2CH_2\text{-})_2$	84.7	86.0	85.7	77.9	73.0	65.5	60.2
$CH_3(CH_2)_{11}SH$	85.1	83.8	82.2	65.5	59.9	54.3	50.3
$CH_2(OH)CH(OH)CH_2SH$	84.6	85.0	84.5	75.0	69.5	63.2	58.1
$HO_2CCH_2CH(SH)CO_2H$	83.3	80.0	80.5	69.6	63.7	56.5	51.9
$SCH_2CH(OH)CH(OH)CH_2S$	85.1	85.7	84.5	74.4	68.1	59.8	54.3
$S_2(CH_2CH_2CO_2H)_2$	84.4	84.6	83.3	73.7	69.2	63.0	58.4

(to be continued)

	Addition		After	Irradiation (min)			
	before	after	storage	15	30	60	90
			2 months storage				
Control	85.1		83.6	65.4	60.0	53.7	50.1
$HSCH_2CO_2H$	84.6	85.3	83.6	71.8	66.2	59.0	54.2
$HSCH_2CH_2CO_2H$	85.6	86.4	84.7	76.2	72.0	65.4	60.8
$(HSCH_2CO_2CH_2\text{-})_2$	85.0	86.1	85.6	77.6	72.3	65.6	60.2
$CH_3(CH_2)_{11}SH$	84.8	83.0	82.5	66.6	61.0	54.7	50.8
$CH_2(OH)CH(OH)CH_2SH$	85.1	86.1	82.7	71.3	65.6	58.3	53.6
$SCH_2CH(OH)CH(OH)CH_2S$	85.0	85.7	84.3	74.7	68.8	60.9	55.8
$S_2(CH_2CH_2CO_2H)_2$	86.0	86.0	84.5	75.0	69.7	63.0	58.1
			3 months storage				
Control	83.9		82.8	65.5	59.4	53.0	49.6
$HSCH_2CO_2H$	85.6	86.0	81.2	72.4	65.5	59.2	55.0
$HSCH_2CH_2CO_2H$	85.4	86.4	83.3	74.6	68.5	62.6	58.7
$(HSCH_2CO_2CH_2\text{-})_2$	82.5	82.7	82.5	75.8	69.2	63.5	59.2
$CH_3(CH_2)_{11}SH$	84.3	82.7	81.6	64.4	59.9	55.6	51.7
$CH_2(OH)CH(OH)CH_2SH$	85.3	86.5	86.3	75.1	69.6	64.3	59.9
$HO_2CCH_2CH(SH)CO_2H$	84.8	83.7	81.8	69.9	63.1	57.7	53.8
$SCH_2CH(OH)CH(OH)CH_2S$	85.6	86.5	84.2	75.5	67.9	62.6	57.6
$S_2(CH_2CH_2CO_2H)_2$	84.4	85.3	83.8	73.9	67.4	62.4	58.2

Figure 1: Photostabilization Effects for Mercapto-Treated BCTMP Handsheets.

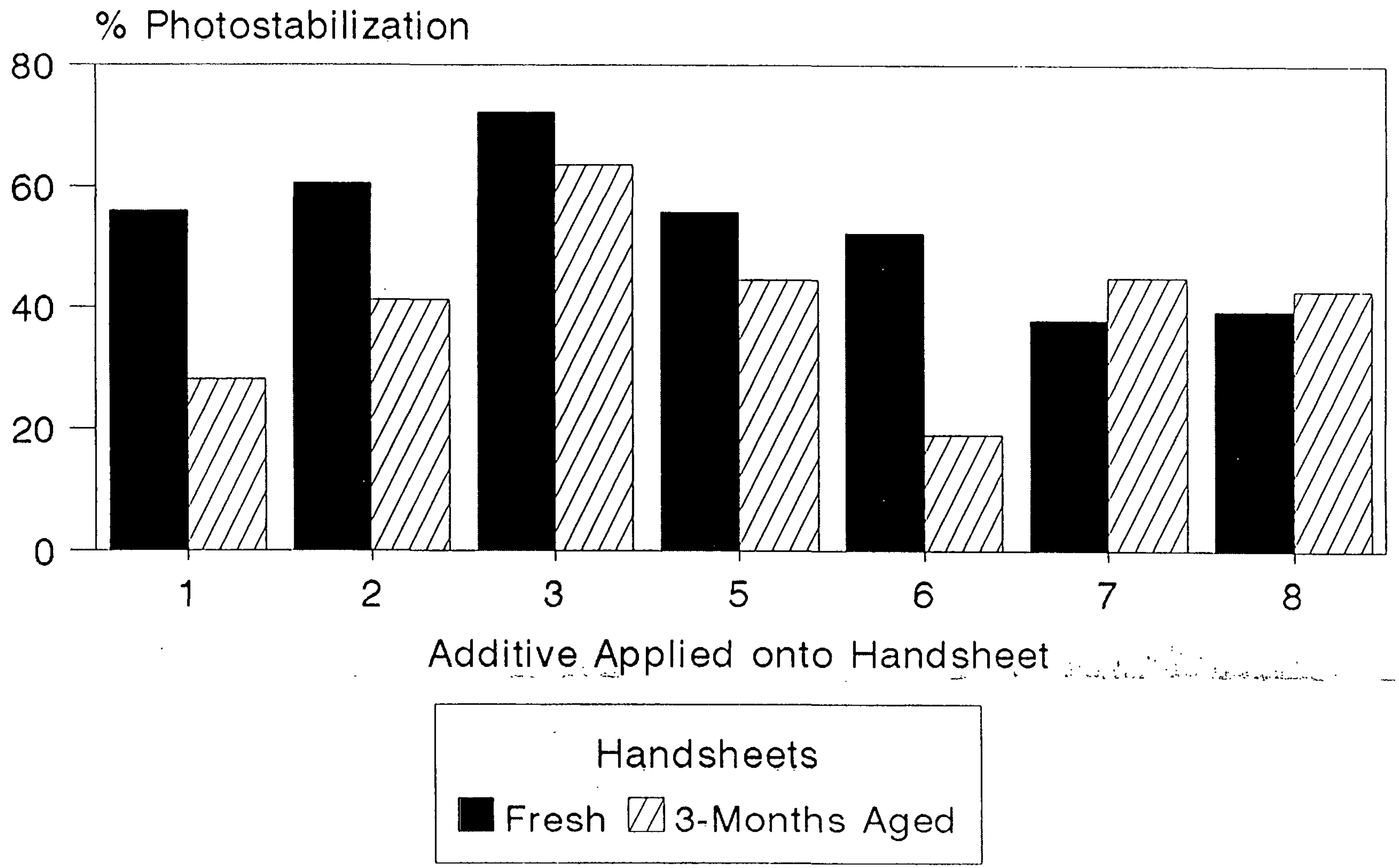


Table 3. Sulfur contents of hardwood BCTMP handsheets before and after addition of various thiols and after extraction and irradiation/extraction.

	%C	%H	%S	%S/C Ratio
Untreated pulp				
	42.69	6.57	<0.05	<0.11
$HSCH_2CO_2H$				
I	45.49	5.69	1.16	2.55
I/E	45.89	6.08	0.13	0.28
I/$h\nu$ 15/E	45.77	5.88	0.35	0.76
$HSCH_2CH_2CO_2H$				
I	45.72	6.05	1.21	2.65
I/E	46.58	6.22	0.075	0.16
I/$h\nu$ 15/E	46.10	6.29	0.44	0.95
$(HSCH_2CO_2CH_2\text{-})_2$				
I	45.94	6.13	2.03	4.42
I/E	46.51	6.06	0.12	0.26
I/$h\nu$ 15	43.59	6.27	1.86	4.27
I/$h\nu$ 6/E	45.15	6.38	0.61	1.35
I/$h\nu$ 15/E	46.00	6.07	0.76	1.65
$CH_3(CH_2)_{11}SH$				
I	47.14	6.65	0.60	1.27
I/E	46.46	6.40	<0.09	0.19
I/$h\nu$ 15/E	46.20	6.42	0.10	0.22

I: impregnation with thiols; E: extraction with organic solvents; $h\nu$ 6: irradiation 6 hours; $h\nu$ 15: irradiation 15 hours.

IMPROVED PERFORMANCE OF MERCAPTO-PHOTOSTABILIZERS

Introduction

Although mercapto-stabilization of mechanical pulps is effective, the malodorous properties associated with these compounds prevents commercial application. Our research efforts over the last year have attempted to address this issue by investigating technologies which could retain the beneficial photoprotective properties of mercapto-compounds while eliminating their unfavorable properties. To date three general approaches were examined including;

- Development of high-molecular weight thio-additives;
- Coating of mechanical pulps with $CaCO_3$/thio-salts;
- Thio-bleaching of BCTMP pulps.

Results and Discussion

Previous studies by Kutney[8] had shown that di-thiols were effective bleaching agents for TMP and SGW mechanical pulps. These studies demonstrated that treatment of mechanical pulps with mercapto-additives afforded brightness gains of 0.5 - 4.8 ISO brightness units. Although the chemical mechanisms contributing to this process were not investigated, it was speculated that the mercapto-compounds were removing lignin chromophores. In light of these observations, we speculated that the thio-bleaching process could potentially improve the brightness reversion properties of mechanical pulps. To investigate this hypothesis, we treated a hardwood BCTMP pulp sample with a monothiol additive, 3-mercaptopropionic acid (8), and a dithiol additive, ethylene glycol bisthioglycolate (9). The thio-bleached pulp samples were then filtered, washed, and formed into handsheets. As a control, a series of BCTMP handsheets were prepared in an analogous manner except that the thio-additive was omitted from the sequence.

Analysis of the thio-treated handsheets indicate that the pulps were brightened by the thiol treatment and washing removed all traces of the thiol additives. The photoaging properties of the control and treated handsheets were determined under standard accelerated photo-reversion conditions[9] and with routine office lighting. The results of these experiments are summarized in Figures 2 and 3. Analysis of these results indicates that the thiol treated handsheets undergo reversion at rates comparable to the untreated handsheets. Nonetheless, at any given time period, the treated testsheets exhibit higher brightness values due to the initial bleaching effect of the thiol agent. Comparison of the rates of photoyellowing for handsheets irradiated with the solar simulator versus office lighting indicates some differences in the long term yellowing properties which we have hypothesized could be due to differences in the light sources.

In summary, thio-bleaching of BCTMP pulps was shown not to be effective at halting brightness reversion. Nonetheless, the apparent absence of mercapto compounds after washing and the observed brightness gains suggest that this process may have application in achieving greater than 90 brightness mechanical pulps.

Based upon the thio-bleaching studies, we believe that the mercapto-compound must be present during the brightness reversion process to effectively halt photoyellowing. To remove the malodorous properties of mercapto compounds, we had hypothesized that a $CaCO_3$ coating, in conjugation with a mercapto-salt, would halt the volatilization of mercapto-additives and still retain the overall antioxidant properties. To explore this hypothesis, we applied a $CaCO_3$/mercapto-salt slurry onto BCTMP handsheets and monitored the overall rates of photoyellowing. Table 4 summarizes the coating conditions employed for these studies.

Table 4. Summary of Thio Additive/$CaCO_3$ Coating Experiments.

Coating Components[a]		% Application	TAPPI Brightness
Control(I)	-no $CaCO_3$ -no thio cpd.	- -	85.3
$CaCO_3$ Control(II)	-no thio cpd.	10	85.8
$CaCO_3/HSCH_2CO_2Na$(III)		10	85.3
$CaCO_3/HS(CH_2)_3SO_3Na$(IV)		10	87.5
$CaCO_3/HSCH_2CH_2N(CH_3)_2.HCl$(V)		9	87.6
$CaCO_3/HSCH_2CH_2CO_2H$(VI)		7	84.2

[a] *coating solution consisted of 10 g of a 7% by weight $CaCO_3$ slurry, 1.5 g of the thiol additive and 8.5 g of water, the slurry was applied onto TAPPI test handsheets with a metering bar and the resulting handsheets were air dried.*

The control and treated handsheets were irradiated with the solar simulator and relative rates of photoyellowing were established. Figure 4 summarizes the results of the accelerated photoyellowing studies preformed with the Solar Simulator. Analysis of these results indicates that the mercapto-additives retain their photostabilization effects when applied onto handsheets with a calcium carbonate slurry. Based upon these results, it appears that the sulfonic salt (i.e., $HS(CH_2)_3SO_3Na$) is one of the most effective agents. Nonetheless, the use of $CaCO_3$ was unable to prevent the complete volatilization of the thio additives from the handsheets.

As a final approach at improving the overall performance of thiol-based additives, we attempted to incorporate mercapto SH units into cellulose. A review of the literature indicates that thiol starch[10] and cellulose[11] additives have been prepared although their antioxidant properties have not been examined. To examine this avenue of research we employed literature procedures to convert cellulose into two thiol-supporting polymers, the general structure of these derivatives is shown below:

Cellulose-CH_2SH	Cellulose-$OCH_2CH(OH)CH_2SH$
<u>Thiol cellulose I</u>	<u>Thiol cellulose II</u>

Analysis of these materials indicated that the mercapto-cellulose polymers were devoid of odor and retained some fiber structure. Following our well established accelerated photoaging procedures, the thiol cellulose derivatives were incorporated into BCTMP handsheets and photolyzed. Unfortunately, the treated handsheets exhibited brightness reversion tendencies comparable to control BCTMP testsheets. Although the exact factors contributing to the failure of these additives remains uncertain, we speculated that a contributing factor may be due to the fibrous nature of thiol cellulose I and II. This tertiary structure could prevent efficient coverage of the BCTMP fibers and thereby limit the effectiveness of these thiol-additives. Alternatively, the failure of the thio-cellulose additives could be due to the polymeric nature of the additive itself.

To test these hypotheses, we prepared several BCTMP handsheets impregnated with a low molecular thiol additive or a high molecular weight thiol additive. The types of additives employed and the application amounts are summarized below:

Test Handsheet VII:

-$HSCH_2CH_2$-O-CH_2CH_2SH (1% charge: 1.5×10^{-4} mols RSH/g handsheet);

Test Handsheet VIII:

-Dithiol polyethylene glycol [$HS-CH_2CH_2-(OCH_2CH_2)_n-OCH_2CH_2-SH$, MW:3400] (25% charge: 1.5 x 10-4 mols RSH/g handsheet);

Test Handsheet IX:

-Polyethylene glycol [$HO-CH_2CH_2-(OCH_2CH_2)_n-OCH_2CH_2-OH$ MW:3400] (25% charge)

Test Handsheet X:

-Polyethylene glycol [$HO-CH_2CH_2-(OCH_2CH_2)_n-OCH_2CH_2-OH$ MW:3400] (25 % charge) &

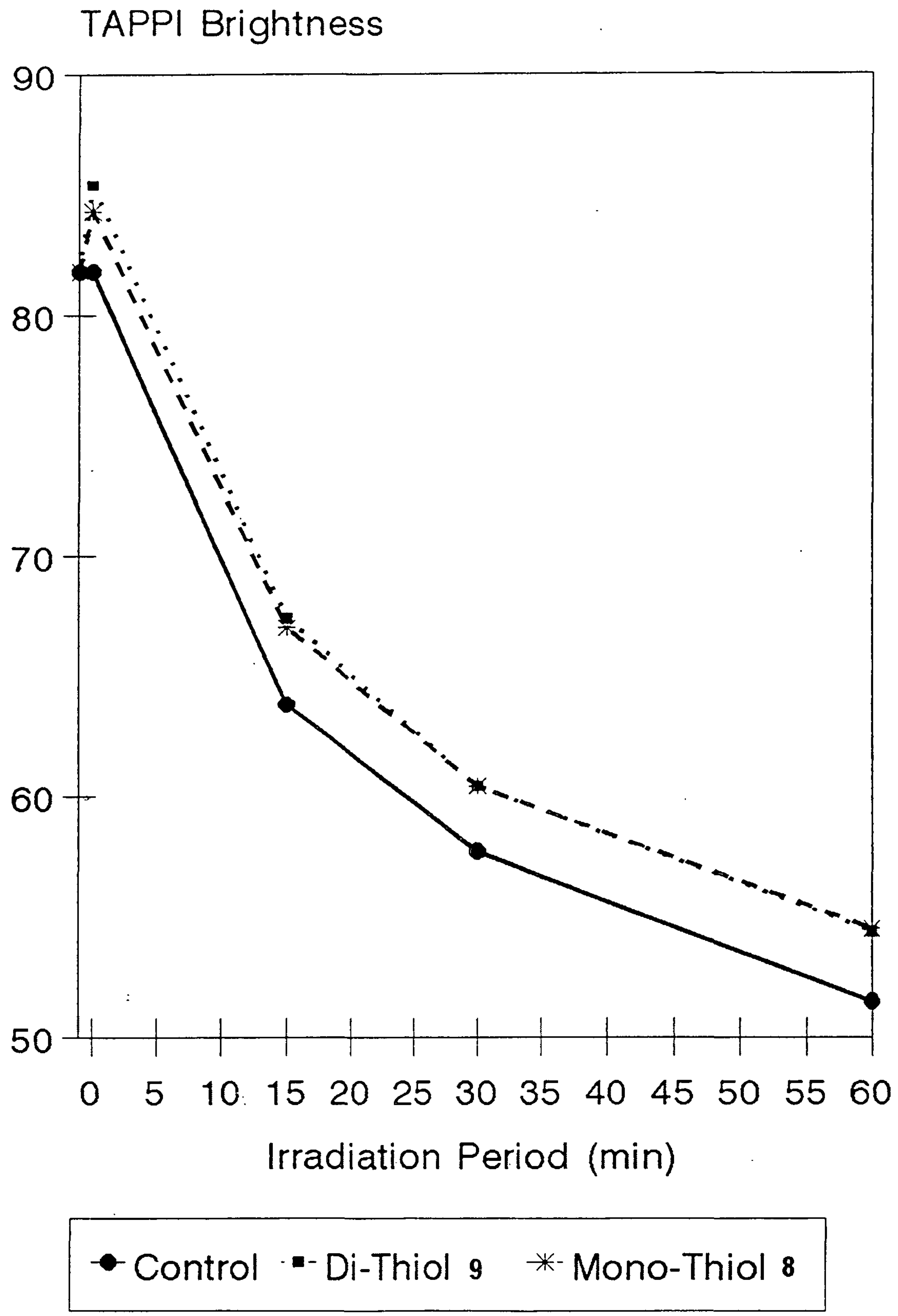
$HSCH_2CH_2-O-CH_2CH_2SH$ (1% charge: 1.5 x 10^{-4} mols RSH/g handsheet).

The two di-thiol additives, dithiol polyethylene glycol and 2-mercaptoethyl ether, were selected as good models for investigating the effectiveness that molecular weight has on the brightness stabilization capabilities of thiol-additives. The two thiol additives were chosen since the low and high molecular weight compounds have similar structural features. The application level of RSH per gram of BCTMP handsheet was maintained at a constant mol value of 1.5 x 10^{-4} mols RSH/g handsheet. Previously research efforts in our laboratory have demonstrated that thio-brightness stabilization effects are sensitive to charge applied onto the handsheet and this necessitated the use of equal charges of RSH/g of handsheet.[9]

Early investigations by Forsskahl et al.[12] have shown that polyethylene glycol additives retard reversion and as a result we prepared BCTMP handsheets IX and X as controls. The handsheets were irradiated in the Solar Simulator and the changes in brightness were monitored. The results of these studies are summarized on Figure 5. Examination of these results indicates several interesting trends. First, our results suggest that the most effective stabilizing system examined was the co-mixture of polyethylene glycol and 2-mercaptoethyl ether (i.e., Handsheet X). The second most effective agent was either polyethylene glycol or the di-thiol polyethylene glycol impregnated handsheets. The relative rates of brightness reversion for these treated handsheets was very comparable and their ordering changed with irradiation time. It is interesting to note that the low molecular di-thiol provided some of the least effective photostabilization effects.

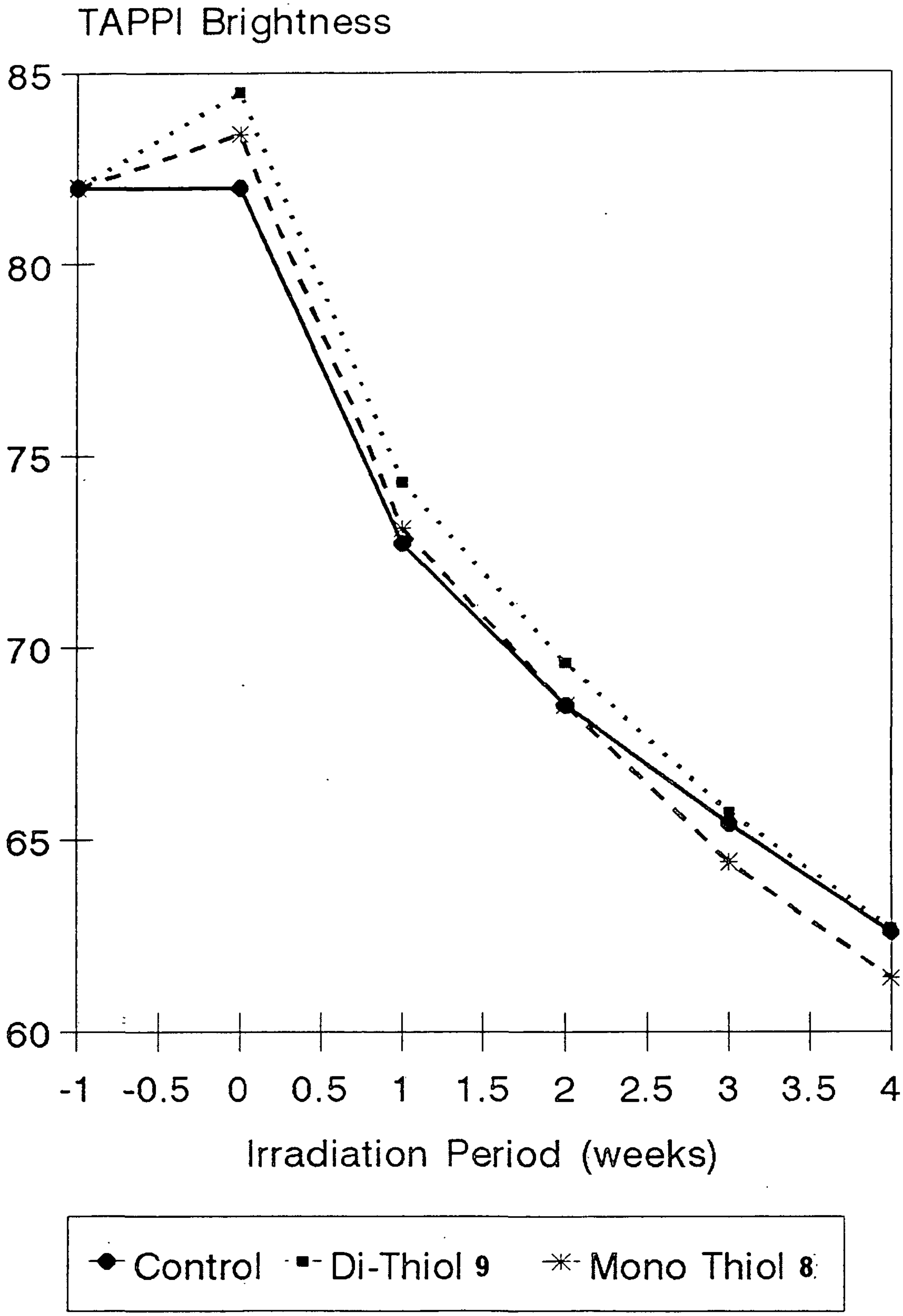
In summary, both polymeric additives applied onto BCTMP handsheets appeared to retard reversion. The incorporation of thiol units onto the "tail-end" of the polyethylene glycol polymer appeared to have little effect on improving the photo-stabilization effect for these handsheets. These results appear to suggest that the thio-additive is most efficient as a photostabilizer when its molecular weight is minimized.

Figure 2: Photoaging of Treated and Control BCTMP Handsheets
Light Source: Xenon-arc Lamp



Note: -1 Brightness values are pre-impregnation values.

Figure 3 Photoaging of Treated and Control BCTMP Handsheets
Light Source: Office Lighting



Note: -1 Brightness values are pre-impregnation values.

Figure 4: Brightness Reversion of Thio/CaCO3 Coated Handsheets

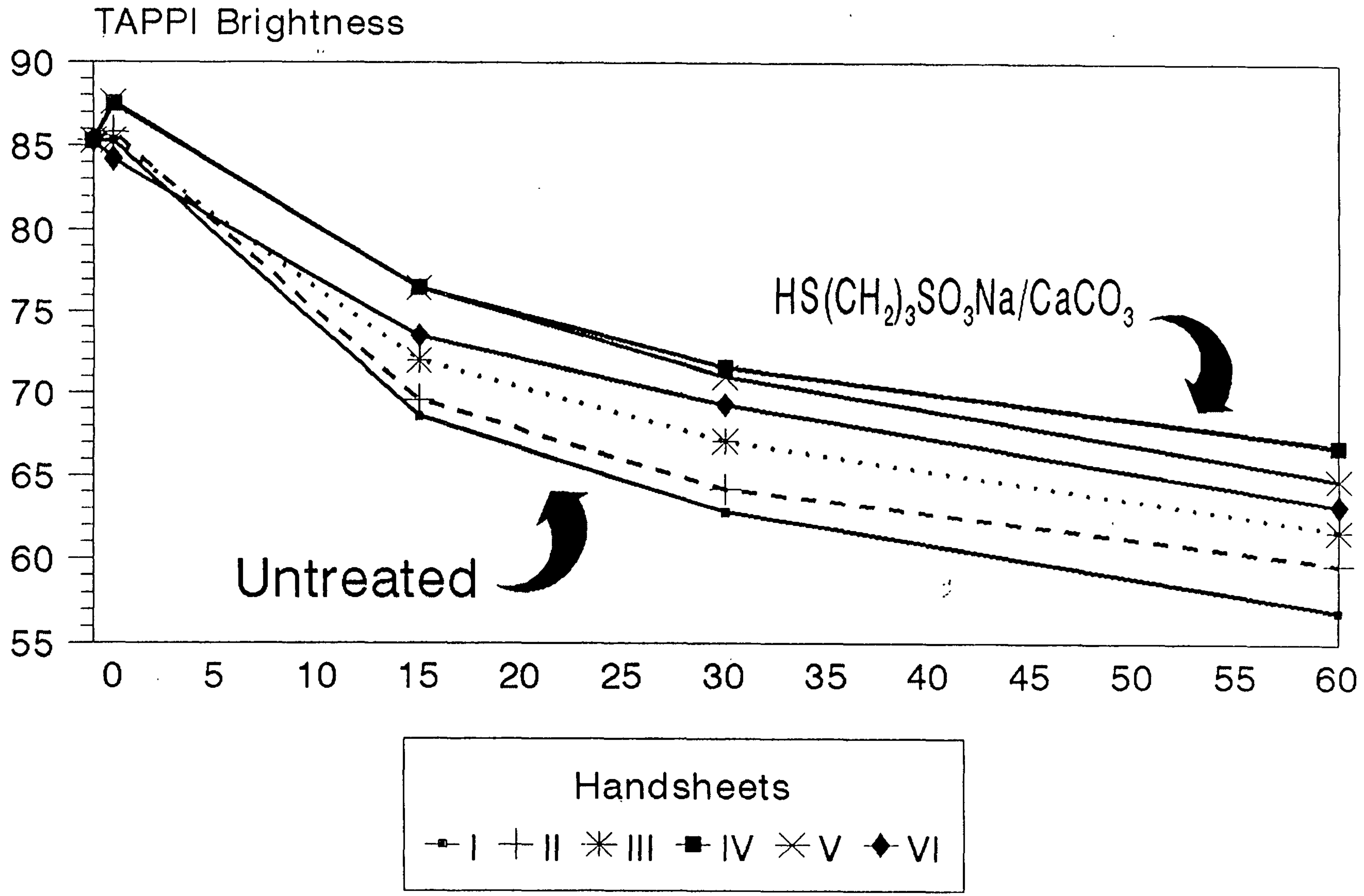
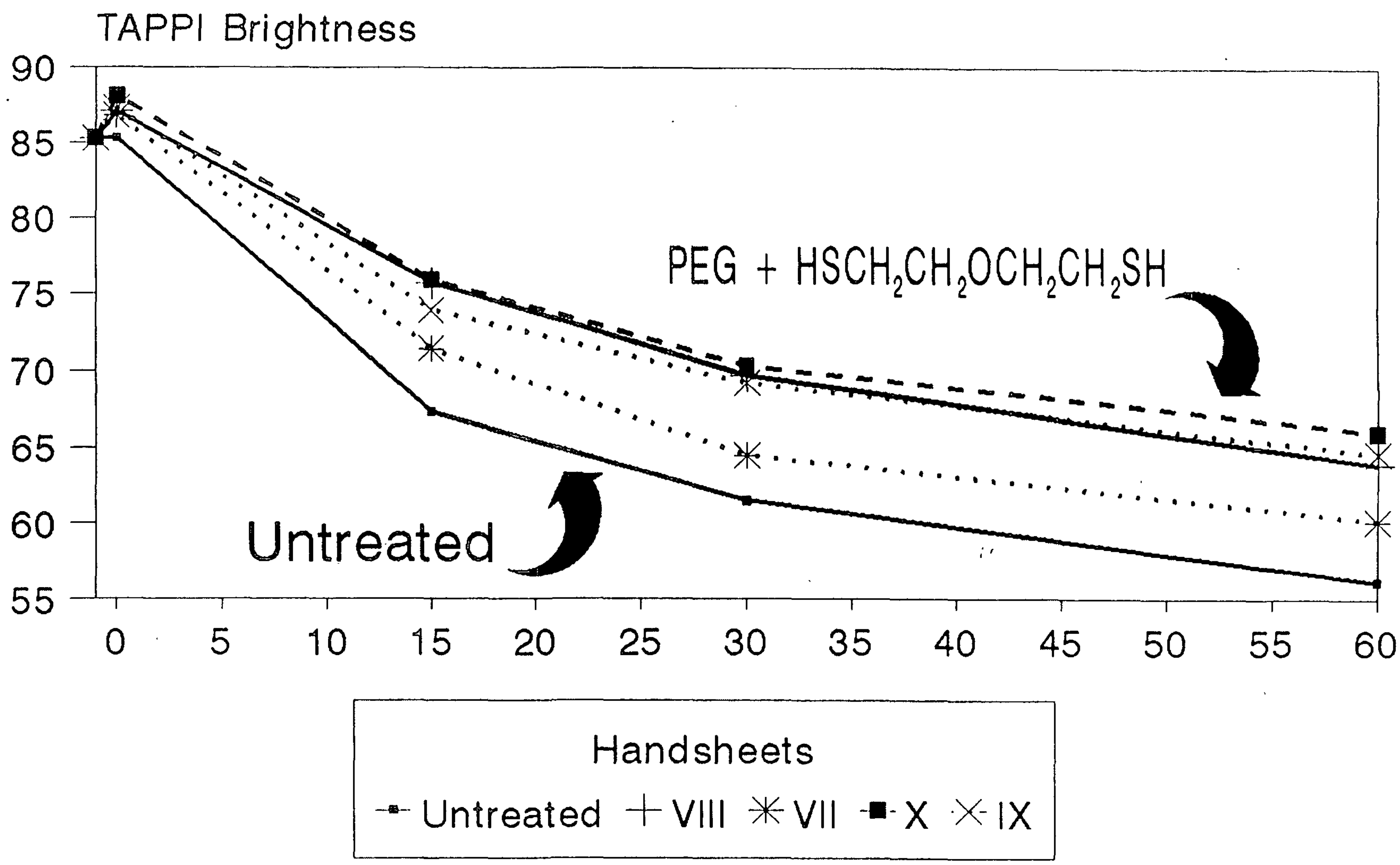


Figure 5: Brightness Reversion of Thio-PEG Additives Impregnated on BCTMP Handsheets



Reference

1. Cockram, R.A., Proceedings of the 1989 International Mechanical Pulping Conference, Helsinki, June, (1989).

2. Heitner, C.; Schmidt, J.A. Proceedings of the 6th International Symposium on Wood and Bleaching Chemistry, Melbourne, *1*, 131 (1991).

3. Stepek, J.; Daoust, H., Additives for Plastics, NY, Springer-Verlag (1985).

4. Heitner, C., In "Photochemistry of Lignocellulosic Materials", ACS Symposium Series 531, ACS Press, Ed. by Heitner, C.; Scaiano, J.C., 192 (1993).

5. Cole, B.J.W.; Sarkanen, K.V., Tappi J., *70*(11), 117 (1987).

6. Ragauskas, A.J., "Brightness Reversion of Mechanical Pulps Part 2: Thermal Aging of Ascorbic Impregnated Lignin-Reatining Pulps", Cellulose Chem. Technol. (in press).

7. Lee, D.Y.; Sumimoto, M., Holzforschung *45* (Suppl.): 15 (1991).

8. Kutney, G.W., J. Pulp Paper Sci. *12*(4), J129 (1986).

9. 1993 Status Report to the Chemical Pulping and Bleaching Project Advisory Committee.

10. Germeiner, P.; Benes, M., Collection Czechoslovok Chem. Commun., *48*(1), 267 (1983).

11. Trimnell, D.; Stort, E.I.; Doane, W.M.; Russell, C.R., J. Applied Polymer Sci., *21*, 655 (1977).

12. Janson, J.; Forsskahl, I., Nordic Pulp and Paper Res. J., *4*(3), 197 (1989).

Supporting Student and Contract Work Directed by A.J. Ragauskas.

External Research Studies:

a) Validation of MoDoCell's Brightness Reversion Technology
-by MoDoCell, Inc., Hoffman-La Roche Inc.

b) Development of Oxygen-Based Bleaching Systems for the Pulp & Paper Industry
-by Forest Products Laboratory, USDA.

c) Fundamental Studies of the Photo-Initiated Oxidation of Lignin in Wood Fibers
-Wood Utilization Program, USDA (92-37103-8237).

d) Application of 17-O and 2-H NMR in Bleaching Technology
-by TAPPI Research Funding Committee.

IPST Graduate Research:

a) Application of On-Line NMR Technologies for The Pulp and Paper Industry
-E. Draheim.

b) Application of DMD and Alternative Oxygen-Based Bleaching
Agents for Recycled Fiber/*F. Chakar.*

c) Investigation of Computational Modeling Techniques for Pulp Additives
-C. Harper.

d) Characterization of Residual Lignin in Conventional and
Extended Delignified Kraft Pulps/*P. Froass.*

Synopsis of Proposal
Submitted
to the
U.S. Department of Energy

Synopsis of Proposal Submitted to U.S. Department of Energy

Research Title: Development of Biobleaching Technology For The Pulp and Paper Industry

Principle Investigators:
Dr. A.J. Ragauskas/IPST
Dr. T.J. McDonough/IPST
Dr. J. Woodward/Oak Ridge National Laboratories
Dr. R. Margalit/JPL, California Institute of Technology

Research Objective: Development of the next generation of biobleaching technologies for pulp bleaching operations.

Research Goals: This program is directed at developing new bioassisted bleaching technology optimized for closed-cycle kraft bleaching operations. Research efforts will be directed at employing biotreatments to substantially reduce the chemical charges/energy requirements needed to produce fully-bleached kraft pulps. This goal will be accomplished in a three-fold manner:

- Development and implementation of new oxo-reductase enzymes which will delignify kraft pulps (i.e., R-stage) and enhance the performance of subsequent bleaching procedures.
- Development of xylanase and/or alternative hemicellulase pretreatment procedures (X-stage) compatible with closed-cycle mill bleaching practices which will enhance the performance of subsequent bleaching procedures.
- Development and implementation of new bioassisted bleaching sequences for closed-cycle bleaching sequences based on either chlorine dioxide or totally chlorine free (TCF) bleaching sequences.

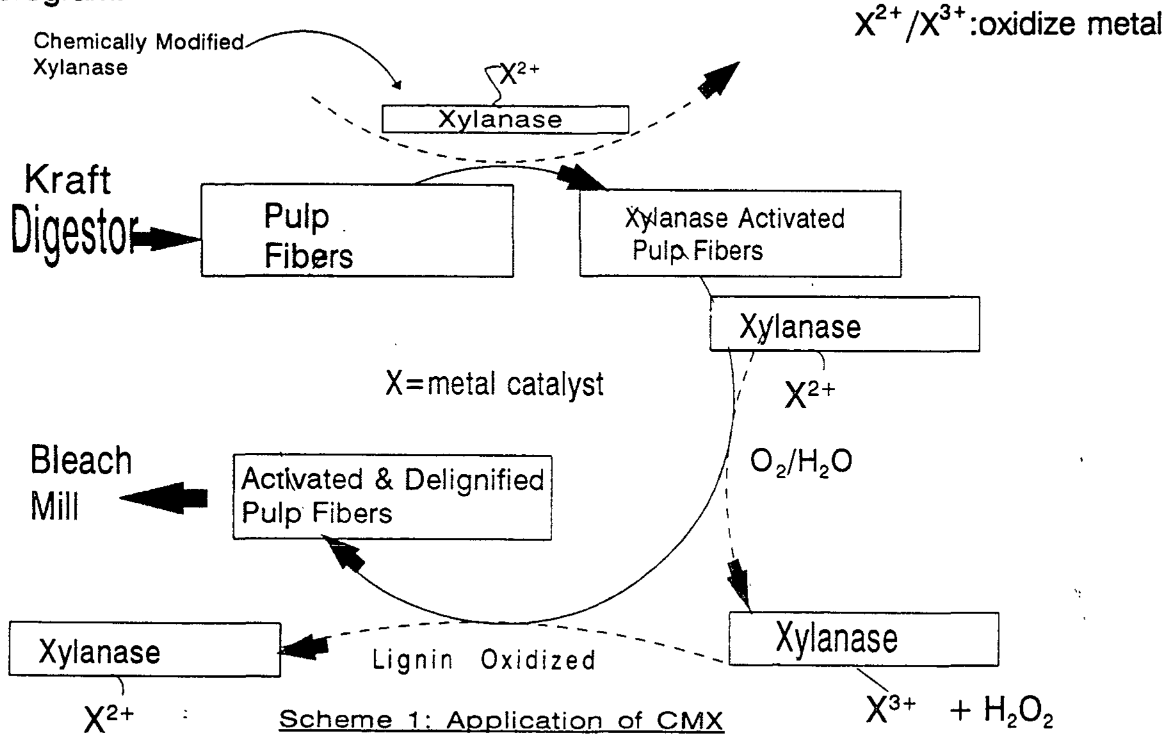
Proposed funding for this project will provide the support needed to develop a center of excellence for bioassisted bleaching technology for the pulp and paper industry. The collaborative effort between the Institute of Paper Science and Technology (IPST), Oak Ridge National Laboratories (ORNL), Jet Propulsion Laboratory (JPL) and private industry will provide a unique opportunity for transferring technology from the national laboratories into the nation's pulp and paper manufacturing industry.

Return on Investment: The studies proposed in this research program will lead to the development of novel bioassisted bleaching technologies which when implemented in commercial bleaching operations will provide several benefits including:

- Reduced energy and chemical cost;
- Improved brightness ceilings;
- Improved strength properties.

Furthermore, our research plans are directed at applying the biobleaching enzyme(s) to brownstock pulps as they emerge from the brownstock washer and pass into the brownstock high density tower just prior to the bleach plant. This site of application ensures that this technology can be readily implemented in modern integrated bleaching mills with minimal retrofit. This site of application will take advantage of existing capital investments and offer the greatest cost-benefit for both chlorine dioxide and oxygen-based closed-cycle bleaching operations.

Research Target: Studies proposed in this program will lead to the chemical modification of biobleaching enzymes so that the enzyme will retain the biobleaching properties and will also be able to actively delignify kraft pulps. Employing well defined chemical modification technologies the xylanase protein will be modified so as to incorporate an oxidative/reductive catalyst onto the surface of the protein. In this manner, chemically modified xylanase will activate the pulp for subsequent chemical bleaching stages while the oxidative/reductive catalyst will delignify the kraft pulp. Scheme 1 summarizes the proposed biobleaching technologies to developed in this program.



Scheme 1: Application of CMX

Along with the development and implementation of this biotechnology the proposed program will examine the use of these biocatalyst with an assorted series of bleaching oxidants (i.e., D, Z, P, *in-situ* dimethyldioxirane). Since future developments in dimethyldioxirane bleaching will require an inexpensive source of peroxymonosulfate this program will examine the use of electro-chemical technologies to develop this valuable agent. In summary, the studies proposed in this program will benefit all manufacturers of bleached kraft pulp regardless of the nature of the bleaching sequence they employ in a closed-cycle bleaching mill.