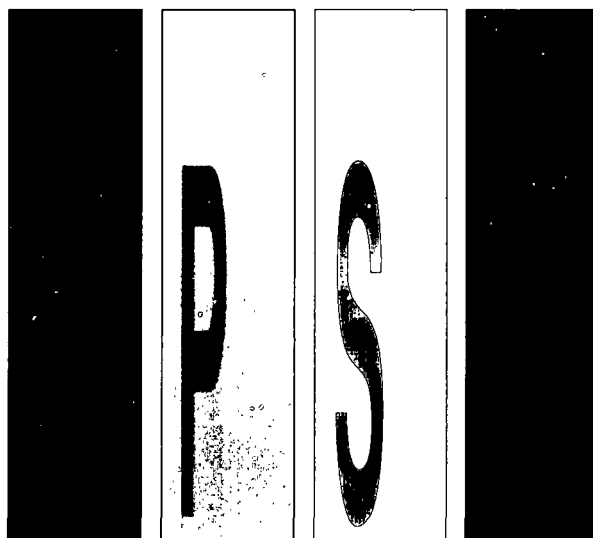*Institute of Paper Science and Technology*

CHEMICAL PULPING AND BLEACHING

ANNUAL RESEARCH REVIEW

April 2, 1991

IPS

Atlanta, Georgia

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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WOOD CHEMISTRY GROUP RESEARCH OVERVIEW

The chemistry which occurs during the pulping and bleaching steps in papermaking is critical to the quality of the end product and to the production economics. The hot issues in the paper industry today are environmental issues - recycling and discharge of chlorinated organics. It is not surprising then that many of the research interests of the Wood Chemistry Group at IPST are related to studying ways to resolve environmental concerns.

PULPING STUDIES

In the pulping area, we are addressing the issues of conservation of wood resources and energy through more selective alkaline pulping processes and extending the value of high yield pulps. The former research is a large effort with DOE financial support and the latter is a dues-funded project.

The complexities of characterizing products from the reactions of major polymeric wood components have led researchers to study model compounds. We too use model compounds in our research. While these investigations have provided valuable insight into carbohydrates and lignin reactions, the models are usually water soluble and flexible - two properties that conflict with the "real world" situation. Therefore, several of the project and student investigations involve reactions of compounds absorbed or attached to solid surfaces.

Project 3661. This DOE funded project is attempting to develop an economical, sulfur-free pulping process based on conversion of lignin to pulping additives which will increase delignification rates and decrease the degradation of carbohydrate fibers.

The research has been divided into two large stages, lignin processing and chemical processing. The lignin processing stage involves selectively isolating a low-molecular-weight fraction by supercritical fluid extraction of a pulping liquor after precipitation of the bulk lignin or simple organic solvent extraction of an organosolv lignin. The first displays good selectivity for low-molecular-weight lignin, but the yields are low; the second is less selective, but provides large amounts of low-molecular-weight material.

The chemical processing of the low-molecular-weight lignin involves: (1) treating with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones and (2) converting the benzoquinones into anthraquinone analogs by treatment with a diene, using the well-known Diels-Alder reaction. The single most important determining factor in the final cost of anthraquinone prepared from lignin is the overall yield of the chemical processing steps. A number of lignin oxidizing agents have been evaluated for generating benzoquinones.

Hydrogen peroxide oxidation yields 80-90% benzoquinones from certain lignin models, but only about 1-2% from isolated lignins. A large excess of oxidant is needed for good yields, thereby reducing its cost-effectiveness. Nitrogen dioxide, a readily available material, has been shown

to be an effective oxidant with syringyl units; the yields of dimethoxybenzoquinone (DMBQ) with simple lignin models are often above 80% and with an extracted lignin in the 20-40% range. In addition, inexpensive oxygen, in the presence of catalytic amounts of certain transition metal complexes, can give yields of benzoquinones as high as 85% from model compounds.

Recent work has centered on the degradation of lignin into smaller fragments before performing NO_2/O_2 oxidation. Some pretreatments, such as acidolysis and copper oxide oxidation, have led to higher yields of benzoquinones after NO_2/O_2 oxidation, while others are detrimental to the yields. Also, several lignin samples have been investigated, in an attempt to find the best starting material for the quinone catalyst synthesis; organosolv lignins appear to be best.

Relative to the formation of one new ring, the yields are high for the second step in the chemical processing, addition of a diene to the benzoquinone mixture to give anthraquinone precursors. However, the formation of two rings simultaneously (benzoquinone directly to an anthraquinone) is a more difficult task; the intermediate naphthaquinone structures react very slowly under standard conditions. The use of catalysis to assist the diene addition and a novel diene addition reaction carried out in water allow for a direct, reasonably high conversion of benzoquinones to anthraquinones, without isolation of non-aromatic precursors.

Project 3524. The commercial use of high yield pulps is limited due to their inherent photo-instability which leads to yellowing. We are investigating the fundamental chemical reactions associated with the brightness reversion of high yield pulps and anticipate that the knowledge gained will lead to methods to retard the yellowing process. The research focuses on the photo-formation and photo-reactivity of chromophoric structures, along with the design of novel photostabilization techniques for mechanical pulp.

The chemical complexity of high yield (mechanical) pulp is such that it is exceedingly difficult to characterize the fundamental photochemical processes which occur during the brightness reversion phenomena. To understand how the photo-initiated oxidation of mechanical pulp leads to the formation of colored structures, we employ lignin model compounds adsorbed onto a solid support as a preliminary means of characterizing these reactions. As the our knowledge of the photo-degradation process increases, research efforts will focus on the yellowing phenomena in-situ.

Quinones appear to be produced during photoyellowing. Their photochemical behavior on a solid matrix may account for color development and is, therefore, being studied in this project. Mono and dimethoxybenzoquinone were synthesized, absorbed onto cotton linters, and photolyzed. Dimethoxybenzoquinone was relatively stable, but monomethoxybenzoquinone (MMBQ) yielded several products, with the predominant compound being the hydroquinone. Apparently, a photo-reduction occurred, which suggests that the cellulose is in turn oxidized. This process is accompanied by a distinctive change in color of the starting material from bright yellow to a dark brownish purple color for the product. The TAPPI brightness dropped from 44 to 32 in 2 hours irradiation.

The photolytic behavior of MMBQ adsorbed onto TMP has also been explored. After 4 hours of irradiation, very little quinone remains on the surface of the fibers. The results suggest that MMBQ is not a final photochemical product in the brightness reversion phenomena, but a reactive intermediate which oxidatively attacks lignin, generates other chromophoric structures and initiates a photo-degradation reaction of mechanical pulp.

Samples of MMBQ and a lignin model compound were adsorbed onto cotton linters and irradiated for 4 hours. Analysis of the product mixture indicated the presence of hydroquinone and several unidentified products, which appear to be oxidized derivatives of lignin model compound. Attempts at separating and characterizing these structures is currently underway. The photolysis reaction is accompanied by a intense darkening of the reaction material and this change will be quantified.

It is known that the photo-fragmentation process is stereochemically dependent. The enhanced conformational freedom of a dimer model suggests that it may not be an accurate model. The synthesis of a lignin trimer is in progress. The decreased flexibility of the lignin trimer, in comparison to simpler dimer models, may have important consequences with respect to the photochemical studies which will follow.

BLEACHING STUDIES

In the bleaching area, we are studying the mechanisms of dioxin formation (and destruction) and the environment consequences of modifying bleaching processes. There are two outside funded projects and a M.S. student research project. In addition, there is a dues-funded project dealing with understanding the chemical and physical factors associated with of the harmful reactions of oxygen-based chemicals on carbohydrate strength properties and a student project comparing an NMR spectral characterization of spent bleach liquors to physical parameters, such as viscosity and heats of combustion.

Projects 3684 and 3685. The goals of these projects are to understand the mechanisms of formation of dioxins (polychlorinated dibenzodioxanes and dibenzofurans) and to use this knowledge to minimize their production in bleached pulp. The research will address: (a) defining the relative importance of different dioxin precursors, (b) determining the reactivity of chlorine and other bleaching agents and pretreatments with one set of precursors, (c) determining if functionalized precursors could still be a source of dioxin upon reaction with chlorine, (d) selectively chlorinating lignin and not the dioxin precursors, and (e) destroying dioxins in partially bleached pulps.

Ultratrace quantities of dibenzodioxane (DBD) and dibenzofuran (DBF) in pulp are chlorinated, in spite of the presence of large amounts of lignin. The selectivity of electrophilic chlorine for the precursors suggests that other electrophilic reagents may be selective for DBD and DBF. Reactions of DBD and DBF with electrophilic reagents, prior to chlorination may prevent the dioxin formation. Consequently, research is being conducted which examines the reactivities of different reagents toward the precursors. The disappearance of DBD and DBF upon selective treatments has been measured for precursors dissolved in water and adsorbed onto cotton linters.

Ozone, nitrogen dioxide, nitric acid, and oxygen under ultraviolet light degraded DBD more effectively than they degraded DBF. Lower concentrations of ozone were required to degrade DBD and DBF in solution and on linters than were required for other reagents. Peroxide degraded DBD and DBF in solution, but did not react with the precursors in the presence of linters. The precursors in solution were also degraded by treatment with O_2/UV.

The DBD and DBF were primarily oxidized, but also substituted to a small extent by nitrogen dioxide. [Traces of mono- and dinitrated DBD and mononitrated DBF were detected.] There was an interesting difference in the reactivities of DBD and DBF to nitrogen dioxide. Under the conditions tested, >99% of the DBD, but only 33% of the DBF, was destroyed. A similar, but even greater difference was observed for reactions with nitric acid; under one set of conditions, all the DBD reacted and none of the DBF reacted. In the case of sulfuric acid reactions, there was basically no degradation of DBD and DBF at moderate H_2SO_4 concentrations, either in solution or absorbed on linters.

The experimental conditions, and methods of analysis, have been established for conducting chlorinations of DBD/F spiked cotton linters to give mono - tetrachloro-DBD and DBF (DBD/F-Cl_x, x=1-4). The latter have been found in both the linters and aqueous phases after reaction with chlorine. The progressive development of DBD/F-Cl_x species during bleaching will provide information on the relative importance of different dioxin precursors.

M.S. student Michael Osborne is beginning a study of how changes in bleaching sequences effect environmental factors, such as AOX, color, and BOD. Another M.S. student, Karen Hodkiewicz, is attepting to characterize spent bleach liquors using NMR spectroscopy.

Project 3475. This project is presently concerned with developing a fundamental understanding of the chemical and physical reactions that control cellulose degradation (chain cleavage reactions) during pulping and bleaching. The reactivity difference observed for amorphous and crystalline cellulose samples has been taken to reflect the importance of "physical effects" in carbohydrate chain cleavage reactions. The viscosity losses as a function of time during simulated alkaline pulping followed the order: amorphous > cotton linters > kraft pulp > crystalline cellulose.

The rate of viscosity loss was increased slightly when amorphous or crystalline cellulose was heated in alkali in the presence of AQ, indicating that AQ may be causing some chain cleavage reactions to occur. Increasing the salt "dead-load" appeared to have little effect on the extent of carbohydrate chain cleavage, since a soda degradation on the amorphous cellulose, performed in the presence of different levels of salt (NaCl), gave nearly the same viscosities.

Additional Fundamental Student Research. In line with becoming "more realistic" in the model compounds used to study pulping and bleaching reactions, there are two student research projects dealing with synthesizing and examining the reactions of polymeric (water insoluble) carbohydrate and lignin models. The research of Rosann Kaylor and David Sawyer will provide insights into the validity of wood chemistry reaction mechanisms obtained from model studies. Kaylor's research project involves binding a cellulose model compound to polystyrene resin and

then initially examining its reactions under pulping conditions. The model will not only lack water solubility, but will also contain inflexible glucose rings that will mimic the situation found in crystalline cellulose.

We have been fairly successful in grafting simple phenol compounds to polystyrene resin and studying condensation reactions of the type which lead to the residual lignin found in unbleached pulp. In an extension of this research, Sawyer's project involves the attempted preparation of a more complex lignin model bound to polystyrene. The model would allow us to study heterogeneous lignin fragmentation reactions, the most important reaction type occurring during pulping and bleaching.

CONCLUSIONS

The research of the wood chemistry group covers a variety of important areas. Except for Don Dimmel, the faculty, technicians, and students in the group have on average less than one year's experience in wood chemistry. However, the group is rapidly developing the experience needed to make significant advances in their related research areas.

The various detailed project summaries, together with information on sources of funding, level of funding, and personnel are provided next. Any further clarification of research directions, beyond the project summaries, can be obtained by contacting the project leader. We welcome your input and suggestions.

PROJECT 3661

SULFUR-FREE SELECTIVE PULPING PROCESS

(DOE FUNDED)

RESEARCH REVIEW

April 2, 1991

Donald R. Dimmel

PROJECT SUMMARY FORM

Project Title:	SULFUR-FREE SELECTIVE PULPING PROCESS
	(DOE FUNDED PROJECT)
Division:	Chemical and Biological Sciences
Project No.:	3661
Project Staff:	Dr. Donald R. Dimmel (professor), IPST Project Leader
	Dr. Earl W. Malcolm (research division director), IPST
	Dr. Ken-Ichi Kuroda (visiting scientist), IPST
	Ms. Patricia Caldwell (technician), IPST
	Mrs. Alison Daube (associate scientist), IPST
	Dr. Joseph Bozell (senior organic chemist), SERI Project Leader
	Dr. David Johnson (senior organic chemist), SERI
	Dr. Helena Chum (manager, Chemical Converstion Branch), SERI
	Ms. Bonnie Hames (staff member and graduate student), SERI
	Mr. Arthur Power, an independent consulting process engineer

FY 90-91 Budget: $205,700 at IPST, $219,300 at SERI

IPST GOAL:

Improved process for bleached chemical pulps.

OBJECTIVE:

To develop a sulfur-free pulping process based on conversion of lignin to pulping additives which will increase delignification rates and decrease the degradation of carbohydrate fibers.

SULFUR-FREE SELECTIVE PULPING PROCESS
(DOE FUNDED PROJECT)

Reporting period: March 1990 - March 1991

OBJECTIVE

To develop a sulfur-free pulping process based on conversion of lignin to pulping additives which will increase delignification rates and decrease the degradation of carbohydrate fibers.

INTRODUCTION

The kraft pulping process has achieved wide acceptance because of its relatively rapid pulping rates, its adaptability to many types of wood feedstocks, its ability to produce a strong pulp, and its low chemical costs. However, the process has a number of shortcomings: the yield of pulp is relatively low, the pulp is highly colored, requiring extensive bleaching, the presence of the sulfur promoter leads to malodorous emissions, and there is an extremely high capital investment associated with the complex chemical recovery system and environmental processing technology.

A possible solution to several of the kraft process disadvantages was discovered in 1977. Holton reported that addition of catalytic amounts of anthraquinone (AQ) significantly promotes alkaline pulping processes.[1] This discovery has become one of the most widely studied effects in paper chemistry in the last 13 years. There are a number of benefits associated with the use of anthraquinone, including an increase in pulping rates, higher pulp yields, a decrease in the amount of the alkali in the process, and adaptability with existing kraft technology. Of course, all of these benefits may not be realized simultaneously. Importantly, the pulp properties are quite similar to kraft, except for a small decrease in tear strength.

Despite the reported advantages of anthraquinone catalyzed pulping, the current cost of AQ (about $4.50/lb) hinders its general use, except under certain circumstances. Where wood costs are high, such as in Japan, pulping yields take on greater importance and AQ-type processes are common. Anthraquinone is also used to give "relief" from a bottleneck, such as a deficiency in recovery furnace capacity.

We have been investigating ways to prepare quinone catalysts at a cost low enough to make it attractive for general industry use and have found lignin to be a suitable starting material.[2-4] Lignin has a number of attractive features as a raw material for anthraquinone production. First,

lignin is inexpensive; it is readily available as a by-product from the paper industry. Its cost is normally calculated as its fuel value which is $0.03-$0.04/lb. Second, a successful synthesis of an anthraquinone analog from lignin will give a new, higher value-added product to the industry. Third, a mixture of lignin and quinone catalysts could probably be used as a pulping promoter without purification and, hence, could be used on site and save several costly processing steps.

In the last two years, our research, supported by the Office of Industrial Technology of the U.S. Department of Energy, has focused on both the scientific and economic aspects of commercialization of a catalysts-from-lignin process. Our approach for the synthesis of catalysts-from-lignin has been divided into two large stages, lignin processing and chemical processing.

The lignin processing stage involves selectively isolating a low-molecular-weight fraction from a lignin source.[5] Lignin is a complex high molecular weight biopolymer which is fragmented during pulping. However, condensation reactions, which occur during pulping, reconnect some of the fragments to give new polymeric and oligomeric materials of widely differing molecular weights. In theory, this crude mixture could be used directly in the subsequent chemical processing stage without separation of a low-molecular-weight fraction. However, our economic evaluation has indicated that this approach is unattractive because of expected non-productive consumptions of chemicals.[6]

Therefore, low-molecular-weight lignins must be isolated to serve as starting materials. Two methods for separation of this low-molecular-weight fraction have been evaluated: extraction of a processed pulping liquor using supercritical carbon dioxide in the presence of small amounts of organic solvents[7] and extraction of an isolated lignin with conventional solvents. At this point, the latter extraction appears to be the more promising.

The second stage of the process involves chemical processing of the low-molecular- weight fraction and contains two critical chemical steps (Fig. 1). In the first step, the low-molecular-weight lignin is oxidized with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones (1). This step attempts to retain the aromatic rings of the lignin while oxidizing away the side chains and cleaving the bonds between monomer units. The aliphatic lignin side chains are not needed and, in fact, will cause problems in subsequent steps in the process. The degree of methoxy-substitution depends on the source of the lignin. Softwoods will give mostly monomethoxybenzoquinone, while hardwoods give a mixture of mono and dimethoxybenzoquinone.
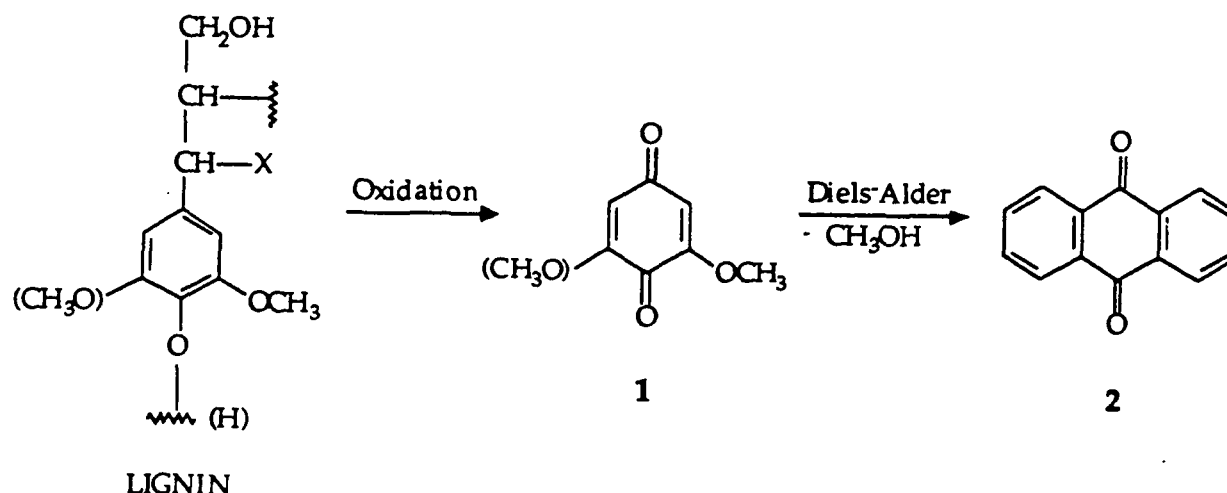
Figure 1. Chemical steps in the conversion of lignin to an anthraquinone analog.

In the second step of the chemical processing sequence, the benzoquinones are converted into nonaromatic AQ-analogs by treatment with a diene, using the well-known Diels-Alder reaction. Final conversion of these AQ-analogs to aromatic quinone catalysts (e.g. **2**) occurs by loss of methanol and hydrogen, either during reaction or in a separate step. The aromatization step may be unnecessary; partially aromatic anthraquinone also functions as a pulping catalyst by in situ conversion to anthraquinone.[8,9]

RESULTS

Progress has been made in each of the areas mentioned in the Introduction Section since our initial disclosure of the preparation and activity of AQ catalysts derived from lignin.[2-4] The most important activities are summarized below.

Process Economics

The single most important determining factor in the final cost of anthraquinone prepared from lignin is the overall yield of the chemical processing steps. An economic evaluation determined that the catalysts cost drop exponentially with increasing overall yield. Because of the strong dependence of catalyst price on chemical yield, the contribution of the preliminary lignin processing stage to the overall cost is not significantly different regardless of whether a supercritical fluid extraction or conventional solvent extraction is employed. Another

conclusion of the economic evaluation is that the catalyst cost drops significantly as the scale of the operation increases. Under optimum conditions, the cost of AQ-analogs could be as low as $1.00/lb. More realistically, a cost between $1.25 and $1.75/lb has been projected.

An economic evaluation also compared the lignin based route to AQ to other competing routes to AQ which are primarily based on fossil fuel-derived starting materials. Five alternative commercial or near-commercial routes were considered. Assuming satisfactory progress in research and development, the lignin route was potentially the most cost-effective anthraquinone process available.

Lignin Processing

A number of lignin processing techniques have been examined. Both supercritical fluid extraction and solvent extraction hold the promise of providing the necessary low-molecular-weight lignin fraction necessary for conversion to anthraquinone. Supercritical fluid extraction, involving carbon dioxide and 15-25% added organic solvent, has been used to remove the low-molecular-weight lignin which remains in the aqueous phase following acid precipitation of the high-molecular-weight lignin from a pulping liquor.[7] While the selectivity for low-molecular-weight lignin is good, the yield has been low.

Recent results indicate that simple organic solvent extraction of organosolv lignins provides significant amounts of low-molecular-weight material. Organosolv lignin has a number of interesting characteristics when considered as a starting material for this process. Structurally, it resembles native lignin more closely than other types of lignin, such as kraft. This property is important since organosolv lignin retains certain functional groups that could make subsequent chemical processing easier. Organosolv lignin also appears to contain a higher proportion of the low-molecular-weight fraction needed for anthraquinone synthesis.

Chemical Processing: Oxidation of Lignin and Lignin Models

A number of oxidizing agents have been evaluated for suitability in the first step of the chemical processing stage. Because of the structural complexity of lignin, initial work was performed on compounds that model lignin's behavior. Fremy salt is an excellent oxidant for the production of benzoquinones from phenols which bear lignin-like functional groups;[2] however, the reagent does not appear suitable for a large industrial process.

Hydrogen peroxide oxidation of certain lignin models to give benzoquinones has been optimized to give yields of 80-90%. However, a large excess of oxidant is needed for good yields, thereby reducing its cost-effectiveness. Also, the yields of benzoquinones from H_2O_2 treatment of isolated lignins have been discouragingly low. For example, the yields of benzoquinones from a lignin by oxidation with $H_2O_2/NaOH$ were about 1/8 the yields by oxidation with NO_2/O_2 (another oxidant to be discussed). These drawbacks have led to the examination of other oxidants.

Inexpensive oxygen has been successfully used as an oxidant in the presence of catalytic amounts of certain transition metal complexes. Yields of benzoquinones from the oxidation of lignin models as high as 85% have been realized under mild conditions. Recent research has been directed at modifying the transition metal complex to achieve a greater range of catalytic activity at a low catalyst/substrate ratio, such as 0.01. The first catalyst tested gave high yields of quinones with only a limited number of lignin models and required a catalyst/substrate ratio of 0.1.

Nitrogen dioxide, a readily available material, has been shown to be an effective oxidant for generating dimethoxybenzoquinone (DMBQ) from lignin. The procedure involves treating lignin, or a lignin model compound, at room temperature with NO_2/O_2 in an alcohol solvent. The yields of DMBQ with simple syringyl lignin models are often above 80%. About 60% of the syringyl units in an extracted (low molecular weight) organosolv aspen lignin were converted to DMBQ. The actual yield of DMBQ was 15% from White Oak organosolv lignin, which contains 25% syringyl units. The yields were enhanced by about 1-1.5% in the presence of N-hydroxysuccimide (NHS), a reagent which can act similar to Fremy salt.

The yields of DMBQ, as a function of isolation procedure, warrant some discussion. We have employed two principal methods of analysis: (1) high performance liquid chromatography (HPLC) of organic solvent diluted reaction mixtures, using UV absorbance values relative to standard mixtures and (2) gas chromatography (GC) of product mixtures containing AQ as an internal standard. In most of our earlier work the HPLC method consistently gave higher yields of DMBQ from lignin that the GC method. Now we known that this was related to the product isolation method.

Two methods were tried to recover more completely the DMBQ from a model system containing known amounts of lignin, DMBQ and AQ. The methods were: (A) extraction by $CHCl_3$ under refluxing and (B) Al_2O_3 column chromatography using $CHCl_3$ as the eluent. Both methods showed that DMBQ was effectively recovered. For an actual oxidized (ethanol organosolv) lignin, method A gave poorer results than method B: 5.2% DMBQ yield before isolation, 4.4% yield by $CHCl_3$ extraction, 3.3% yield by $CHCl_3$ extraction after addition of water, and 5.1% with Al_2O_3 column chromatography (these data are also summarized later in Table 1).

The recovery yields, after addition of water, of known amounts of DMBQ and AQ from solutions of lignin in $CHCl_3$ were determined using GC. The recovery yields of DMBQ decreased gradually with increasing amounts of lignin, while the yields of AQ internal standard were consistently near 100%. Also, the recovery yields of DMBQ depended on the reaction times for (acidolysis) pretreatment of the lignin. Therefore, the amount and the property of lignin have detrimental effects on the recovery of DMBQ in DMBQ/lignin mixtures. These effects are probably due to the incorporation of DMBQ into the lignin macromolecular structure, during precipitation by water. These findings suggest that some of the earlier yield values of DMBQ have been underestimated.

We have also compared the GC and HPLC yields of DMBQ from the oxidation of white oak organosolv lignin with NO_2/O_2 to observe any changes in the % yield of DMBQ due to filtration and/or dilution of the mixture. The % yield was basically the same for both analytical methods

for (1) the non-diluted, non-filtered reaction mixture, (2) the non-diluted, filtered reaction mixture, and (3) the diluted, filtered reaction mixture. The procedure of refluxing twice for 30 minutes with $CHCl_3$ gave about 1% lower yields by GC.

The most reliable yields come from a direct analysis reaction mixture analysis by either HPLC or GC. The yields reported here are by the direct analysis method, unless stated otherwise. For any commercialization of a process for producing DMBQ (and MMBQ) from lignin, we will need to take into consideration the association of simple quinones with precipitated lignin and design our recovery system accordingly.

The predominate lignin unit (75%) in White Oak organosolv lignin is a guaiacyl unit (aromatic ring with one methoxyl group). Oxidation of guaiacyl units would lead to monomethoxybenzoquinone (MMBQ). Unfortunately, the yields of MMBQ from White Oak organosolv lignin were consistently low (1%). The stability of MMBQ to NO_2/O_2 was checked; it showed no significant loss after 90 minutes, 20% loss after 3 hours, and 77% loss after 20 hours of treatment. Poor MMBQ yields from NO_2/O_2 oxidation presents a serious drawback to the NO_2/O_2 procedure since most common wood species are rich in guaiacyl units and the sum of the benzoquinone yields (MMBQ and DMBQ) will be low.

The NO_2/O_2 oxidation of vanillyl alcohol (a guaiacyl model) was studied in order to understand the low yields of MBQ from organosolv lignin. Several unsuccessful attempts were made to duplicate an earlier _estimated_ 56% yield of MBQ from vanillyl alcohol in ethylene glycol solvent. Yields in the 11-18% range were found for the NO_2/O_2 oxidation of vanillyl alcohol in MeOH. A similar oxidation of _p_-hydroxybenzyl alcohol, a non-methoxylated model, gave essentially no 1,4-benzoquinone. Thus, it appears that the presence of methoxy groups on the 3,5 positions of the aromatic ring favors good oxidation yields.

Vanillyl alcohol disappeared when treated with NO_2/O_2. If quinone yields are low, what then were the products? A large scale (1 gram) oxidation of vanillyl alcohol with NO_2 was performed in order to obtain enough products to isolate and characterize via NMR and GC/MS. Isolation was accomplished using silica gel column chromatography and prep TLC on condensed fractions containing the compounds of interest. Results of analytical tests indicate the major product was 5- or 6-nitrovanillyl alcohol. This finding suggests a preference for addition of the NO_2 to vanillyl alcohol over oxidation to a quinone, and could explain our unsuccessful efforts to obtain good overall quinone yields in the oxidation of organosolv lignin. The preference for ring addition reactions of NO_2 may be due to a localized overabundance of NO_2 in the reaction mixture. A higher O_2/NO_2 ratio might increase the yields of MBQ.

An experiment was set up in which a stream of O_2 was maintained while quickly sweeping a large excess (10X molar ratio) of NO_2 through the reaction mixture several times, recondensing the NO_2 prior to each "sweep". The recondensation aspect failed and the yields of DMBQ from syringyl alcohol and MBQ from vanillyl alcohol with this experimental design were substantially lower than the normal procedure. Additional modifications will be pursued before abandoning this approach.

The oxidation of syringyl alcohol by NO_2/O_2 in various solvent systems and lengths of time has been extensively investigated. The solvents tested were mixtures of water/methanol or ethanol, together with nonhydroxylic solvents, such as methyl isobutyl ketone. The latter produced a 4.7% yield of DMBQ. Methanol proved to be the superior solvent for DMBQ production. The stability of DMBQ was good for all solvents tested.

Peroxide and, especially, acidolysis were the effective treatments (Table 1). The yields of monomethoxybenzoquinone were only a trace in these cases. Some pretreatments of ethanol lignin hurt DMBQ yields (in comparison to no pretreatment). For example, the combination, acidolysis followed by $H_2O_2/NaOH$, was poor. Aqueous peracetic acid pretreatments at room temperature and under more harsh conditions gave DMBQ in 1-3% yields. A $Na_2S/NaOH$ treatment (kraft cooking) led to only a 2.9% yield.

Table 1

Yields of DMBQ after Oxidation of Pretreated Ethanol Lignin

Pretreatment Type - % DMBQ yield[a]

work up procedure	no pretreat.	H_2O_2	acidolysis	acidolysis H_2O_2	CH_3CO_3H	Na_2S	CuO	$NaBH_4$
direct GC	5.2		10.7[b]	3.0	1-3	2.9	9.5	6.4
Al_2O_3 chrom.	5.1							
hot $CHCl_3$	4.4							
ppt./$CHCl_3$	3.3	5.0						

[a]The yield is the best of several time tested.
[b]Pretreatment followed by an NO_2/O_2 oxidation done at 40-45°C.

It is well known that CuO/NaOH oxidation extensively depolymerizes lignin into low molecular fractions, having increased levels of phenols and a-carbonyl groups. A CuO/NaOH pretreatment at 100°C led to a slight yield increase of DMBQ (5.8%), while pretreatments with CuO/NaOH at 170°C at 1, 3, 5, and 8 hrs gave, after NO_2/O_2 oxidation, yields of DMBQ of 3.3, 9.5, 6.2 and 6.8%, respectively. The yield (9.5%) at 3 hr is the largest observed for a room temperature NO_2/O_2 oxidation of this particular lignin. Also, the observed values might be slightly lower than real ones because the CuO/NaOH reaction mixtures were neutralized and extracted by $CHCl_3$-dioxane prior to NO_2/O_2 oxidation and some water soluble lignin may have been lost.

Reduction of ethanol lignin by NaBH$_4$ was carried out in order to reduce a-carbonyl groups, if present, to a-carbinol groups; the latter gives higher yields of DMBQ than the former when oxidized by NO$_2$/O$_2$. Two reduction procedures were tried. One involved powdered NaBH$_4$ being added to ethanol lignin in 0.1 N NaOH; after 4 and 16 hr reaction, the samples were neutralized, extracted with CHCl$_3$-dioxane, and oxidized with NO$_2$/O$_2$ to give the same yield (3.9%) of DMBQ. Another involved adding a 0.1 N NaBH$_4$ aq. soln. to ethanol lignin in ethanol. The sample obtained after 48 hr gave DMBQ in 5.5% yield by NO$_2$/O$_2$ oxidation. Repeating this last experiment, only employing a milder work up, gave a 6.4% yield (1.3% better than the control) after NO$_2$/O$_2$ oxidation. While NaBH$_4$ on its own does not give substantial yield increases, the combination of NaBH$_4$ with other pretreatments may be beneficial.

Several other lignin samples have been investigated, in an attempt to find the best starting material for the quinone catalyst synthesis. The NO$_2$/O$_2$ oxidations of a 2:1 lignin to polyepichlorohydrin sample and a 1:1 lignin to alum sample received from a member company gave very poor yields of DMBQ (0.4% and 0%, respectively). Methoxybenzoquinone was detected in trace levels in the first case. The NO$_2$/O$_2$ oxidation of the REPAP lignin phenolic by-product gave a 6.0% yield (by HPLC analysis) after 30 min reaction time and, in another experiment, a 6.7% yield (by GC analysis) of DMBQ after 3 hrs reaction time. In comparison, the yields range from 7.5 - 10.2% DMBQ for a SERI white oak organosolv lignin over the same oxidation time period.

The reactions of potassium dichromate with selected lignin model compounds and lignin were also examined; yields of DMBQ in the 10-55% range for models and 1.2% for a hardwood kraft lignin were not encouraging enough to pursue further. No formation of MBQ was observed.

Chemical Processing: Diene Addition

The second step in the process of producing quinone catalysts from lignin is addition of a diene to the benzoquinone mixture to give anthraquinone precursors. Each of the benzoquinones expected from lignin oxidation has been tested for its ability to under go Diels-Alder reactions. The yields of these reactions can be high, especially for formation of one ring. However, the formation of two rings simultaneously (benzoquinone directly to an anthraquinone) is a more difficult task; the intermediate naphthaquinone structures react very slowly under standard conditions.

benzoquinone (DMBQ)   diene   AQ analog
(R$_1$, R$_2$ = H, CH$_3$)
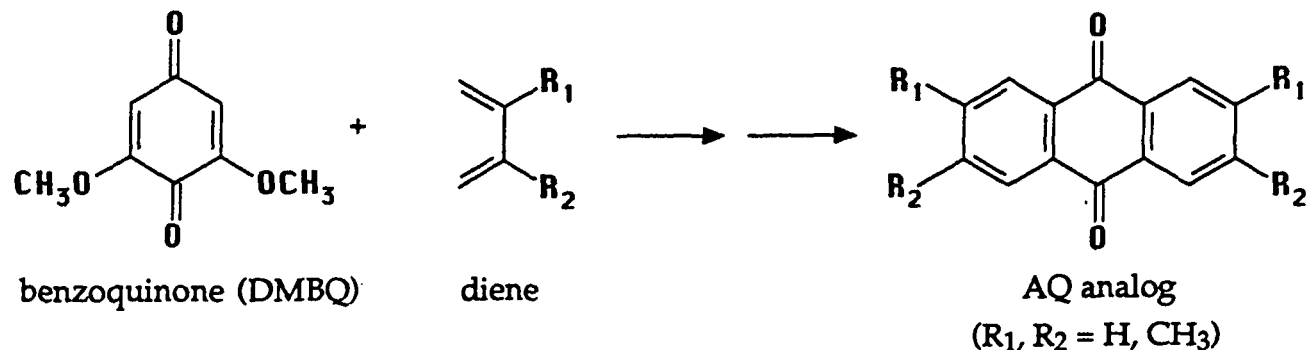
Through the course of our research, we have found that Diels-Alder reactions between two water insoluble reactants can proceed in water with quite favorable results. The reaction between DMBQ and a diene in water at 170°C gives a mixture of naphthoquinones and anthraquinone analogs in roughly a 1:4 ratio and overall yields generally in 65-85% range. The terms "analogs" and "adducts" refers to the fact that not all of the products are fully aromatized and there may be methyl groups on the rings (AQ itself is fully aromatic and unsubstituted). We have been examining several factors related to optimization of yields, both in pure water and mixed water/organic solvents.

The effects of ethanol and 1,4-dioxane co-solvents in the aqueous Diels-Alder reactions were determined for a 10:1 ratio of 2,3-dimethyl-1,3-butadiene, the diene, and DMBQ, the benzoquinone. At low concentrations of dioxane, the AQ and NQ adduct yields improved over a pure aqueous control by 3% and 2%, respectively. At higher concentrations of dioxane, the AQ adduct yield was comparable with the control and the NQ adduct yield increased. Ethanol had a slightly negative effect on NQ/AQ adduct yield at either a high or low concentration. The appearances of the dioxane and ethanol product GC chromatograms were considerably different. The dioxane runs had a strong signal indicative of the NQ adduct increase. GC-MS of the ethanol samples allowed for the characterization of many of the adducts and clarified the presence of dimers and trimers of the diene.

Another set of ethanol and dioxane co-solvents experiments was carried out at a diene to dienophile ratio of 5:1 and yield improvements, versus the control, of 5 - 9% AQ and NQ adducts were noted. This led to an experiment to determine the effect of diene to dienophile ratios on product yield using isoprene (a diene) and DMBQ in pure water. The data in Table 2 for isoprene were generated from simultaneous reactions; the data for 2,3-dimethyl-1,3-butadiene were done on a different day, but same conditions. The isoprene adduct yields were (1) high for this set, (2) substantially better than the other diene, and (3) low at the low diene/DMBQ ratio.

Table 2
AQ + NQ Adduct Yields as a Function of Diene Ratio

Diene/DMBQ ratio	2,3-dimethyl-1,3-butadiene NQ + AQ Adduct Yields	2-methyl-1,3-butadiene (isoprene) NQ + AQ Adduct Yields
2.5/1		25 + 30 = 55%
5/1	8 + 42 = 50%	18 + 69 = 87%[a]
7.5/1		17 + 61 = 78%
10/1	7 + 36 = 43%[b]	18 + 67 = 85%

[a]A recent bulk reaction gave 15 + 57 = 72% result.
[b]A bulk reaction gave 5 + 58 = 63% result.

A direct comparison of methanol and water as the Diels-Alder solvent for isoprene and DMBQ at 5:1 at 170°C for 8 hr gave quite different results. The water run gave 15% NQ and 52% AQ adducts (67% total). The methanol solvent gave very high yields of NQ, but AQ adduct yields of only about 4%. Methanol was investigated because this is the solvent used in the preparation of the DMBQ and possibly a simple set of consecutive reactions could be developed.

A set of no solvent Diels-Alder reactions was run at 170°C for 6 hours. AQ and NQ adducts were not formed at 2.5:1 reactant ratio; DMBQ was still present after 6 hours. The number and intensity of product GC signals, relative to the internal standard, increased as the diene/DMBQ ratio increased; however, AQ adducts were not produced. Dimers and trimers of isoprene appeared abundant. In summary, solvent-free reactions do not appear to be promising.

Reactions of isoprene in water and 2,3-dimethyl-1,3-butadiene in water, without any quinone coreactant, were run at conditions duplicating diene concentrations and vapor space conditions of typical Diels-Alder reactions. The samples were removed from the oil bath at 2, 4, and 8 hour intervals, extracted, and analyzed using GC. The odor of limonene (isoprene dimer) was evident in the isoprene product extractions. The chromatograms allowed for the identification of dimer and trimer peaks in previous and subsequent Diels-Alder runs.

Cyclopentadiene reactions were then run to determine the suitability of this diene in the conversion of DMBQ to AQ and NQ adducts. The Diels-Alder reaction was run at 170°C for 8 hr with a ratio of cyclopentadiene:DMBQ of 2.5:1 and 5:1. The samples proved difficult to extract. Two solvents were used, chloroform/ethanol and dichloromethane; yet a small portion of a brownish-black product was insoluble in either solvent. Both extracts were analyzed. The resulting gas chromatograms revealed a large number of strong signals eluting prior to naphthoquinone internal standard, which are presumably dimerization products of the cyclopentadiene. Quantification of products was difficult, but it appeared that the overall yield of NQ adducts was <15% and the AQ adduct yields were insignificant. Further cyclopentadiene reactions will not be pursued.

The effect of cyclohexene on the reaction of isoprene with DMBQ at 5:1 in water was also examined. The cyclohexene was tested as an additive since it could possibly function as a hydrogen acceptor in disproportionation reactions and, thereby, promote adduct aromatization steps. The cyclohexene was present at 3, 6, or 10 equivalents relative to DMBQ. The control (no cyclohexene) had the best yield (15% NQ and 55% AQ adducts). The products and the amounts were somewhat similar (ie., no large aromatized AQ analog signal) with and without cyclohexene, indicating that very little reaction occurred between cyclohexene and the intermediate adducts. The yields with cyclohexene were as follows:

1) 3 eq.   ---> 10% NQ adducts, 55% AQ adducts, 65% total;
2) 6 eq.   ---> 20% NQ adducts, 43% AQ adducts, 63% total;
3) 10 eq. ---> 31% NQ adducts, 20% AQ adducts, 51% total.

Dr. Joe Bozell at SERI has found that Diels-Alder reactions of benzoquinones on solid surfaces give 30-55% yields of aromatic anthraquinone analogs; he will be pursuing this area in much greater depth.

These recent encouraging results, using catalysis to assist the diene addition and a novel diene addition reaction carried out in water, suggest that a direct one-step conversion of benzoquinones to anthraquinones, without isolation of non-aromatic precursors, is possible. Isoprene appears to be an excellent diene reactant and with simple benzoquinones will produce a product mixture which should have high catalytic activity. We now suspect that the Diels-Alder step will not be a significant contributor to the overall process cost. We will continue to pursue efforts to understand the yield variations and to increase the Diels-Alder yields further. Any improvements in the Diels-Alder yields will compensate for deficiencies in the oxidation step leading to the benzoquinones.

Pulping Studies

Several large scale Diels-Alder reaction have been performed to obtain sufficient quantities of the NQ/AQ adduct product mixture to test for catalytic pulping activity. The product mixture, which contained oil from the high temperature bath, was purified by chromatography. The resulting mixture was added to pine chips (0.1%) and pulped under standard soda conditions; in comparison to three control soda/AQ cooks, the Diels-Alder mixture was close in activity to a 0.1% level AQ; however, the alkali level was high due to a miscalculation and the experiment was repeated.

Two large scale preparations were performed by combining the products of several small scale runs between diene and DMBQ. The one set employed isoprene at a 5:1 ratio with DMBQ and the other set employed 2,3-dimethyl-1,3-butadiene at a 10:1 ratio with DMBQ. The product mixture from combining seven small runs with the isoprene was atypical, in that the product mixture was richer in NQ-type adducts (31%) than AQ-type adducts (28%). The bulk run with 2,3-dimethyl-1,3-butadiene and DMBQ resulted in adduct yields of 5% NQ and 58% AQ.

Both the 31/28 isoprene adduct mixture and 5/58 DMBD adduct mixture were tested for pulping activity on pine. The Kappa numbers were as follows:

1) 64.2 with no additives (control);
2) 34.3 with 0.1% isoprene product;
3) 26.7-27.7 with 0.25% isoprene product;
4) 34.6 with 0.1% 2,3-dimethyl-1,3-butadiene product; and
5) 31.9-32.8 with 0.25% 2,3-dimethyl-1,3-butadiene product.

The additives slightly decreased the pulp yield (1-2%) in comparison to the control. The 2,3-dimethyl-1,3-butadiene samples had a much higher concentration of AQ-type products in the mixture, yet had higher Kappa numbers (more lignin) than the isoprene samples at the 0.25% level. This demonstrates that the AQ adducts from isoprene likely have a higher pulping activity than the DMBQ products.

The target yield from previous isoprene reactions is 55-60% AQ adducts and approximately 15% NQ adducts. The bulk reaction with isoprene is being repeated. The products will then be examined for pulping activity versus a control with 0.1% AQ. Also, reactions of butadiene and

DMBQ (and MMBQ), which will lead to non-methylated AQ adducts, will be performed and the products tested for catalytic activity.

FUTURE STUDIES

We have demonstrated the feasibility of each step in the overall process under certain cost constraints. The objective of our research in the next year is to develop and optimize our lignin extraction and chemical conversion efficiencies to further lower the cost of pulping catalysts from lignin. In the synthesis area we will continue to examine different lignin sources for their capacity to be oxidized to benzoquinones, ways to convert guaiacyl structures to monomethoxybenzoquinone, ways to degrade an isolated lignin into small pieces capable of conversion to quinones, and the best conditions for performing Diels-Alder reactions that give high yields of anthraquinones. The catalyst mixtures will be tested for activity. The successful laboratory research will be moved to larger scale in future years.

Development of a cost effective soda/AQ process will greatly reduce the air emissions typically associated with present processes and simplify chemical recovery and environmental processing. If catalyst cost can be kept low, an anthraquinone process offers opportunities to improve productivity, conserve raw materials, and save significant amounts of energy.

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PROJECT 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

RESEARCH REVIEW

April 2, 1991

Arthur J. Ragauskas

PROJECT SUMMARY FORM

FY 90-91

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

IPST GOAL:

Increase the usefulness of high yield fibers

OBJECTIVE:

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

FUNDAMENTALS OF BRIGHTNESS STABILITY

Reporting Period: March, 1990 -- March, 1991

OBJECTIVES

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

INTRODUCTION

The use of high yield mechanical pulp has received increasing attention for the last two decades. Several timely reviews have highlighted the current and future demands for these types of pulps[1,2]. Despite the recent interest in high yield pulps, their commercial use is often limited to low value or short life-cycle paper products due to the inherent photo-instability of mechanical pulps. The photochemical initiated reactions result in the yellowing of both bleached and unbleached mechanical pulps and therefore decreases the brightness of these pulps[3]. It is this fundamental problem that has hindered further use of mechanical pulps for a variety of commercial applications. Research efforts directed at examining the photo-yellowing process have been successful in defining some of the important parameters involved in this reaction.

Early investigations by Leary[4a,b] and others clearly[5a,b] determined that the yellowing of high yield pulp is initiated by the absorption of near UV light (λ=300-400 nm) by the lignin component of the pulp. Furthermore, the presence of oxygen was shown to be crucial for the photo-yellowing process to occur.

Further studies at IPST and at other research institutes have clearly defined the kinetics of yellowing[6] for various types of mechanical pulp and the rate of yellowing as a functional of spectral distribution. The brightness reversion phenomena has been examined by various analytical means, such as solid-state electronic spectroscopy[7], FT-IR[8], ESCA[9], ultraviolet microscopy[10], ^{13}C CPMAS[11] and ^{31}P NMR[12]. These studies have defined a variety of the physical changes which accompany the yellowing phenomena. The ^{31}P NMR studies clearly identified the important role that ortho-quinones play in the yellowing phenomena. The presence of para-quinones has also been suggested as a contributing yellowing reagent based upon FT-IR studies.

A variety of other factors, such as pH[13], metal salts[14], bleaching procedures[15], moisture content[16], common antioxidants[17], and extractives content[18] have also been examined to determine their role in the photo-degradation process. To date, these investigations have not been successful in finding manufacturing conditions which would significantly reduce the rate of photo-yellowing.

Based upon these results and a variety of model studies reported in the literature it was proposed[19] that the current research studies would focus on the photoformation and photoreactivity of quinones in the solid state. It is anticipated that a refined understanding of how quinones are formed and the reactivity of these structures under the brightness reversion conditions could lead to novel methods of retarding their formation.

RESULTS FROM PHOTOLYSIS STUDIES

Initial photochemical studies were focussed on the photoreactivity of dimethoxybenzoquinone (DMBQ) and monomethoxybenzoquinone (MMBQ). Both of these compounds have been suggested to contribute to the yellowing process.

DMBQ   MMBQ
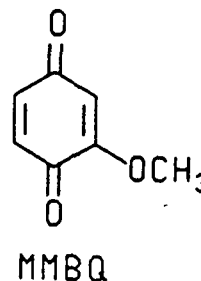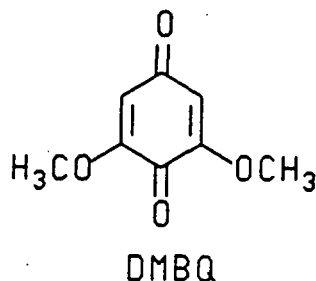
These compounds were also selected as a starting point in this investigation since it was known that their reactivity and ease of preparation would permit facile development of the techniques needed to study the more reactive ortho-quinones. Synthetic efforts directed at preparing these and other structures is highlighted in the latter part of this report.

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

Due to the chemical complexity of mechanical pulp the initial photochemical studies were performed on extracted cotton linter fibers (i.e., cotton linters fibers which were washed with distilled water and then exhaustively extracted with methanol followed by dichloromethane).

The para-quinones were applied onto the cotton linters, dried under high vacuum and irradiated with vigorous stirring. Samples of the irradiated material were then periodically removed from the photoreactor, extracted and analyzed by GC and/or GC-MS.

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

Period of Irradiation (h)	% DMBQ Recovered[a]
1	81
2	73
4	69
8	76

[a]GC Yields

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

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

Period of Irradiation (h)	Sample	TAPPI Brightness
0	Cotton Linter	89
0	Cotton Linter\DMBQ	38
1	Cotton Linter	88
1	Cotton Linter\DMBQ	40
2	Cotton Linter	88
2	Cotton Linter\DMBQ	44
4	Cotton Linter	89
4	Cotton Linter\DMBQ	56

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

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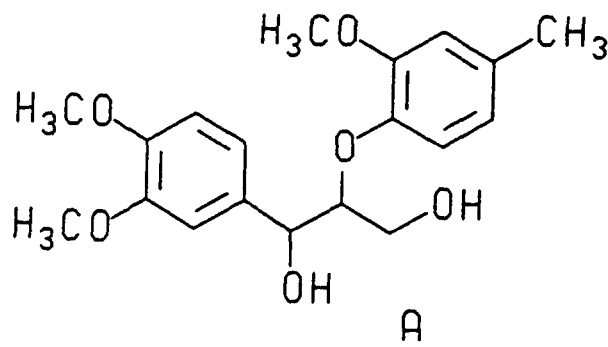
Clearly these results suggested that any DMBQ formed under the brightness reversion conditions is photostable and will not initiate any further reactions.

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

Period of Irradiation (h)	% DMBQ Recovered[a]
1	83
2	>100
4	76
8	>100

[a]GC Yields
[b]the results for the 2 and 8 h samples gave greater than 100% yields since the samples were not completely homogeneous

The photoreactivity of MMBQ was also examined in this research term. The behavior of this quinone was of interest since Forsskahl[20] has shown that solution photolysis leads to complete consumption of starting material and formation of an intensely colored dimer compound.
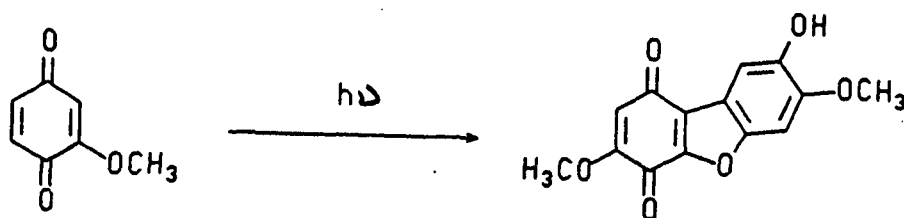
To explore the photoreactivity of MMBQ in the solid state, samples were applied onto cotton linters fibers and were irradiated in much the same manner as described above for DMBQ. GC-MS analysis of the product mixture indicated that the reactivity of MMBQ in the solid state was distinctively different than that reported for the solution phase. The photolysis of MMBQ, adsorbed onto cotton linters gave largely a product mixture containing MMBQ and monomethoxyhydroquinone (MMHQ).

Period Irradiation (h)	% MMBQ[a]	%MMHQ[a]
1/2	65	6
1	58	5
2	65	5
4	70	8

[a]GC Yields

The presence of MMHQ was not expected and repetition of the experiments confirmed its formation. The exact ratio of MMBQ:MMHQ did vary and was shown to be dependent upon the effectiveness of stirring. The formation of MMHQ was attributed to a photo-reduction, which suggests that the cellulose was undergoing an oxidation. This process is accompanied by a distinctive change in color of the starting material from bright yellow to a dark brown\purple color for the product. Samples of MMBQ were applied to sheets of cotton linters, irradiated and the color change was monitored by TAPPI brightness measurements

Period Irradiation (h)	TAPPI Brightness
0	44
1	35
2	32
4	33

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

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

The photolytic behavior of MMBQ adsorbed onto TMP has also been explored. In contrast to the cotton linter studies it appears that after 4 h of irradiation very little quinone remains on the surface of the fibers.

Period Irradiation (h)	% MMBQ Recovered[a]
1	21
2	25
4	20

[a]GC Yields

The fate of MMBQ on TMP currently remains uncertain but these results clearly suggest that MMBQ is not a final photochemical product in the brightness reversion phenomena. Instead it appears that MMBQ is a reactive intermediate which oxidatively attacks lignin, generates other chromphoric structures and initiates a photo-degradation reaction of mechanical pulp.

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

Samples of 4-methyl ortho quinone have been prepared but difficulties encountered in isolating this compound and in applying this material to a solid support have delayed the photolysis studies. The reactivity of 4-methyl ortho quinone does suggest that it will also be photo-labile under the brightness reversion conditions.

RESULTS FROM SYNTHETIC STUDIES

The photolysis of para and ortho quinones requires an efficient source of these starting materials. Following the literature procedure of Matsumoto[21] 1,3,5-trimethoxybenezene was efficiently converted to DMBQ. The preparation of MMBQ was shown to be readily achieved by oxidizing MMHQ with either Clayfen (Iron(III) Nitrate supported on K 10 clay) or bis-acetoxy iodobenzene. Both of these reagents were shown to efficiently oxidize MMHQ and allow for facile work-up procedures. Since the oxidation of lignin like structures is of general interest in the wood chemistry literature the reactivity of these reagents with several lignin like structures was examined (i.e., vanillin, 4-methyl catechol, syringaldehyde, acetovanillin, 1,2 catechol and 1,4-hydroquinone). Analysis of the product mixtures indicated that the Clayfen usually yielded a complex mixture unless the starting material was a hydroquinone-like structure. The oxidizing potential of bis-acetoxy iodobenzene was such that it could efficiently convert either the catechol or hydroquinone structures to the corresponding quinone compounds. The preparation of 4-methyl ortho-quinone has been accomplished using this latter reagent.

The chemical complexity of mechanical pulp is such that it is exceedingly difficult to characterize the fundamental photochemical processes which occur during the brightness reversion phenomena. To understand how the photo-initiated oxidation of mechanical pulp leads to the formation of colored structures this research project has elected to employ lignin model compounds adsorbed onto a solid support as a preliminary means of characterizing these reactions. It is anticipated that as the our knowledge of the photo-degradation process increases research efforts will re-focus on the yellowing phenomena in-situ.

The lignin model compounds to be employed in studying the fundamental photochemical reactions contributing to brightness reversion were described in the previous PAC report and are summarized in Figure 1. Current research efforts have been successful in preparing several dimeric lignin structures and one trimeric compound. Scheme 1 highlights some of our recent synthetic efforts. Furthermore, studies directed at controlling the stereochemistry of the lignin side chain have also been relatively successful. The ability to control the stereochemistry of the lignin side chain is important due to practical and theoretical considerations which were described in the previous PAC report.

The synthesis of the lignin trimer has also provided the opportunity to investigate the conformation of these lignin structures. As expected, the lignin trimer appears to be more rigid than the dimer, based upon ^{13}C NMR measurements. The decreased flexibility of the lignin trimer may have important consequences with respect to recent photochemical studies of - carbonyl- -aryl ether lignin structures which were shown to be photolabile[22]. It is known that the photo-fragmentation process is stereochemically dependent. The enhanced conformational freedom of the dimer may therefore suggest that the use of dimeric structures as model compounds for photolysis is not an accurate model.

Finally the research efforts directed at preparing these lignin model compounds will also have potential applications in other fields of investigation.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

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

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

Figure 1

R_1 = H, CH_3

R_2 = H, OCH_3

K_2CO_3

$ClCH_2CO_2CH_3$

LDA

R_3 = H, OCH_3

$R_4 = CH_3, Bn, Si(t-Bu)(CH_3)_2$

LAH

Scheme 1

For R$_4$= Si(t-Bu)(CH$_3$)$_2$
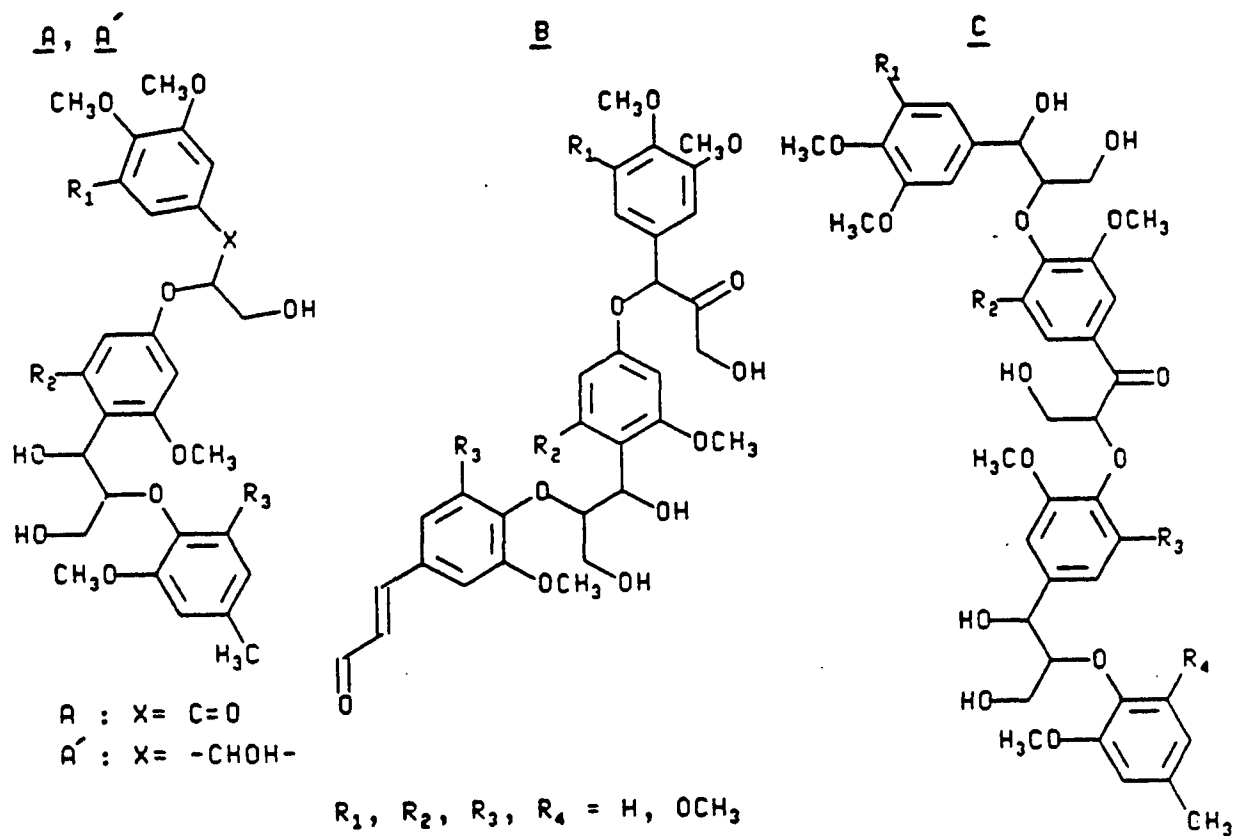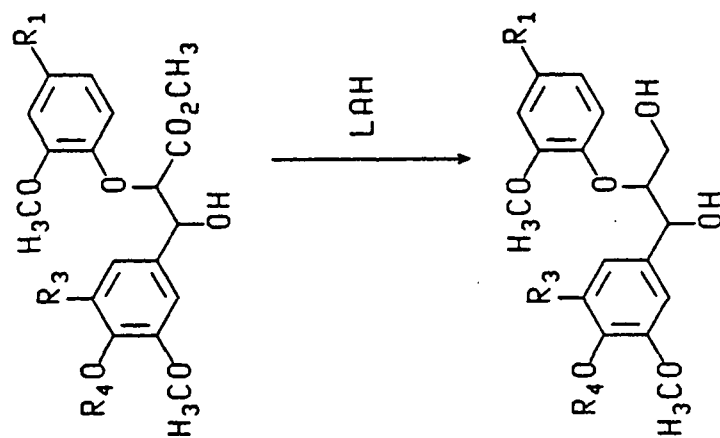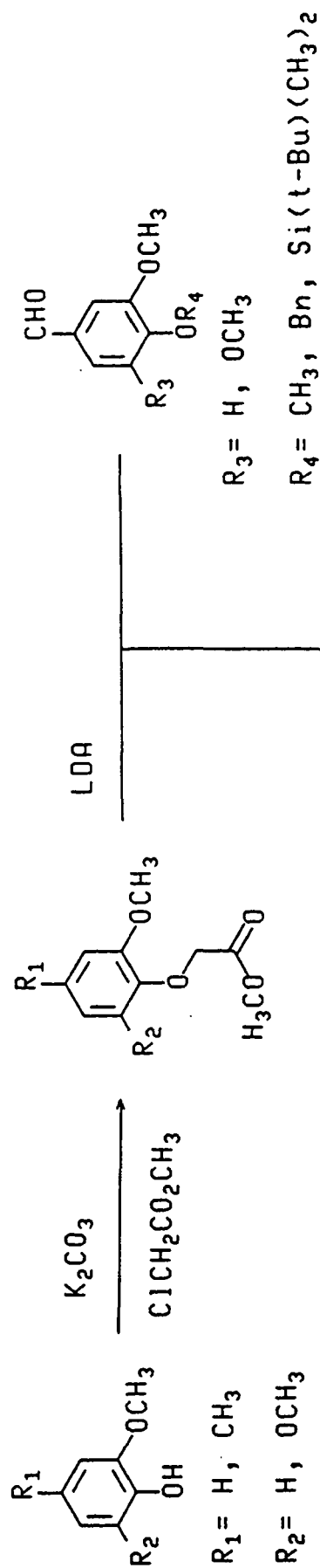
Scheme 1-a

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

POTENTIAL FUTURE ACTIVITY

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

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

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

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

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

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PROJECT 3684

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTIVITY.

PART I: PRECURSOR FORMATION AND REACTIVITY

(API/NCASI FUNDED)

RESEARCH REVIEW

April 2, 1991

Lucinda B. Sonnenberg

Project Title:	MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION. PART I: PRECURSOR FORMATION AND REACTIVITY (API/NCASI FUNDED PROJECT)
Division:	Chemical and Biological Sciences
Project Number:	3684
Project Staff:	L.B. Sonnenberg, D. Dimmel, C. Tucker
FY 90-91 Budget:	$76,000

IPST GOAL:

Eliminate or minimize chlorinated dioxins and chlorinated furans in bleached pulp production.

OBJECTIVE:

The unchlorinated compounds, dibenzodioxin (DBD) and dibenzofuran (DBF), are probably the major precursors to the tetrachlorinated dibenzodioxins (TCDD) and tetrachlorinated dibenzofurans (TCDF) sometimes found in effluent from chlorine-bleached pulp. Under-standing the reactivities and the sources of the precursors is necessary to eliminate the production of TCDD and TCDF. The goal of this research is to investigate chemical methods of modifying the precursors in order to prevent their conversion to the chlorinated analogs.

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION.
PART 1: PRECURSOR FORMATION AND REACTIVITY

Reporting Period: March 1990 - March 1991

OBJECTIVE

In order to eliminate the production of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the chlorine bleaching of pulp, it is necessary to understand the reactivities and the sources of their major precursors, dibenzodioxin (DBD) and dibenzofuran (DBF). The goal of this research is to investigate chemical methods of modifying the precursors in order to prevent their conversion to the chlorinated analogs.

INTRODUCTION

The chlorination of wood pulp appears to lead to low levels of tetrachlorinated dibenzodioxins (TCDD) and tetrachlorinated dibenzofurans (TCDF) which are extremely toxic to some animal species (1,2). The paper industry is concerned over the public's reaction to dioxins and meeting limits imposed by state and federal regulations. Consequently, reduction of levels of dioxins in paper products and mill discharges has been a recent major research thrust.

Dibenzodioxin and dibenzofuran are present in pulp (3,4) and there is strong evidence that chlorination of these compounds leads to a significant portion of the observed TCDD and TCDF. Control of TCDD and TCDF formation will be greatly aided if the fundamental chemistry of the precursors is better understood.

Ultratrace quantities of DBD and DBF in pulp are chlorinated in the presence of lignin, which is present in percentage levels. The selectivity of electrophilic chlorine for the precursors suggests that other electrophilic reagents may be selective for DBD and DBF. Greater stability of ionic intermediates of the DBD and DBF chlorine substitution reactions could explain the higher reactivity of the precursors relative to lignin (or other reactants) in bleaching liquors. Electrophilic radical intermediates of DBD and DBF may be similarly stabilized.

Selective reactions of DBD and DBF with electrophilic reagents, other than chlorine, may prevent the subsequent chlorination of the precursors to form TCDD and TCDF. In addition, a study of the reactions of DBD and DBF with several electrophilic reagents may yield useful chemical information about TCDD and TCDF formation.

This report describes work in which the reactivities of different reagents toward the precursors have been evaluated and compared. The disappearance of DBD and DBF upon treatment with ozone, hydrogen peroxide, oxygen under ultraviolet light, nitrogen dioxide, nitric acid and sulfuric acid, was measured. The reactions were evaluated for precursors dissolved in water and adsorbed to cotton linters.

METHODS

Each reagent, O_3, H_2O_2, O_2/UV, HNO_3, and H_2SO_4, was reacted with a mixture of DBD and DBF in solution under the conditions listed in Table 1. The solutions were extracted with hexane and the DBD and DBF in the extracts were quantified using gas chromatography with flame ionization detector (GC/FID) and 2-methoxybiphenyl as an internal standard (GC: 30 M DB-1 column; Oven T = 90 - 295°C at 4°C/min; Injector T = 245°C; Detector T = 295°C; 2mL/min He carrier gas). Gas chromatography/mass spectrometry (GC/MS) was used to identify products. Sample spectra were obtained using an HP Model 5985 quadrapole mass spectrometer. The products were identified by matching library mass spectra, standards mass spectra or by spectral interpretation.

For reactions of adsorbed DBD and DBF, the analytes were initally adsorbed onto clean, dry cotton linters from a methylene chloride solution. The solvent was removed by rotoevaporation. Generally about half of the DBD and DBF that was in the spike was retained by the linters. Following reaction, (conditions are summarized in Table 1), the solids were soxhlet extracted overnight in hexane and the aqueous portions were extracted with hexane in separatory funnels. The DBD and DBF in the extracts were quantified as described above.

The O_3 was generated by a Welsback T 816 ozonator at 115 V with a 2.5 L/min O_2-O_3 flow rate. In the O_2/UV studies, a Rayonet Photochemical Chamber Reactor equipped with a merry-go-round and 3000 Å lamps (approximately 21 W) was used. All reactions were conducted at room temperature (20-25°C).

RESULTS AND DISCUSSION

The results from the solution experiments are shown in Figure 1. The results from the degradation of DBD and DBF adsorbed onto linters are given in Table 2.

There are two potential sites of reaction in DBD and DBF: the aromatic ring or ether oxygens. The ring may become oxidized (5,6), cleaved (7) or substituted (8) when exposed to electrophilic reagents such as chlorine, ozone and nitrogen dioxide. The electron-rich oxygen in DBD and DBF may also be reactive. Although the reactivity of phenolic and alkoxyl oxygen toward many electrophilic oxidants has been well investigated (5,8,10), there is less information about chemical activity of the oxygen in diaryl ethers. In both DBD and DBF, the cyclized nature of the two linkages may impart unusual stabilization to the intermediates, compared to the electron-donating substituents in lignin aromatics.

Ozone, nitrogen dioxide, nitric acid, and light degraded DBD more effectively than they degraded DBF, suggesting that the limiting step in the reaction is dependent on the differences in structures of DBD and DBF. Reactions in which DBD and DBF reactivities were similar to each other may involve a limiting reaction that is independent of the precursor structure, such as the formation of the active species in the reaction. The reactions of each reagent are discussed below.

Ozone

The precursors degraded at ozone concentrations considerably lower than concentrations required by the other reagents. Some DBD and DBF in solution remained after treatment with 500 μM ozone (36% and 21% of DBF and DBD, respectively), but similar concentrations of ozone completely degraded DBD and DBF adsorbed to cotton linters. (While the ozone concentrations were the same, the molar ratio of ozone to total initial DBD and DBF was 250 for the solids experiments and 12 for the aqueous experments). The results from the linters experiments are in agreement with Pentek (13) who found that a 3.5 to 1 molar ratio resulted in complete DBF destruction by ozone in methylene chloride (and that aqueous reactions were faster than methylene chloride reactions). However, degradation of aqueous DBD and DBF in the reaction conditions in this work was less than reported by Pentek (13). In addition, Hoigne and Bader (14) stated that a molar ratio of 10 generally destroys nonionizing organics directly with ozone.

The differences may be due to the relative abundances of potentially active species. Generally, OH, O_2^- and OOH radicals, O_3^-, and HOO$^-$ ions are present in ozone reaction mixtures, along with O_3, in relative amounts that are dependent on reaction conditions.

It is possible that reactive radicals and anions were present in these reactions. However, since the ozonations were conducted under clean reaction conditions for fairly short times and at a neutral pH, it is likely that radical reactions (e.g. peroxy radical, hydroxy radical, superoxide radical anion) were minimized (14), although probably not eliminated.

The precursors are likely to have reacted with O_3 (O-O-O$^+$) by a 1,3 dipolar addition of ozone to an aromatic bond (15) producing carboxylic acids, aldehydes and carbon dioxide through ozonide intermediates. Coupling reactions may also occur. Although no degradation products were detected, high molecular weight materials (from coupling reactions), CO_2, and highly polar compounds such as carboxylic acids may not have been detected under these analytical conditions.

The 1,3 dipolar addition is electrophilic; the rates of ozonolysis of benzene and substituted benzenes increase with electron-donating capacity of the substituents (16). Factors that decrease reactivity to electrophilic substitution decrease the reactivity of ozone (7,16). The electrophilic nature of the reaction may be important in understanding the differences between DBD and DBF reactivities and between the precursors and lignin.

Peroxide

The precursors were fairly resistant to hydrogen peroxide; even at 6 M H_2O_2, 3% of DBD and 9% of DBF remained in solution. In contrast to the ozonation, there was less degradation on solids than in solution at similar concentrations (even though the molar ratio of H_2O_2 to total DBD and DBF was about 2 times higher in the linters reactions than in the solution reactions). If the OH, OOH and O_2^- radicals were the active species in DBD and DBF degradation, the linters may have competed with DBD and DBF for the radicals, which would decrease the extent of reaction of the precursors.

The difference in the extent of the degradation between DBD and DBF that was observed for ozone (and nitrogen dioxide, nitric acid and light) was not observed for peroxide. The similarity between DBD and DBF reactivities towards peroxide is consistent with radical formation limiting the overall DBD and DBF reactions; the precursors would then be uninvolved in the limiting step.

However, preliminary work suggests the degradation of DBD and DBF was inhibited by NaOH. Peroxide decomposes to radicals under alkaline conditions (17,18) produced by NaOH. Solution experiments showed that 1 g of NaOH increased the amount of precursors that remained after reaction with 0.9 M peroxide by 30 to 45%. The decrease in reactivity with NaOH suggests that the reactive species was not created; therefore, radicals do not appear to be important species in these reactions. However, the presence of the radicals in the reaction mixture was not verified.

If radicals are not active species, then the peroxides may undergo electrophilic displacement reactions (16) in which a polarized oxygen acts as the electrophile, similar to ozone (nucleophilic oxidation by peroxide probably did not occur).

O_2/UV

Rose Bengal (a photosensitizer) under UV irradiation produces singlet oxygen and photo-excited Rose Bengal, (20-22), although their presence was not verified in these samples. The reaction of DBD and DBF in oxygen-saturated water under irradiation in the presence and absence of Rose Bengal, suggested that DBD and DBF underwent direct photolysis more readily than indirect photolysis. The sensitizer decreased the reactivity of DBD and DBF, indicating that singlet oxygen and photo-excited Rose Bengal do not react readily with DBD and DBF under these reaction conditions. Precursor reactions in 10^{-3} M solutions of fluoroscein diacetate and anthracene gave similar results. The lack of reactivity was unexpected since singlet oxygen reacts with aromatics such as 1,4 benzodioxins and naphthodioxins (23), biphenyl (24), dimethylnaphthalene, anthracene (25), and aryl olefins (26). The inhibition of the degradation in the sensitizer may have been due to the attentuation of the light by the 10^{-3} M Rose Bengal solution (27).

Nitrogen Dioxide

The DBD and DBF were primarly oxidized, but also substituted to a small extent by nitrogen dioxide. (Traces of mono- and dinitrated DBD and mononitrated DBF were detected.)

Nitrogen dioxide, a radical species, frequently abstracts a nonaromatic hydrogen initially (6,28) or substitutes by way of a nitrocyclohexadienyl radical intermediate (15,28). Oxidative reactions of DBD and DBF with nitrogen dioxide suggest that a nonaromatic hydrogen, (e.g. phenolic, methanolic) is unnecessary for NO_2 attack (6,28).

Potential initial reactions are 1) abstraction of the aromatic hydrogen, 2) displacement by the nitrogen dioxide, or 3) single electron transfer from the ether oxygen. Aromatic hydrogen abstraction to form an aryl radical is unlikely (15); however, unusual stabilities of the precursors may allow it. An aryl or phenoxy radical formed by displacement would be well stabilized as would the radical oxycation that would be formed from a single electron transfer. There is little information in the literature that considers these latter two types of reactions.

There was an interesting difference in the reactivities of DBD and DBF to nitrogen dioxide. The difference may reflect the differences in stabilization of neutral radical intermediates or charged radical intermediates of the two analytes (15,28). Neutral radical reactions exhibit some substituent effects (15) (perhaps similar to reactions with neutral, even-electron electrophiles), but to a smaller extent than reactions involving charged intermediates. (radical or even-electron). Since 67% more of the DBD disappeared than the DBF, it appears that DBD intermediates are significantly more stabilized and that charged intermediates may be involved.

Nitric Acid

DBF proved to be quite resistant to reaction by nitric acid. DBF in solution required a nitric acid concentration between 8 and 10 M to be destroyed. Even though DBD on linters was completely destroyed at 4M, none of the DBF reacted. These results suggest there is a strong substituent effect in these reactions, whether they are oxidations or substitutions. Substitution products were detected in the nitric acid treatment of DBD and DBF (mono- and dinitrated DBD and mononitrated DBF) in very small quantities indicating that oxidative reactions were more significant than nitration. The nitronium ion is associated with electrophilic reactions by nitric acid. However, nitric acid mixtures contain nitrogen oxides and nitrous acid as well. Although free radical substitution on aromatics can occur (15), in general, the nitrogen oxides are responsible for the oxidation reactions and the nitronium ions are largely responsible for the substitution reactions.

Nitronium ion and nitrogen oxides are present in small and variable amounts suggesting that their formation could limit the overall reaction. However, the nitric acid reacted differently to DBD and DBF, indicating that the limiting reaction was dependent on DBD and DBF structure. These results are in agreement with the nitrogen dioxide results. If most of the degradation of DBD and DBF with nitric acid treatment is due to oxidation by nitrogen oxides, then there should be a similar substituent effect in the nitrogen dioxide reactions, which was observed.

Sulfuric Acid

Solutions of DBD and DBF were exposed to 0.5 to 10.2 M H_2SO_4. There was no degradation of DBD and DBF up to 6 M H_2SO_4 while only 20% of both analytes degraded at 10.2 M H_2SO_4. The reactions on linters were consistent with the aqueous results; no degradation of either analyte was apparent. The high degree of reversibility of the sulfonation reaction with sulfuric acid may have contributed to this apparent lack of reactivity.

Summary

Lower concentrations of ozone were required to degrade DBD and DBF in solution and on linters than were required for other reagents. Peroxide degraded DBD and DBF in solution, but did not react with the precursors in the presence of linters. The precursors in solution were also degraded by treatment with O_2/UV. Nitrogen dioxide reacted with adsorbed DBD and DBF more than nitric acid, sulfuric acid and hydrogen peroxide (NO_2 in solution and O_2/UV on linters were not examined).

CONCLUSIONS

The precursors were reactive toward a number of the reagents examined under conditions where few competing reactions occurred. Results suggest that radical and neutral electrophiles are reactive to DBD and DBF, in addition to charged electrophiles such as chlorine and nitronium ion.

While micromolar concentrations of ozone degraded dissolved and adsorbed DBD and DBF, molar concentrations of the other reagents were necessary. A 1,3 dipolar addition of ozone to the aromatic compounds, an electrophilic reaction, is a likely mechanism for ozone reaction with the precursors.

There were differences between the reactions of DBD and DBF in solution and adsorbed DBD and DBF in the cases of ozone and peroxide, but the differences were opposite for the two reagents. Ozone reactivity was enhanced and peroxide reactivity was inhibited by the presence of linters, suggesting a significant difference in reaction mechanism.

The results of the peroxide degradations were inconclusive with respect to likely modes of degradation; reaction optimization may produce more effective degradation.

Lability of DBD and DBF to direct photolysis was indicated; indirect photolysis, including through singlet oxygen, appears to be insignificant compared to direct photolysis.

There was apparently little reactivity of DBD and DBF to singlet oxygen and possibly hydroxy radicals. This result was unexpected since other aromatics are reactive (15,24). The lack of reactivity may be related to the absence of free phenols or activated aliphatic side chains.

A difference between the reactivities of DBD and DBF toward nitrogen dioxide suggests that the radical reagent may have oxidized DBD and DBF by way of charged intermediates. Only very small quantities of substitution reactions were detected, indicating the relative importance of oxidation reactions. Nitrogen oxides in nitric acid were probably mostly responsible for the disappearance of DBD and DBF in nitric acid.

Now that it has been determined that ozone is highly reactive toward DBD and DBF, it is necessary to determine its selectivity for the precursors in the presence of pulp. The ozone may be consumed by other pulp components before trace amounts of DBD and DBF react. The reactive species in peroxide mixtures needs to be more fully investigated.

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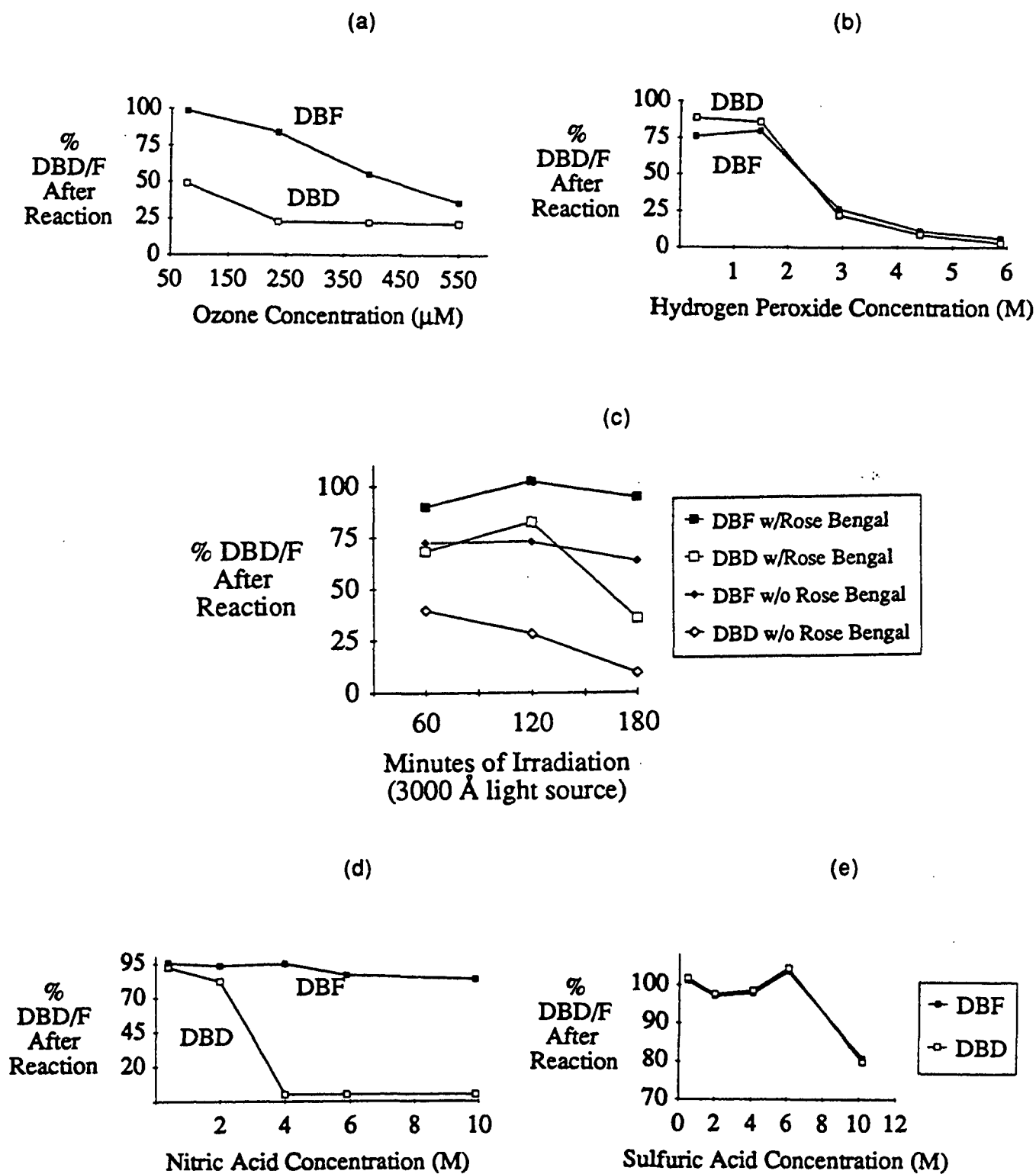
Figure 1.   Reactions of DBD and DBF in Solution; a) O_3, b) H_2O_2, c) O_2/UV, d) HNO_3, e) H_2SO_4.

Table 1. Reaction Conditions of DBD and DBF in Solution and Adsorbed onto Cotton Linters.

	Solution Conditions				Adsorbed Conditions		
Reagent	Initial μmoles DBD DBF		Initial μM DBD DBF		Initial mmoles Rgt.	Initial μmoles DBD DBF	
O_3	0.9	1.0	22	25	0.25	0.6	0.5
	79 μM to 550 μM O_3 Reaction time: 15 min.				2% Consistency Reaction time: 15 min.		
H_2O_2	1.6	1.8	53	58	290	1.1	1.1
	0.3 M to 6 M H_2O_2 Reaction time: 1 hr.				17% Consistency Reaction time: 1 hr.		
O_2/UV	0.5	0.5	17	17	-		
	O_2-saturated water Reaction times: 0,1,2,3 hr. 10^{-3} M Rose Bengal (sensitizer)						
NO_2	-				5	3.1	2.2
					Dry linters Reaction time:10, 40 m		
HNO_3	1.5	1.7	150	170	400	1.6	1.5
	0.4 M to 9.9 M HNO_3 Reaction time: 1 hr.				9% Consistency Reaction time: 1 hr.		
H_2SO_4	2.0	2.2	56	62	650	0.3	0.6
	0.5 M to 10.2 M H_2SO_4 Reaction time: 1 hr.				9% Consistency Reaction time: 1 hr.		

Table 2.   Reactions of DBD and DBF Adsorbed onto Cotton Linters

Reagent		ug/g DBD/F Before Reaction	ug/g DBD/F After Reaction [1]	% DBD/F Reacted [1]
O_3	DBD	10	≤ 1	≥ 92
	DBF	8	≤ 1	≥ 88
H_2O_2	DBD	19	19	0
	DBF	18	19 [3]	0
NO_2 [2]	DBD	58	≤ 1	≥ 99
	DBF	37	24	33
HNO_3	DBD	28	≤ 1	100
	DBF	26	30 [3]	0

[1] Average of duplicate or triplicate experiments.

[2] 10 minute reaction time.

[3] Values for DBD/F may be slightly greater after reaction than before due to experimental error, inhomogeneity in the spiked cotton linters, or due to internal standard degradation.

PROJECT 3685

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION

PART II: CHLORINATION AND DIOXIN REACTIONS

(CHLORINE INSTITUTE FUNDED)

RESEARCH REVIEW

April 2, 1991

Donald R. Dimmel

PROJECT SUMMARY FORM

Project Title: MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION
PART II: CHLORINATION AND DIOXIN REACTIONS
(CHLORINE INSTITUTE FUNDED)
Division: Chemical and Biological Sciences
Project No.: 3685
Project Staff: Donald R. Dimmel and Battelle
FY 90-91 Budget: $180,000

IPST GOAL:

To understand the mechanisms of formation of chlorinated dioxins and chlorinated furans, and to use this knowledge to eliminate or minimize their production in bleached pulp.

OBJECTIVE:

The objective of this project is: (1) to develop a fundamental understanding of chemistry which leads to dioxins in bleached pulp, (2) study the reactions of dioxins with selected bleaching reagents, and (3) lay the foundations for developing new technologies for chlorinating pulps without dioxin production. Conditions will be sought that will (a) define the relative importance of different dioxin precursors, (b) determine the reactivity of chlorine with functionalized precursors, (c) selectively chlorinate lignin and not the dioxin precursors, and (d) destroy dioxins in partially bleached pulps.

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION
PART II: CHLORINATION AND DIOXIN REACTIONS
(CHLORINE INSTITUTE FUNDED)

Reporting Period: July, 1990 - March, 1991

OBJECTIVE

The objective of this project is: (1) to develop a fundamental understanding of chemistry which leads to dioxins in bleached pulp, (2) study the reactions of dioxins with selected bleaching reagents, and (3) lay the foundations for developing new technologies for chlorinating pulps without dioxin production. Conditions will be sought that will (a) define the relative importance of different dioxin precursors, (b) determine the reactivity of chlorine with functionalized precursors, (c) selectively chlorinate lignin and not the dioxin precursors, and (d) destroy dioxins in partially bleached pulps.

INTRODUCTION

The production of dioxins during chlorine bleaching is a major concern to the paper industry. The principal source of dioxins appears to be the chlorination of dibenzo-*p*-dioxane (DBD) and dibenzofuran (DBF). Evidence exists that some DBD/F compounds are absorbed on the pulp during brownstock washing that employs certain oil based defoamers. Other potential sources of DBD/F are (1) the wood, (2) formation from wood components during pulping or bleaching, and/or (3) outside sources, such as the makeup water, air, etc. Certain simple phenols have been shown to convert to dioxins during chlorine bleaching. Present evidence suggests that the extraction step following chlorination is not a significant source of dioxins.

Besides nonchlorine bleaching sequences, several measures can be taken to reduce dioxin production during bleaching technologies that use chlorine. These measures include reducing the level of chlorine during chlorination, substituting chlorine dioxide for chlorine, employing an oxygen delignification stage, and washing the pulp thoroughly before bleaching. Many of these changes are being done without a good understanding of dioxin precursor sources, properties, and chemistry.

The research being conducted in Projects 3684 and 3685 is directed towards developing a more thorough understanding of the properties and reactivities of dioxin precursors and of dioxins

themselves. The results of this research should help explain existing effective control measures ensure they don't fail, and to suggest more effective technologies for reducing dioxin levels. The research of companion Project 3684 (Part I) deals with nonchlorine, destructive reactions of DBD/F compounds, while Project 3685 focuses on chlorine reactions of DBD/F, formation of dioxins from non-DBD/F precursors, and possible destructive reactions of dioxins.

The bulk of the laboratory work is being conducted at Battelle in Columbus, Ohio. Battelle is specifically equipped to handle toxic materials and is capable of performing ultratrace analyses. Project research began in late July 1990. Due to diversion of Battelle personnel to war related projects, progress has been considerably behind schedule. The war-related activities have ended and our project is now receiving extra attention in order to meet the July 1991 conclusion date.

RESULTS

Most of the planned experiments involve DBD, DBF, and lignin models absorbed onto cotton linters. This very clean system should provide valuable fundamental information about reactivities without possible by-product problems. The simplified analytical procedures will also allow a greater number of experiments to be performed at a reasonable cost.

Background levels of DBD and DBF for cotton linters and the solvent extraction procedure have been determined and appropriate DBD/F spike levels established. Reasonable conditions for conducting chlorinations of DBD/F spiked cotton linters were also established. The conditions selected to produce mono - tetrachlorodioxins were: 5 g of (spiked) linters with 0.015 g of Cl_2 in 500 mL of water at room temperature for two reaction times, 10 and 120 minutes. Analysis of the reaction system after 10 minutes with unspiked linters showed nearly 50% of the Cl_2 charge was in the headspace.

Analysis of the initial chlorination experiments of DBD and DBF spiked cotton linters and various controls produced some unexpected results. Specifically, extraction of selective chlorinated spiked and unspiked linters and solvents led to substantial quantities of a pale yellow residue which interfered with simple analysis for chlorinated DBD/F compounds. Analysis of the samples indicated that unchlorinated and mono - tetrachloro-DBD and DBF (DBD/F-Cl_x, x=0-4) were present in both the linters and aqueous phases. There appears to be a direct correlation between the number of chlorines present in the products and the ratio of the aqueous/linters distribution; the more chlorines, the less product found in the water phase.

Two samples of cotton linters were spiked with unchlorinated and mono - tetrachloro-DBD and DBF (DBD/F-Cl_x, x=0-4) and taken through the sample workup. These "extraction check samples" were analyzed for DBD/F-Cl_x (x=0-4) and spike recoveries determined. The recoveries, generally in the range of 120-180%, indicated that the analytical procedures effectively removed the DBD/F-Cl_x components from linters. The data, however, exhibited poor internal standard recoveries.

A sample of cotton linters, which was not spiked with DBD/F, was chlorinated for 2 hours and, following workup, was analyzed for DBD/F-Cl_x. Several mono, tri, and tetrachloro-DBF isomers were observed. The corresponding DBD compounds were not observed. However, the extensive losses of labeled DBD/F internal standards associated with repeated attempts to separate the compounds of interest from the "yellow residue" shed doubts on the validity of the results.

A set of follow up experiments have recently been completed. These experiments used a solvent extracted linters and gave very little interfering residue. A modified work up procedure was also employed; simple chromatography through alumina provided clean samples. Excellent recovery of labeled internal standards were observed and the reproducibility of the results was much better.

SUMMARY

Indications are that the selected chlorination conditions will be ideal for seeing the progressive development of ring chlorination of the DBD/F. The sample work up procedure and ability to accurately analyze for the mono-tetra chloro DBD and DBF look to be appropriate.

FUTURE STUDIES

Battelle will perform a series of runs to determine chlorine content in DBD and DBF as a function of chlorination time for spiked cotton linters samples. One set of experiments will address the issue of the source of the dioxin precursors. The distribution of mono-, di-, tri-, and tetrachlorodioxins (DBD/F-Cl_x) as a function of chlorination time will be compared for a DBD/F spiked cotton linters sample and an unspiked pulp sample. If the time development profile of the DBD/F-Cl_x components for the two substrates differ substantially, precursors other than DBD/F will be indicated. The profile of tetrachloro isomers for the two samples will also indicate possible sources of precursors and provide an estimate of the relative importance of different precursors.

Another set of experiments will provide rate data for the appearance and disappearance of DBD/F-Cl_x on a lignin model. Done at different temperatures, the chlorination rate data should provide energies of activation (Ea) for the substrates. Such information may lead to chlorination processes that will give greater selectivity for lignin vs. DBD/F. A follow-up competitive experiment will verify the expected selectivities under different chlorination conditions. We will also examine how the selectivity changes with the addition of chlorine dioxide to the chlorination reactions. DBD/F spiked cotton linters, which have been treated with NO_2 or O_2, will be chlorinated to show if substituted precursors will still give rise to dioxins upon chlorination.

Finally, we will treat bleached pulp (which contains trace levels of dioxins) with ozone, peroxide, oxygen, and other possible commercial electrophilic reagents to test the stability of dioxins to various post-chlorine bleaching stages.

PROJECT 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

RESEARCH REVIEW

April 2, 1991

Donald R. Dimmel

DUES-FUNDED PROJECT SUMMARY FORM

Project Title: FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

Division: Chemical and Biological Sciences

Project Code: PBSEL

Project No.: 3475

Project Staff: Donald Dimmel and Lynn Boysen

FY 90-91 Budget: $120,000

IPST GOAL:

Improved process for bleached chemical pulps.

OBJECTIVE:

Provide a fundamental understanding of the chemical and physical reactions that control both:

(1)   the rate of lignin removal, hemicellulose dissolution, and cellulose degradation, and

(2)   the structures of the lignin, hemicelluloses and cellulose that remain in the pulp after pulping and bleaching.

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

Reporting Period: March, 1990 - March, 1991

OBJECTIVE

The objective of this project is to provide a fundamental understanding of (1) the chemical and physical reactions that control the rate of lignin removal, hemicellulose dissolution, and cellulose degradation, and (2) the structures of the lignin, hemicelluloses, and cellulose that remain in the pulp after pulping and bleaching. The knowledge gained should lead to improved processes for bleached chemical pulps.

INTRODUCTION

The detailed mechanistic studies of pulping delignification chemistry conducted in this project have led to a greater understanding of the factors which control lignin fragmentation and condensation reactions. A significant portion of the research was directed towards understanding the reactions of anthrahydroquinone (AHQ) with lignin substrates. Our interest here relates to the fact that anthraquinone (AQ) pulping systems show improved selectivities.

The project has also been concerned with understanding the chemistries associated with carbohydrate chain cleavage reactions that occur during alkaline pulping and bleaching. Such reactions cause a lowering of the degree of polymerization (DP) and thus a loss in paper strength properties. Changes in DP are seen by changes in pulp viscosities and molecular weight distributions.

Research activity in the past few years has concerned comparing the reactivity difference of amorphous and crystalline cellulose samples; any observed difference should reflect the importance of "physical effects" in carbohydrate chain cleavage reactions. A "peeling"resistant, amorphous cellulose sample and crystalline cellulose sample have been prepared from cotton linters. The viscosity losses as a function of time during simulated alkaline pulping followed the order: amorphous > cotton linters > kraft pulp > crystalline cellulose. The rate of DP loss was further increased slightly when amorphous or crystalline cellulose was heated in alkali in the presence of AQ.

Similar reactivity trends were observed for the various cellulose samples in a simulated oxygen-alkali bleaching reaction at 100°C and a hydrogen peroxide bleaching reaction at 50°C and pH 11. The viscosity losses for amorphous cellulose in oxygen-alkali were inhibited by the presence of magnesium. The addition of cobalt, above a certain level greatly accelerated the amorphous cellulose viscosity losses. The combination of Mg and Co was even more harmful. A combination of added magnesium sulfate and sodium silicate prevented viscosity losses during hydrogen peroxide reaction with the amorphous cellulose.

A detailed review of this work was presented in the March 20, 1990 IPST Pulping Processes Project Advisory Committee Report, pages 83-97.

RESULTS
(March-October 1990)

There is a certain "art" to the preparation of a proper amorphous cellulose sample. Often the cotton linters fail to completely dissolution in the cellulose solvent. The mode of heating and the exact timing for mixing in additional amounts of DMSO, SO_2, and diethylamine is critical to getting a high viscosity amorphous cellulose product. Even so, not all amorphous cellulose samples behave similarly during simulated pulping and bleaching reactions. The differences do not appear to be related to the samples' crystallinity, since most have been shown to be amorphous by X-ray diffraction.

During the first year in our new Atlanta facilities, we were unable to confirm samples' crystallinity. During this time the principal researcher on the project was a part time Georgia Tech coop student. The viscosities of amorphous and crystalline cellulose prepared by the student were equal to or better than previous samples. Yet, for reasons which are still unclear, the samples displayed different reactivities, relative to earlier samples. For example, the magnitude of viscosity losses at early reaction times for the kraft and highly crystalline cellulose were variable and the viscosity often increased slightly, rather than dropping, towards the end of a treatment.

The student's amorphous cellulose samples were generally much less reactive than earlier ones. For example, treatment with hydrogen peroxide for various time periods, consistencies, and concentrations, led to only minor degradation (as noted by viscosity changes), even though residual peroxide was present in the reaction samples. Degradation was greater in oxygen/alkali runs. A viscosity drop from 40 to 32 (20%) occurred in 1 hour with 0.1M $NaOH/O_2$ at 100°C; however, previous amorphous cellulose samples dropped more than 50% under these conditions. The addition of vanillyl alcohol had little effect on the $NaOH/O_2$ degradation rate. A $NaHCO_3/O_2$ treatment at 100°C showed small viscosity decreases; while a Na_2CO_3/O_2 treatment gave moderate decreases.

RESULTS
(October 90 - March 91)

The student has been replaced by a Lynn Boysen, a technician who duties are split between the Analytical Group and the Wood Chemistry Group. After experienced the usual problems of preparing amorphous cellulose, she performed several reactions on a new 25 cps viscosity, amorphous cellulose. The purpose of these experiments was to determine whether coop student's results (no viscosity change with time) or the previous results (large viscosity changes with time) were the true response. X-ray diffractograms showed that Boysen's amorphous cellulose sample was amorphous. Her results were mixed.

A set of time-variable reactions on the amorphous cellulose in 1M NaOH at approximately 125°C led to a decrease of viscosities from 25 to 8 cps. In another set of time-variable degradation reactions performed at 115°C, the amorphous cellulose viscosities again dropped substantially, while a crystalline cellulose sample run simultaneously display only a small viscosities drop with time. An oxygen-alkali cook on both amorphous and crystalline cellulose for 30, 60 and 90 minutes gave viscosities decreases from 25 to 13 cps for the amorphous and from 31 to 28 cps for the crystalline. In contrast, a set of peroxide reactions with the amorphous cellulose, using 0.2% peroxide at pH 11, showed very little change in viscosities with time (Table 1).

Conditions employing a higher peroxide concentration (1%), to encourage more reaction, were examined next. A new batch of amorphous cellulose was also examined. The results are presented in Table 1. The regular loss in viscosity with time for the 33 cps amorphous cellulose confirms earlier project work; the absolute magnitude of the loss is somewhat variable.

Table 1.

Viscosity Values after Treating Amorphous Cellulose with Hydrogen Peroxide[a]

Time - min	0.2% H_2O_2 25.2 - Amor.[b]	1% H_2O_2 25.2 - Amor.	1% H_2O_2 32.7 - Amor.	1% H_2O_2 32.7 - Amor.	1% H_2O_2 32.7 - Amor.
10	24.4	22.1	27.1	25.0	22.4
20	24.4	23.9	-----	18.8	19.3
40	22.7	22.0	25.3	14.3	16.3
80	23.4	20.1	18.3	16.0	11.9

[a]pH 11.0, 55°C; [b]Amorphous cellulose with a 25.2 cps viscosity

A comparison of extent of degradation with the strength of H_2O_2 employed showed peculiarities. The above 1% H_2O_2, 40 min sample had a viscosity of 16.3. An experiment done in duplicate at 55°C for 40 minutes with 0.5% H_2O_2 at pH 11 gave viscosities of 26.4 and 26.5 cps. The third identical experiment, except using 0.2% H_2O_2 gave viscosities of the duplicate samples of 19.7 and 19.8 cps. This weakest peroxide experiment should have had the highest viscosity of the set.

An oxygen-alkali reaction was performed on the 32.7 cps amorphous cellulose. The samples were left in boiling 0.1N NaOH for 30, 60, and 120 minutes. The viscosities were 31.4, 26.2, and 23.2 cps, respectively.

A soda degradation at 116°C for 40 minutes was completed on four samples of the 32.7 cps amorphous cellulose. An addition of 0, 25, 50 and 100 mg of NaCl was made to four bombs. The mean viscosities were 13.4, 16.3, 11.5, and 16.5 cps, respectively. Increasing the NaCl "dead-load" appeared to have little effect on extent of carbohydrate chain cleavage.

Following preparation of a new amorphous cellulose sample (viscosity 35.3 cps), Lynn Boysen became involved with a high priority analytical project and work has been temporarily halted Project 3475.

SUMMARY

It is apparent that amorphous cellulose degrades much more rapidly than highly crystalline cellulose samples and kraft pulp under pulping and bleaching conditions. The experimental verification for this statement comes from the fact that amorphous cellulose shows either a rapid or slight viscosity loss upon treatment, while the crystalline cellulose and kraft pulp samples invariably display little or no viscosity loss upon treatment. Why the amorphous cellulose exhibits somewhat erratic behavior is a mystery.

FUTURE ACTIVITIES

The large backlog of results of the project's carbohydrate research has been organized in preparation for internal and external publications. Publication of the research results and performing supporting experiments for the publications will be the focus of the fiscal year 1991 activities.

This project is scheduled to be terminated at the end of this fiscal year. Some aspects of the research will, however, be incorporated into a new project which deals with developing a more fundamental understanding of the chemistry associated with nonchlorine bleaching systems. Specifically, the amorphous cellulose bleaching chemistry studies will consider carbohydrate reactions of ozone in the presence of stabilizers, etc.

PROJECT 3477

DEVELOPMENT OF NEW ANALYTICAL METHODS

RESEARCH REVIEW

April 2, 1991

Sujit Banerjee

PROJECT SUMMARY FORM

Project Title: DEVELOPMENT OF ANALYTICAL TECHNIQUES
Division: Chemical and Biological Sciences
Project Code: ANALT
Project No.: 3477
Project Staff: Sujit Banerjee
FY 90-91 Budget: $5,000

IPST GOAL:

To develop an algorithm for automatically identifying components in mixtures by infra-red spectroscopy.

OBJECTIVE:

To develop new analytical methodolgy for characterizing components relevant to the industry

DEVELOPMENT OF NEW ANALYTICAL TECHNIQUES

Reporting Period: July, 1990 - March 1991.

OBJECTIVE

To develop an algorithm for automatically identifying components in mixtures by infra-red spectroscopy.

RESULTS

Infrared spectroscopy is used extensively in the industry, e.g., to identify "pitch" components. Usually there is more than one major component present, and deconvoluting the spectrum into its components is presently very difficult (1-8).   When a constituent is removed from a multicomponent spectrum, the number of bands in the spectrum usually declines, i.e. the complexity of the residual decreases. Consider the spectrum in Fig. 1A which comprises two signals and its derivative. As one of the signals is progressively removed, the absolute value of the overall intensity (positive and negative) of the first derivative decreases until the signal is exactly stripped out in Fig. 1B. Further stripping of the signal increases the intensity of the derivative (Fig. 1C). Thus, the derivative, which relates more closely to spectral complexity than to the intensity, minimizes when a component is exactly removed. Hence, in principle, the intensity of the derivative can be used as a tool for identifying component spectra.

A complication arises if a signal very similar to a constituent is stripped. In Fig. 1D, a signal that is identical to a component signal, but displaced just slightly from it, is subtracted. The intensity of the derivative minimizes as before, although to a lesser extent. However, the likelihood of a non-component signal giving rise to a minimum becomes progressively smaller as the complexity of the signals increases, since in all likelihood, a simplification in one spectral region will be offset by increased complexity in another. Thus, the technique is best suited to spectra rich in detail rather than to broad unstructured bands.

Consider the spectrum in Fig. 2A which contains components from Figs. 2B and 2C. A computer program was written to subtract various fractions (n) of the Fig. 2B spectrum from Fig. 2A and to take a derivative after each stage. A plot of the absolute integrated intensity (positive and negative) of the derivative is plotted against n in Fig. 3. The minimum occurs at n=0.85, indicating that 85% of the Fig. 2B spectrum is contained in Fig. 2A.

In summary, the procedure is able to automatically and objectively interpret a complex spectrum without prior knowledge of any of its components. The procedure utilizes all the information in the region where the multi- and pure-component spectra overlap. It is unnecessary for a signal in the mixture to be associated exclusively with any pure component band; ie. no restrictions are placed regarding overlapping pure-component bands. Unlike conventional subtraction schemes where one component is scaled and factored out before analysis of another is attempted, our scheme separately considers each pure component spectrum against the original multi-component spectrum. Thus, the progressive uncertainty of subtractions is removed.

Computer code has been written to process an unknown spectra against each of the 300+ spectra in the IPST spectral library. Plots such as that in Fig. 3 are generated (internally) for each library spectrum. If a minimum exists, the library spectrum is scaled and plotted along with the unknown as illustrated in Figure 4. It is, therefore, possible to automatically interpret a complex spectrum. In preliminary trials, our computer program has been much more successful in identifying components than the search software provided by the instrument vendor.

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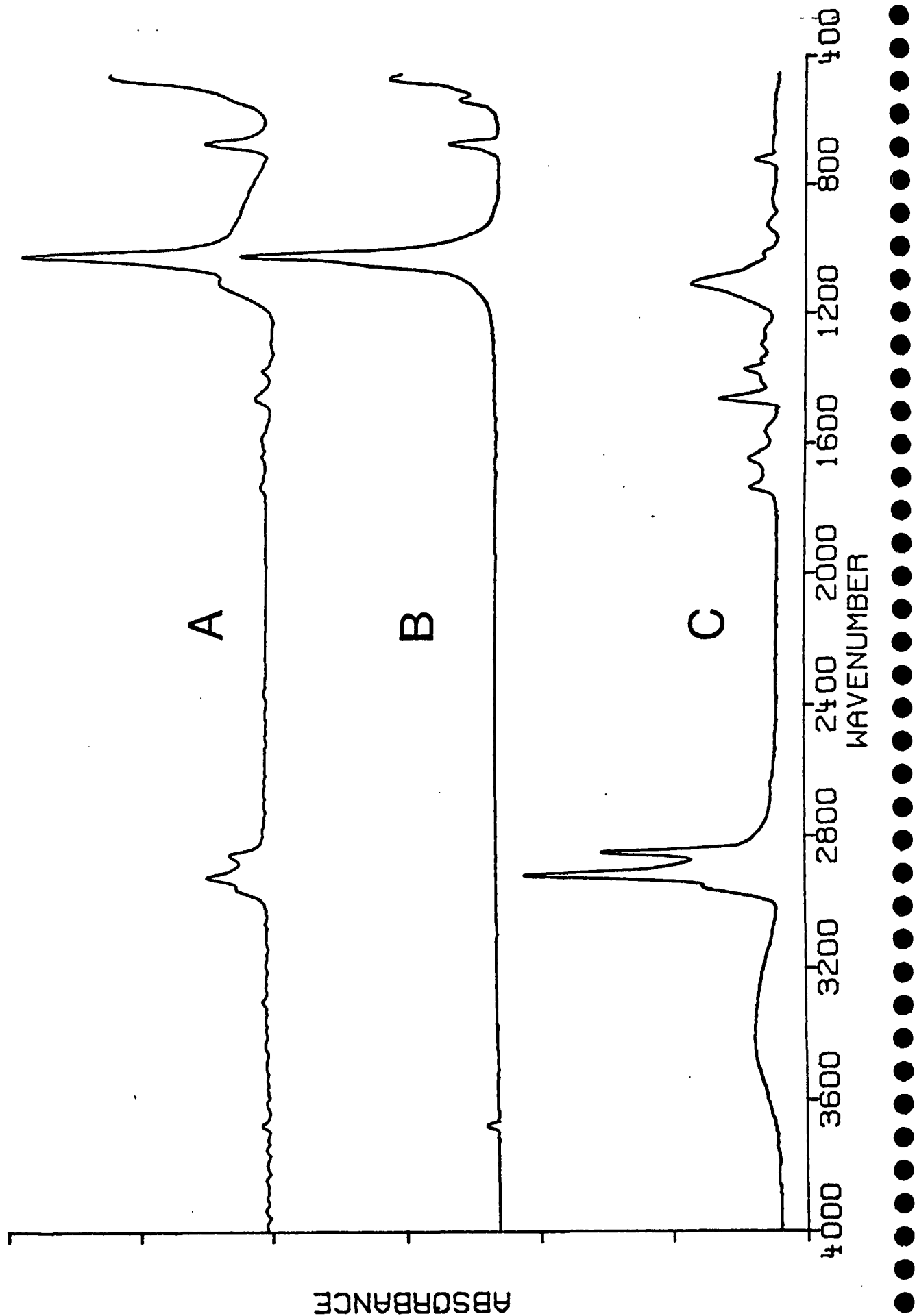
Fig. 2 Spectrum of a mixture (A) including components from (B) and (C).
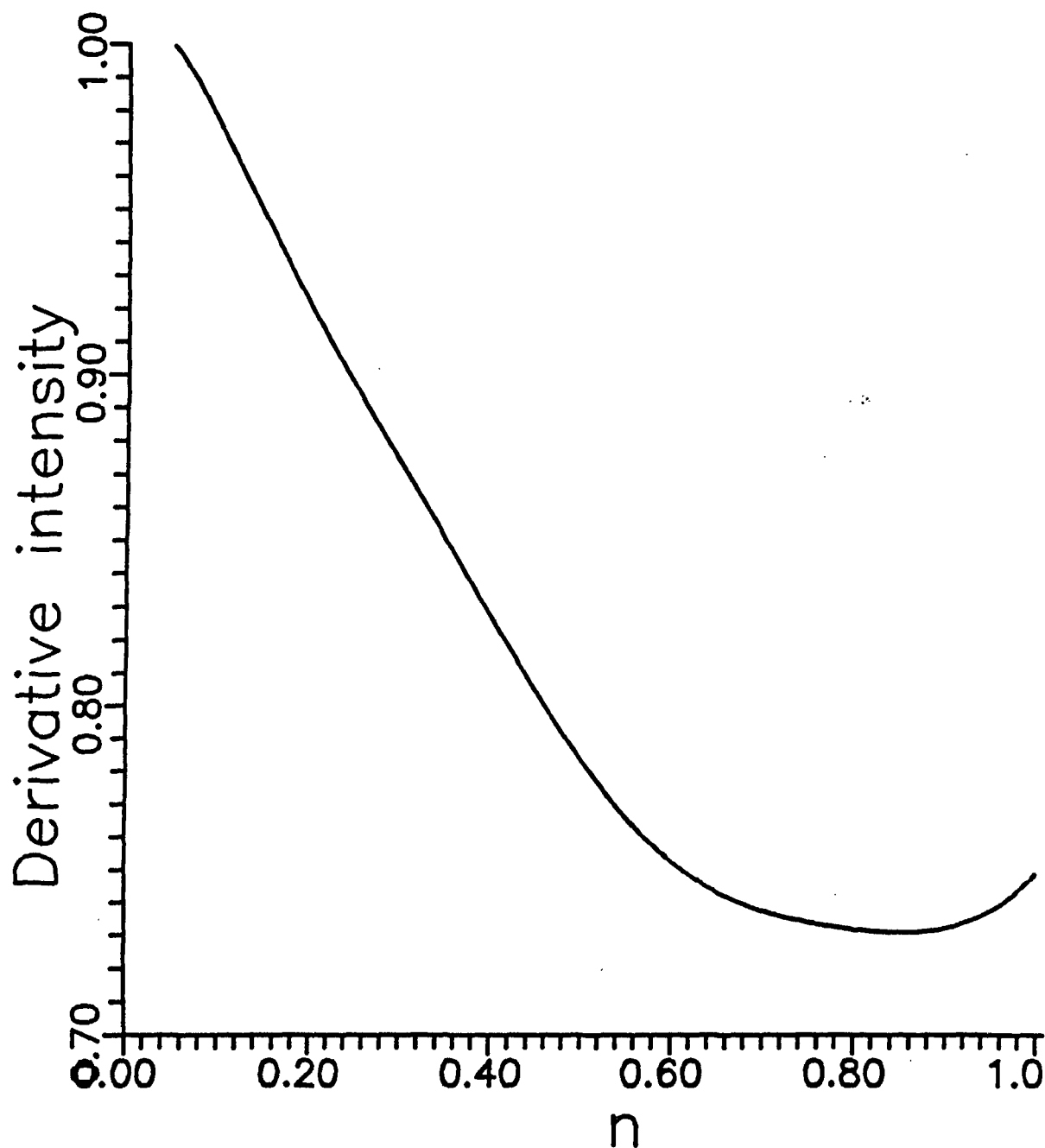
Fig. 3 Integrated absolute intensities (positive and negative) of derivatives of the Fig. 2A spectrum taken after stepwise subtraction of n times the Fig. 2B spectrum.
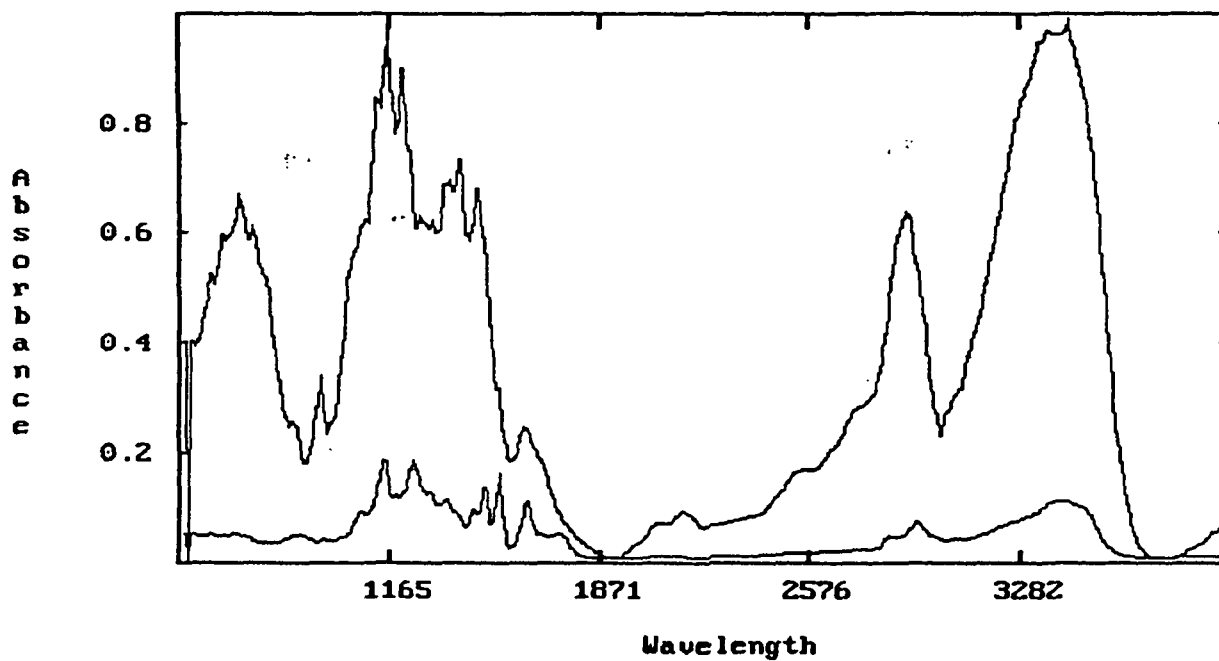
Component (): 18.40%

Fig. 4 Computer-generated identification of a component in a mixture. The top trace is the target spectrum; the lower trace is the scaled library match.

PULPING AND BLEACHING GROUP RESEARCH OVERVIEW

April 2, 1991

PULPING AND BLEACHING GROUP RESEARCH OVERVIEW

INTRODUCTION

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

PROJECTS

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

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

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

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

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

A NOTE TO THE PROJECT ADVISORY COMMITTEES

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

ORGANIZATION OF THE REPORT

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

CHEMICAL PULP BLEACHING

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

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

Dioxins

Project 3664, as yet unmentioned, is closely related to Project 3474. It was entitled "Precursors and Variables in Dioxins Formation". This project, funded by the API through the National Council of the Paper Industry for Air and Stream Improvement (NCASI), was established in late 1989 to address questions concerning the mechanism of dioxins formation during kraft pulp bleaching. Bleaching experiments funded by NCASI were conducted at IPST and analysis of the resulting pulps and effluents was provided by NCASI at their Corvallis, Oregon, analytical facility. This work has resulted in one publication[1] and a second one is pending.

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

Within the past year, a statistically designed study of effects of changes in chlorination stage variables was completed and a study of mixing effects was performed. The appended report entitled "Factors Affecting Formation of PCDD/F in Kraft Pulp Bleaching" (Appendix 1) describes the results of both studies, as well as those of an analysis of data acquired during an earlier investigation of destruction of dioxin precursors by chlorine dioxide. The nature of the mixing experiments is summarized below, under the AOX heading.

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

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

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

AOX

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

The second set of experiments consisted of trials at the two different mixing conditions and two different consistencies, 4 and 6%. These experiments all employed a relatively high chlorine charge, corresponding to a kappa factor of 0.25.

Consistency had no effect on the amount of AOX produced, but the degree of mixing had a significant effect which was the same at both consistencies. Poor mixing gave 20% lower total AOX and 5% less delignification. At this high kappa factor, making the mixing poorer concentrates the added chlorine in "pockets". Within these pocketsconversion of precursors to AOX is complete and excess chlorine remains. Outside of them, aox precursors remain

unconverted. The net result is inefficient conversion to AOX when the mixing is poor. Delignification is also inefficient, but in regions of low chlorine concentration delignification is less hindered by lack of chlorine than is AOX formation. This behavior is to be expected in situations where AOX increases linearly with increasing chlorine concentration, since delignification is known to be more efficient (albeit less complete) at low chlorine concentration than when the chlorine concentration is high. Linear dependences of AOX on kappa factor have been reported in the literature[2,3].

The third set of experiments was designed to investigate the effect of mixing on the relationship between AOX formation and kappa factor. Chlorinations were conducted at both mixing conditions and kappa factors ranging from 0.1 to 0.22. The results showed that the negative effect of mixing on AOX, observed previously at high kappa factor, underwent a reversal as the kappa factor was decreased below about 0.15. At the lower values, poor mixing gave higher AOX. Concentrating the chlorine in pockets, where the chlorine concentration nevertheless remained low enough (because of the low kappa factor) so that it was all consumed, resulted in efficient local AOX generation which was not compensated for by the limitation placed on AOX precursor conversion by low chlorine concentration elsewhere. This requires an AOX-chlorine concentration relationship that is nonlinear in the concave upwards sense (less AOX formed per unit increase in chlorine concentration at low chlorine concentrations), in apparent contradiction to linear relationships that have been reported in the literature[2,3]. A possible explanation may be that the literature correlations were developed, at least in part, by progressively replacing chlorine with chlorine dioxide rather than simply reducing the amount of chlorine added. Berry[4], on the other hand, has presented AOX-kappa factor data that approximate a concave upwards nonlinear relationship.

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

Academic Research on AOX

Mr. Todd Schwantes has begun work on a thesis concerned with the kinetics of formation, and characterization, of AOX generated during the bleaching of kraft pulp in "chlorine-free" sequences. The particular sequences to be investigated are based on the use of oxygen predelignification, 100% substitution of chlorine dioxide for chlorine, and various types of oxidatively reinforced extraction stages.

One objective is to better define, in chemical and physical terms, just what AOX consists of in sequences likely to be used by the industry. Characterization of the AOX formed will include determination of chloroform and other volatile chlorinated compounds, partitioning into ether extractable and non extractable fractions, determination of the molecular weight distributions of

both fractions, further partitioning of the ether extractable material into chlorophenols, acids, and neutrals, and determinations of the chlorine:carbon ratio in each fraction. A second objective is to determine how the concentration, molecular weight distribution, and chlorine:carbon ratio of each of these classes of chlorinated compounds develops over time in the chlorine dioxide stage, for all of the sequences to be examined.

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

Academic Research on Chlorination Kinetics

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

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

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

PROJECT 3474 NONCHLORINE (DUES-FUNDED) AND RELATED ACTIVITIES

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

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

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

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

The report appended as Appendix 3 summarizes recent results.

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

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

A Related, Privately Funded Project

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

Oxygen at 80 psig and 80° C will raise the brightness of mechanical pulps by one to two points if used at a pH around 8. The brightness gain does not appear to be additive with second stage bleaching processes using other bleaching agents such as hydrogen peroxide and sodium hydrosulfite. Higher brightness gains are possible when hydrogen peroxide is added to the oxygen process but net bleached brightness is well below what is achievable with peroxide alone.

Additional sodium hydroxide can be added in a second stage to make use of the considerable peroxide residual remaining after the oxygen/peroxide treatment. This process raises the overall brightness gain to within several points of what can be achieved with peroxide alone.

When oxygen is used at 120 psig of oxygen and 120° C a substantial loss in brightness is obtained which cannot be recovered in a second stage peroxide or hydrosulfite bleach stage.

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

CHEMICAL PULPING AND PULP PROPERTIES

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

ACADEMIC RESEARCH ON PULPING

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

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

API PROJECTS RELATED TO PULPING

Semichemical Pulp Yield Determination (API-CKPG Funded)

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

Work to date has centered on near infrared reflectance spectroscopy (NIR) and UV-visible fluorescence spectroscopy. Laboratory pulps have been prepared at different yield levels and subjected to both types of measurements. Both have given promising results. NIR wavelengths have been identified where spectral properties can be used to differentiate between yield levels. Similarly, it has been shown that when dry pulp samples are irradiated with light of a suitable wavelength, the intensity of their fluorescence at 490 nm is apparently related to yield. The results are summarized in the report attached as Appendix 5.

Conductivity of Pulping Liquors (API-MTC Funded)

This project, Project 3699, has as its major objective the evaluation of three commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams. A test stand was constructed, incorporating a laboratory digester to serve as a liquor reservoir and heater, a circulating pump, a pipe loop to accomodate the sensors, and a data acquisition system. Results to date are presented in the appended report (Appendix 6). Temperature-sensor output relationships have been developed for all 3 sensors simultaneously, using sodium hydroxide solutions. Subsequently, it was established that liquor velocity had no effect, and white liquor testing over a range of temperatures and concentrations of sodium hydroxide, sodium sulfide, sodium carbonate, sodium sulfate and calcium carbonate. The testing is now in progress. Multiple regression analysis will be used to determine the influence of each variable on the conductivity. Present indications are yhat the conductivity can be strongly correlated with active alkali.

Evaluation of a Pulp Additive (Privately Funded)

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

MECHANICAL PULPING AND PULP PROPERTIES

PROJECT 3566 (DUES-FUNDED) AND RELATED ACTIVITIES

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

CHYPS Support and Effects of CHIP Compression on Fiber Properties

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

In November CHYPS conducted a project to evaluate operating capabilities of the pilot plant and develop data in support of the proposed projects. The project was implemented as a 2^{3-1} fractional factorial design with main factors of southern pine tree age (10 and 24 years), density (0.37 g/cc to 0.53 g/cc), and chip size (1/8 - 3/4 and 1/4 - 5/4).

Analysis of the Tensile Index, specific energy relationship for the five wood samples confirms a decrease in strength when pulping lower density southern pines.

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

Effects of Chip Compression on Fiber Properties

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

Evaluation of Interstage Chemical Treatment of Chemimechanical Pulp

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

MECHANICAL PULP BLEACHING AND BRIGHTNESS REVERSION

PROJECT 3694 (DUES-FUNDED) AND RELATED ACTIVITIES

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

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

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

When oxygen is used at 120 psig of oxygen and 120° C a substantial loss in brightness is obtained which cannot be recovered in a second stage peroxide or hydrosulfite bleach stage.

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

A Modified Peroxide Bleaching Process (Privately Funded)

Project 3701 evaluated a modified peroxide bleaching process for CTMP.

PROJECT 3524 (DUES-FUNDED; WOOD CHEMISTRY GROUP)

This recently-established project is under the leadership of Dr. A.J. Ragauskas of the IPST Wood Chemistry Group. This work is summarized in the first overview.

PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION

OF BLEACHED PULP

PART 1: FACTORS AFFECTING FORMATION OF PCDD/F
IN KRAFT PULP BLEACHING

RESEARCH REVIEW

April 2, 1991

Thomas J. McDonough

PROJECT SUMMARY FORM

Project Title:	ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP
Division:	Chemical and Biological Sciences
Project Code:	BLECH
Project No.:	3474
Project Staff:	T.J. McDonough, A.R. Malcolm, K.R. Reed
FY 90-91 Budget:	$250,000

OBJECTIVE:

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

PROJECT 3474
ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

PART 1. FACTORS AFFECTING FORMATION OF PCDD/F IN KRAFT PULP BLEACHING

SUMMARY

A statistically designed study of effects of changes in chlorination stage variables has been completed and a study of mixing effects performed. This report describes the results of both studies, as well as those of an analysis of data acquired during an earlier investigation of destruction of dioxin precursors by chlorine dioxide.

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

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

Analysis of all tetra- through octachlorinated dioxin and furan congeners provided some insight into relevant mechanisms. The TCDF fingerprint, for example, suggests a low probability of chlorination of the ring position adjacent to the ether linkage. This may be an indication of steric hindrance resulting from interaction of the furan oxygen with a pulp component. Another example is the occurrence of a relatively large amount of the 123467/123478 isomer pair, in

which both members have a "lopsided" distribution pattern. This is unexpected in view of the ring-deactivating effect of chlorine substituents, and suggests the participation of a non-DBF precursor or steric interaction of partially chlorinated DBF with a fiber component.

INTRODUCTION

The part of Project 3474 that is concerned with dioxins is being conducted in collaboration with the National Council of the Paper Industry for Air and Stream Improvement (NCASI). According to the terms of this collaboration, pulping, bleaching and other chemical treatments are conducted at IPST, and the resulting pulp and effluent samples are analyzed for dioxins by NCASI at their Corvallis, Oregon analytical facility. Both IPST and NCASI participate in the design of the experiments. The principal investigators at NCASI are L.E. LaFleur and R. Brunck.

DIOXINS IN BLEACHING EFFLUENTS AND BLEACHED PULPS

Initial indications that pulp bleaching is a source of chlorinated dioxins and furans were confirmed in the United States by a cooperative industry - Environmental Protection Agency study begun in 1986 and reported in early 1988[1]. The latter study, conducted on effluents, sludges and pulps from five bleached kraft mills, also showed that the bleaching process was primarily responsible for dioxins formation. A contemporary investigation in Sweden[2] confirmed the bleaching process as a source. Subsequently, unchlorinated dibenzodioxin (DBD) and dibenzofuran (DBF) were found in unbleached kraft pulp and identified as precursors for the corresponding chlorinated compounds[3,4,5,6].

A study of the effect of DBD/DBF addition and removal on the formation of a variety of chlorinated dioxin and furan congeners[7] provided evidence for the existence of precursors other than DBD or DBF. This study also showed that dioxins were formed almost exclusively in the chlorination stage and that virtually none found their way into the liquid phase issuing from this stage.

The "fingerprint," or relative amounts of the various congeners formed was earlier shown[2] to be characteristic and dominated by the 2,3,7,8 isomers of TCDF and TCDD, the former being present in larger amounts. These observations have subsequently been confirmed and amplified by bleaching pulps that produced higher levels of dioxins and by spiking studies[7].

At least two studies[7,8] have addressed the fate of the dioxins formed in the chlorination stage. In the laboratory, virtually all of the dioxins passed from the C-stage to the E-stage with the pulp. The amount and composition were nearly unchanged by the E-Stage, from which they emerged in both the pulp and liquid phases, in roughly equal amounts. The mill study found that most of the dioxin formed in the C-stage left the bleach plant in the E-stage filtrate and the bleached pulp.

Considerable knowledge of control methods has been gained by recent research. Kringstad and co-workers[9] stressed the importance of keeping the ratio of the charge of chlorine (as % of o.d. pulp weight) to unbleached kappa number (chlorine multiple) below a critical value of about 0.15. Below that value, they observed no detectable dioxins, while above it there was an exponential increase in the amount of dioxins formed. They also recommended improved brownstock washing, elimination of chlorination filtrate recycle and avoiding the use of evaporator condensate for brownstock washing. Canadian researchers[3,5,6] have confirmed the importance of the chlorine multiple, and also demonstrated beneficial effects of high chlorine dioxide substitution, careful defoamer selection, oxygen delignification, adding chlorine before chlorine dioxide, decreasing consistency and increasing pH. The success of each of these changes can be traced to a decrease in the concentration of either molecular chlorine or dioxin precursors. These studies predicted, but did not demonstrate, a detrimental effect of recycling chlorination filtrate. In addition, they failed to detect beneficial effects of increasing temperature or divided charges ("split addition") of chlorine, both of which decrease the concentration of molecular chlorine. A beneficial effect of split addition was, however, demonstrated by Hise[10], who combined the effect with that of increased pH for dioxins control. Hise and Hintz[11] also confirmed the importance of good brownstock washing and provided further evidence for the existence of precursors other than DBD or DBF.

With one exception[6] (where chlorine multiple and substitution were studied together), none of the studies referred to above has examined the interactions between the recommended process changes, or the effect of combinations of them. Similarly, none has directly addressed the effect of mixing and none has examined the reasons for the beneficial effect of chlorine dioxide substitution. We judged all of these issues to be worthy of further research, which is the subject of this paper.

EXPERIMENTAL APPROACH

The experiments consisted of laboratory simulations of the chlorination stage, followed by analysis of the resulting pulps and effluents for dioxins. In most of the experiments, all of the tetra- through octachlorinated dibenzodioxins and dibenzofurans were determined. In some cases, pulping and oxygen bleaching were also performed in the laboratory, to track precursor concentrations or to determine effects on dioxins formation in the subsequent stages.

Chlorinations were conducted in a Quantum Technologies high-shear mixer to ensure good mixing and good control over the timing of chlorine and chlorine dioxide additions. The mixer was located in an enclosure equipped with a carbon-filtered air supply, to minimize contamination by airborne precursors and dioxins.

EFFECT OF CHLORINE DIOXIDE ON PRECURSORS

It is now well known[6,9] that chlorine dioxide substitution decreases dioxin formation. In addition, it is likely that adding chlorine before chlorine dioxide gives lower dioxin levels than the reverse procedure. These observations have been explained by postulating that chlorine

dioxide is inert toward dioxin precursors and that chlorine converts precursors to dioxins much more slowly than it reacts with lignin. It follows that adding chlorine first results in its being rapidly consumed by lignin before it has time to generate dioxins from precursors. On the other hand, adding chlorine dioxide first satisfies a major part of the lignin's oxidant demand and thereby slows consumption of chlorine when the chlorine is finally added. As a result, an appreciable concentration of chlorine remains, to serve as a driving force for reaction with dioxin precursors.

The above hypothesis assumes that chlorine dioxide is inert toward dioxin precursors. However, relaxing this assumption does not impair the ability of the hypothesis to explain the observations. It may, for example, be possible that chlorine dioxide destroys dioxin precursors and it fails to do so when added before chlorine simply because it is consumed by lignin before it has the opportunity.

We judged it highly desirable to learn more about the mechanism by which chlorine dioxide has its beneficial effect. Improved knowledge in this area should lead to more effective use of chlorine dioxide in dioxins control and to effective alternatives. As an initial step in this direction, we undertook experiments designed to determine whether chlorine dioxide destroys dioxin precursors. They consisted of a series of chlorinations preceded by chlorine dioxide treatment, and a similar control series in which chlorine dioxide was omitted from the pretreatment. In the event of precursor destruction by chlorine dioxide, more dioxin formation is expected in the control series than in the series where the final chlorination comes after chlorine dioxide treatment.

An additional feature of these experiments was the inclusion of a prechlorination with a limited amount of chlorine in all cases. Its purpose was to satisfy much of the lignin's immediate oxidant demand and thereby minimize the chances that the chlorine dioxide would be destroyed by lignin before having the opportunity to manifest its ability to destroy precursors. The chlorine charge in this stage was chosen to be below the known threshhold value for dioxins formation[6,9] so that it would not consume precursors and generate a background level of dioxins, thereby complicating the interpretation of the results.

To summarize, these experiments took the form of three-stage chlorinations in what could be described as a (CDC) sequence. The first stage was constant for all experiments and consisted of chlorination at a kappa factor of 0.12. The second stage was initiated by injection of chlorine dioxide solution without intermediate filtration or washing, in an amount corresponding to a kappa factor of 0.08. In the third stage, chlorine was injected to convert surviving precursors into dioxins, the determination of which served as a measure of the precursor concentration in the pulp after the chlorine dioxide treatment. In a series of control experiments, the chlorine dioxide solution was replaced by pure water.

The results of analyses of the stage 3 chlorinated pulps for for 2378-TCDD, 2378-TCDF, and 1278-TCDF are summarized in Table 1. All 3 compounds showed a similar response to the experimental variables, as illustrated by the TCDD data plotted in Figure 1. The control experiments, with no chlorine dioxide in the stage preceding final chlorination, exhibited the expected behavior: no detectable dioxin formation was observed until the total chlorine charge

exceeded a threshhold value. When chlorine dioxide treatment preceded final chlorination, similar behavior was observed, with the important exception that the amounts of dioxin produced were higher.

This observation is open to 3 possible interpretations. One is that chlorine dioxide converts precursors to dioxins. This seems unlikely in view of the known beneficial effect of increasing substitution. Another is that it creates new precursors or liberates precursor initially chemically bound to a pulp component. The third, and perhaps most likely, is that chlorine dioxide has no effect on the precursor concentration, and acts simply by reducing the oxidant demand of the lignin, leading to higher chlorine concentrations and consequently more efficient conversion of existing precursors in the final stage. In any case, the results show that chlorine dioxide does not readily destroy precursors, since such destruction would lead to decreased dioxin levels relative to the control experiments.

MIXING EFFECTS

Kringstad et al.[9] and Berry et al.[6] have clearly shown that the amount of dioxins formed in the chlorination stage is a strongly nonlinear function of initial chlorine concentration. None can be detected at low chlorine charges, but the amount formed increases exponentially with increasing chlorine charge after the latter has exceeded some critical threshhold level. This can be explained by again invoking the hypothesis that chlorine reacts much more rapidly with lignin than with dioxin precursors. Below the critical level, all of the added chlorine is immediately consumed by lignin in the initial rapid phase of that reaction. Only at higher chlorine charges does sufficient residual chlorine remain to participate in the slower reaction with dioxin precursors. It also follows from this hypothesis that continued increases in chlorine charge will convert increasing fractions of the available precursors to dioxins.

All of the above arguments apply on a local level as well as the global one, suggesting that poor mixing is likely to result in higher dioxin levels at a given chlorine charge. Under this hypothesis, high chlorine residuals in those parts of the pulp suspension receiving disproportionately high fractions of the total chlorine applied will efficiently convert precursors to chlorinated dioxins. Because of the exponential shape of the response curve, the amounts formed will more than compensate for the lack of formation in chlorine-starved parts of the suspension, leading to an overall increase.

A related hypothesis predicts that dioxins formation should increase with increasing consistency. At higher consistency, the concentration of molecular chlorine will be higher, because of the smaller amount of water present. Furthermore, this effect will be enhanced by a corresponding shift in the equilibrium between molecular chlorine and hypochlorous acid.

To test both hypotheses, we conducted experiments in the Quantum Technologies high-shear laboratory mixer at two levels of consistency and two different conditions of mixing. The consistency levels used were 4% (24 g water/g pulp) and 6% (15.7 g water/g pulp). Two extreme mixing conditions were used at each consistency, one corresponding to very good mixing, the other to poor mixing. The conditions for either extreme were chosen, and the

corresponding degrees of mixing quantified, in a series of preliminary experiments employing a dye tracer technique. Runs conducted under each of the four combinations of consistency and mixing conditions were run twice, so the experiment took the form of a replicated 2x2 factorial design.

These experiments were conducted on an unbleached softwood kraft pulp that had been artificially enriched in the known dioxin precursors, DBD and DBF. This was done to exaggerate the effects of chlorine concentration gradients, thereby making their dependence on the experimental variables more apparent.

The experimental design is further illustrated by Table 2, which also gives partial results and further information about the mixing conditions. Results for individual isomers are summarized in Tables 3, 4, and 5.

The data in these tables show that improved mixing gave significantly lower E-stage kappa number, but did not result in any decrease in the amounts of any measured single isomer or class of chlorinated dioxins or furans. This surprising result suggests that the increase in conversion of precursors to dioxins in regions of high chlorine concentration was insufficient to compensate for the unavailability of residual chlorine to convert precursors in regions of low chlorine concentration. This is inconsistent with a simple exponential increase in dioxins formation with increasing chlorine concentration, which would demand that the effect of an increase in chlorine concentration in one region must always be less (in an absolute sense) than the corresponding decrease in a different region. Rather, it suggests that the rate of formation of dioxins levels off sharply as the chlorine concentration is increased beyond the range of exponential dioxin increase.

This may be illustrated with a hypothetical example comparing a perfectly mixed chlorination with chlorine charge C_{av} to another which is poorly mixed in such a way that half of the pulp receives a chlorine charge of $C_{av}+d$ and the other half receives $C_{av}-d$. It is apparent from Figure 2(a) that an exponentially increasing dioxin response curve would result in the poorly mixed chlorination giving a higher dioxin level. It is equally apparent from Figure 2(b) that a response curve characterized by an exponential increase, followed by a sharp levelling off, would result in the poorly mixed sample giving a lower dioxin level, as was actually observed.

In fact, Berry et al. did observe such a levelling off in formation of 2378-TCDD and 2378-TCDF, and attributed it to progressive conversion of these tetrachlorinated compounds to congeners containing larger numbers of chlorine substituents. The present study, however suggests that some other mechanism is responsible for the levelling off, since the poorly mixed samples showed no increases in the higher congeners. It may be postulated, for example, that oxidative ring opening competes favorably with substitution after four chlorine atoms have been introduced.

Increasing the chlorination consistency from 4 to 6% caused a small but statistically significant increase in total TCDD formation, as expected on the basis of the resulting increase in chlorine concentration. Larger increases were observed in the amounts of polychlorinated dibenzofurans.

The dioxin/furan fingerprint typically observed in these experiments is represented by the overall average concentrations of the measured isomers and groups of isomers in Figures 3-6. The TCDD pattern, shown in Figure 3, is similar to that found in our earlier study[7] and to that reported by Swanson et al.[2]. It is characterized by the dominance of the 2378 isomer, the occurrence of a smaller amount of 1278-TCDD, and the near absence of all other tetrachlorinated isomers. In our earlier study, we showed that both isomers were enhanced by spiking with DBD. The 1379 and 1289 isomers observed by de Sousa et al.[12] have not been observed in our studies.

The pattern for the higher CDD congeners is shown in Figure 4. It, too, is similar to that published earlier by de Sousa et al., in that the dominant isomers are 12378-PeCDD, and the hepta- and octa- CDD's. The amounts we observed in our heavily spiked sample were similar to those observed earlier in unspiked samples, suggesting a precursor other than DBD for the higher congeners.

The TCDF fingerprint (Figure 5) shows the expected preponderance of the 2378 and 1278 isomers, together with significant quantities of 1248/1346, 1268/1478/1369, 1238/1467, 1239/2348, 2367 and 1289. A summarizing observation may be made with regard to the approximate relative probabilities of finding a chlorine substituent at each of the four types of DBF carbon. Relative to the ring position immediately adjacent to the carbon-carbon bond joining the rings (1 or 9) the adjacent lateral position is about 5 times more likely to be substituted, the other lateral position about 4 times more likely, and the position adjacent to the ether linkage only about one-third as likely. The low probability of chlorination of the last position may be an indication of steric hindrance resulting from interaction of the furan oxygen with a pulp component. Berry et al.[6] have invoked this idea to explain the absence of 1278-TCDD in their chlorinated pulps.

The pattern for the higher chlorinated furan congeners, shown in Figure 6, is also dominated by 2378-substituted isomers. An interesting feature is the occurrence of a relatively large amount of the 123467/123478 isomer pair, in which both members have a "lopsided" distribution pattern. A similarly larger than expected amount of the 123489 isomer was also observed. Full chlorination of one ring while the other contains two unsubstituted positions is inconsistent with the known deactivating effect of chlorine substituents and with the expected statistical effect. This is an indication of either a non-DBF precursor or steric interaction of partially chlorinated DBF with a fiber component. The former interpretation is favored by our earlier observation[7] that the amounts of these isomers observed in chlorinated pulp were relatively unaffected by spiking the unbleached pulp with DBF or by extracting it with solvents before bleaching.

EFFECTS OF CHLORINATION STAGE VARIABLES

Previous work in other laboratories has demonstrated that chlorination stage conditions can influence the amounts of 2378-TCDD and 2378-TCDF formed. The order of addition of chlorine and chlorine dioxide has been shown to affect TCDF formation, and preceding the chlorination stage by an oxygen stage or by improved washing has been shown to be beneficial. In addition, it has been predicted, but not demonstrated, that increasing temperature or

decreasing chlorination filtrate recycle will reduce dioxins formation.

Because combinations of such changes may constitute effective and economical strategies for avoiding dioxins formation, and because knowledge of their effects is incomplete, we undertook a systematic study of effects of changes in chlorination stage variables, both singly and in combinations. The approach we adopted involved the use of a statistically designed factorial experiment and analysis of the resulting chlorinated pulps for tetra- through octachlorinated dibenzodioxins and dibenzofurans.

All chlorinations were conducted on mill softwood kraft pulp in a Quantum Technologies high shear mixer/reactor using a total active chlorine multiple of 0.25 and a chlorine dioxide substitution level of 25%. The variables and their levels were:

(A) timing of chlorine dioxide addition (15 sec before or 15 sec after chlorine),

(B) temperature (30 or 60 degrees C),

(C) chlorination stage filtrate recycle (0 or 30%),

(D) degree of oxygen delignification before the chlorination stage (0 or 40%), and

(E) degree of washing of the unbleached pulp (either near-perfect or normal, i.e. no black liquor carryover or a normal level of carryover.

The experimental design was a one-half fraction of a 2^5 factorial. Two complete replications were done, each replication being performed on a different set of unbleached pulp samples from the same mill. The results were subjected to analysis of variance, assuming a statistical model containing main effects and two-factor interactions.

The experimental results are summarized in Table 6, and a detailed tabulation of relevant means for each important isomer is presented in Table 7. Only isomers that were detected in more than half of the samples analyzed are included in Table 7. The results of the statistical data analysis are summarized in Table 8.

Effect of Oxygen Bleaching

The introduction of an oxygen stage before chlorination had a greater effect than any other variable. With very few exceptions, the levels of all dioxin and furan congeners were sharply reduced by introducing the oxygen stage. The average levels of 2378-TCDD and 2378-TCDF were reduced by 88% and 82% respectively. Only the higher dioxin (as opposed to furan) congeners were unaffected; the average level of OCDD formed was slightly, but not significantly, higher after oxygen bleaching.

A possibly related observation is that the reductions in chlorinated furan levels became progressively smaller with increasing chlorine substitution. This suggests that the higher congeners arise partly from precursors that are unaffected by oxygen bleaching. Since the beneficial effect of the oxygen stage is probably attributable to precursor volatilization it is likely that nonvolatile precursors exist, and possible that they are identical to the nonextractable precursors we postulated earlier. The level of the 123467/123478 HxCDF isomer pair, for example, was reduced by only 43%, and was shown earlier to be relatively unaffected by solvent extraction or by spiking with DBF.

The effect of the oxygen stage on the levels of the tetrasubstituted congeners depended on whether the chlorine dioxide was added before or after chlorine. As discussed below, adding chlorine first was effective in reducing dioxins formation. When this was done, taking the additional step of adding an oxygen stage had a much smaller effect. Similarly, the effect of changing the order of addition from chlorine dioxide first to chlorine first was small after an oxygen stage. This relationship between oxygen bleaching and order of addition is exemplified by 2378-TCDD. Oxygen bleaching reduced 2378-TCDD from 4.6 to 0.4 ppt when chlorine dioxide was added first and from 1.8 to 0.4 ppt when chlorine was added first. The interaction was, in general, not observed for higher congeners, probably because they were less affected by changing the order of addition. This is another indication of a second mechanism of formation that is more important for higher congeners than lower ones.

A practical implication of the interaction between these two variables is that, because their effects are to some extent mutually exclusive, it is possible that incorporation of both modifications into the same sequence may not be economically justified. A corollary is that, when a remedial measure is needed, it may be advisable to consider changing the order of addition before adopting the more capital-intensive oxygen bleaching alternative.

There was a similar, but less pronounced, interaction between oxygen bleaching and temperature. Oxygen had a smaller effect on a high temperature chlorination because the temperature increase accomplished part of the reduction which could otherwise be attributed to oxygen. For example, oxygen reduced 2378-TCDF from 22 to 3 ppt in a low temperature chlorination and from 10 to 3 ppt in a high temperature chlorination.

Order of Addition of Cl2 and ClO2

Formation of 2378-TCDD and most of the tetrachlorinated furans was significantly decreased by adding chlorine before chlorine dioxide. The average levels of 2378-TCDD, 1278-TCDF and 2378-TCDF were decreased by 56%, 43% and 55%, respectively. As already mentioned, the size of the effect depended on whether or not an oxygen stage was present in the sequence, and it was not observed for higher congeners.

Besides depending on whether or not oxygen bleaching was used, this effect also depended on the degree of washing of the unbleached pulp and on the temperature of the chlorination stage. Reversing the order of addition proved to be of little value when the pulp was washed free of any residual black liquor before bleaching. For example, the average level of 2378-TCDF

formed after normal mill washing was reduced from 18 to 4 ppt by adding chlorine first. The corresponding reduction after thorough removal of spent liquor was from 8 to 7 ppt. Similarly, adding chlorine first was more effective in a low temperature chlorination than in a high temperature stage, principally because a beneficial effect of increasing temperature made reversing the order of addition redundant.

A notable exception to the general beneficial effect of reversing the order of addition on tetrasubstituted congeners was the behavior of 2468-TCDF. In fact, this isomer is unusual in several respects. The mixing study reported above and our earlier publication[7] both indicate that its formation is suppressed by spiking the unbleached pulp with DBF. We also observed that its level is unaffected by prior exhaustive extraction of the unbleached pulp. These observations strongly suggest that 2468-TCDF is not formed by chlorination of DBF.

It is also notable that the formation of higher congeners is not inhibited by adding chlorine first.

Effect of Chlorination Temperature

Increasing the chlorination stage temperature from 30 to 60 degrees C decreased the amounts of 2378-TCDD, 2378-TCDF and several other chlorinated furans, most notably the 123467/123478 pair. The average reductions were 50, 49 and 40%, respectively. In contrast, the temperature increase caused an average 38% increase in the observed amount of OCDD, which may therefore be formed by a different mechanism than TCDD.

The magnitude of the temperature effect was dependent on several other variables. Its dependence on order of addition of chlorine and chlorine dioxide has already been referred to; it is typified by the behavior of total TCDF, which was reduced, on the average, from 47 to 27 ppt when chlorine dioxide was added first, but remained approximately constant at an average of 25 ppt when chlorine was added first. An interaction with oxygen has also been referred to. For example, increasing the temperature reduced the average level of 2378-TCDF from 22 to 10 ppt in the absence of oxygen, while after an oxygen stage it was roughly constant at about 3 ppt, regardless of temperature. A final, weaker interaction of the temperature effect was with recycle, which had a beneficial effect at low temperature, but not at high temperature.

Recycling Chlorination Filtrate

The effects of chlorination filtrate recycle were generally small and were statistically significant at a high confidence level only for 2 pentachlorinated furan isomers. Their levels were slightly increased by the recycled filtrate. On the other hand, some significant interaction effects suggested that recycled filtrate may have a beneficial effect under certain conditions.

Black Liquor Carryover

The effect of the black liquor in normally washed pulp was small and in most cases not statistically significant. It did, however, interact with the order of addition of chlorine and chlorine dioxide in the case of several TCDF's. As already described, the black liquor in the unbleached pulp increased TCDF if chlorine dioxide was added before chlorine but not if the reverse order was used.

EXPERIMENTAL

Effect of Chlorine Dioxide on Precursors

Materials

Softwood kraft pulp was supplied by a north central mill. Upon receipt, the pulp was squeezed to remove dilute spent pulping liquor and washed thoroughly with distilled water. The liquor separated from the pulp before washing was stored under refrigeration for later use. The kappa number of the pulp was 31.3.

Distilled water was used for all experiments. Chlorine was research purity grade (99.99% pure), obtained from Holox. Sodium hydroxide was analytical reagant (AR) grade (98.6% pure), obtained from American Science Products. Sodium chlorate was AR grade (99.1% pure) from Baker, oxalic acid was AR grade from Mallinckrodt (99.8% pure) and the sulfuric acid was Reagant A.C.S. (98.0% pure) form Fisher.

Chlorine dioxide was generated from sodium chlorate and oxalic acid in sulfuric acid solution. Its chlorine content, expressed as a percentage of the total active chlorine was between 0.04 and 2.60%.

Bleaching Experiments

Bleaching experiments were conducted in a Quantum Technologies high shear mixer-reactor in a (CDC) sequence. A 120 g (o.d. basis) sample of unbleached pulp was placed in the mixer with sufficient dilution water to give a consistency of 5.5% after addition of the chlorine required for the first stage. An aqueous solution containing 3.76% chlorine (o.d. pulp basis - chlorine factor 0.12) was placed in one of the reactor's injector reservoirs, which was then pressurized with nitrogen. The mixer was actuated, causing the chlorine solution to be injected when the rotor had attained a preset speed. Mixing was continued at 600 rpm for 10-15 sec and was repeated for 3 sec at intervals of 5 minutes. The same mixing schedule was used in the subsequent stages, described below.

After an elapsed time of 30 minutes, chlorine dioxide (0.95% based on o.d. pulp, kappa factor 0.08) was injected with enough water to reduce the consistency to 4.5%. The reactor remained

closed, and, with the exception of a small sample of filtrate withdrawn through a sampling line, no pulp or filtrate was removed prior to injection of the chlorine dioxide. In control experiments, an equal volume of pure water was substituted for the chlorine dioxide solution.

After a further 30 minutes, and again without opening the reactor, a calculated quantity of chlorine solution was injected. Dilution water, sufficient to give a final consistency of 3.5%, was injected with the chlorine. Reaction of the chlorine with the pulp was allowed to proceed for 30 minutes, after which the reactor was opened and the filtrate sampled for pH and residual determination. The pulp was then diluted to 3% consistency, thoroughly mixed and thickened to 15% consistency. The thickened pulp was transferred to an ultraclean jar and submitted for dioxins analysis.

MIXING EFFECTS

Defining Mixing Conditions

Conditions that would provide respectively poor mixing and good mixing in the Quantum Technologies laboratory mixer/reactor were defined and quantified by a dye tracer technique. A bleached softwood sulfite pulp was used in these experiments, together with phenolphthalein as dye tracer. The pulp (120 g at either 4 or 7.7% consistency) was buffered at pH 10 with sodium carbonate-bicarbonate, and a volume of dye solution (1 L) comparable to the normal volume of chlorine water was injected while mixing the pulp at various rotor speeds. Mixing was then immediately stopped or continued for varying lengths of time.

At the end of the mixing period, the reactor was immediately opened and the liquid phase sampled at approximately 25 randomly chosen points throughout the fibrous mass. Sampling consisted of withdrawing 0.5 mL samples with a syringe. The samples were then volumetrically diluted and their visible light absorbance was measured at a wavelength of 552 nm. The coefficient of variation of the resulting absorbance measurements was then taken as an inverse measure of mixing efficiency.

On the basis of these measurements we adopted, for poor mixing, standard conditions of 60 rpm and a mixing time that corresponded to the time required for injection of 1 L of solution (11-13 sec). This gave a coefficient of variation of 15-37% at 4% consistency and 15% at 7.7% consistency. Good mixing was similarly defined as mixing at 1800 rpm for 180 sec, which gave a coefficient of variation equal to that obtained in a control series of measurements on a homogeneous solution (2-3%).

Bleaching

A mill-made jackpine kraft pulp was thoroughly washed in the laboratory and determined to have a kappa number of 26.4 and viscosity of 28.2 cp. 120g. o.d. (4% consistency) or 200 g.o.d. (6% consistency) samples were chlorinated with 6.6% chlorine at 45 degrees C for 30 minutes. No chlorine dioxide was used.

The chlorinated pulp was sampled for tetra through octachlorinated dioxins analysis and then extracted with 3.63% NaOH (o.d. pulp basis) for 1 hour at 70 deg. C and 7% consistency, prior to determinations of kappa number and viscosity.

Chlorination Stage Variable Effects

Several pulp samples taken from the same mill over a short time span were used for this work. The kappa number of each sample was accurately determined before bleaching and the amount of chemical to be used in the first stage of bleaching was chosen accordingly. When the first stage was chlorination, the amounts of chlorine and chlorine dioxide were chosen to give a ratio of total active chlorine to kappa number of 0.25 at a level of 25% substitution (active chlorine basis) of chlorine dioxide for chlorine. The average kappa number of the unbleached pulps was 34.

The unbleached pulp was thoroughly washed with distilled water using a fritted glass funnel. The liquor initially expressed from the pulp was reserved and in those experiments that called for it was added back to the pulp at a level of 6 mL/g o.d. pulp before bleaching.

The oxygen stage, if used, was carried out in the Quantum Mixer at 9 % consistency with 2.0 to 3.6 %NaOH for 60 minutes at 93 deg. C. Oxygen was charged once at 100 psi. After bleaching, the pulp was removed, diluted to 4%, and thickened to 20 % consistency and transferred to the chlorination stage without further washing.

The chlorination stage was conducted at 4% consistency for 30 minutes at 30 or 60 deg. C. Chlorine water was iodometrically titrated and the required volume was carefully transferred to the injector reservoir to minimize losses due to volatilization. Chlorine dioxide solution was titrated for both chlorine dioxide and chlorine and the required volume was imilarly transferred to the second injector reservoir. The kappa factor was 0.25 and the level of substitution 25%. At the end of the chlorination stage the pulp was thickened to 20% consistency, sampled for dioxins analysis and transferred to the extraction stage without further wasing.

Caustic extraction was conducted in the Quantum mixer with % NaOH at 0.55 * % total Cl2 charge at 9% consistency and 70 degrees C for 60 min. At the end of this time, the pulp was removed, diluted to 4 % consistency, and thickened to 20% consistency.

CONCLUSIONS

When chlorine dioxide treatment preceded chlorination, the amounts of dioxin produced were higher. These results show that chlorine dioxide does not readily destroy precursors, since such destruction would lead to decreased dioxin levels relative to the control experiments.

Improved mixing gave significantly lower E-stage kappa number, but did not result in any decrease in the amounts of any measured single isomer or class of chlorinated dioxins or furans. This suggests that the rate of formation of dioxins levels off sharply as the chlorine concentration

is increased beyond the range of exponential dioxin increase. Berry et al. did observe such a levelling off in formation of 2378-TCDD and 2378-TCDF, and attributed it to progressive conversion of these tetrachlorinated compounds to congeners containing larger numbers of chlorine substituents. The present study, however suggests that some other mechanism is responsible for the levelling off, since the poorly mixed samples showed no increases in the higher congeners. Increasing the chlorination consistency from 4 to 6% caused a small but statistically significant increase in total TCDD formation, as expected on the basis of the resulting increase in chlorine concentration.

The TCDF fingerprint suggests that, relative to the ring position immediately adjacent to the carbon-carbon bond joining the rings (1 or 9) the adjacent lateral position is about 5 times more likely to be substituted, the other lateral position about 4 times more likely, and the position adjacent to the ether linkage only about one-third as likely. The low probability of chlorination of the last position may be an indication of steric hindrance resulting from interaction of the furan oxygen with a pulp component. The occurrence of a relatively large amount of the 123467/123478 isomer pair, in which both members have a "lopsided" distribution pattern, and of a similarly larger than expected amount of the 123489 isomer was also observed. This is an indication of a non-DBF precursor or steric interaction of partially chlorinated DBF with a fiber component.

The levels of all dioxin and furan congeners were sharply reduced by introducing an oxygen stage before chlorination. The reductions in chlorinated furan levels became progressively smaller with increasing chlorine substitution. This suggests that the higher congeners arise partly from nonvolatile precursors, possibly identical to the nonextractable precursors we postulated earlier. The effect of the oxygen stage on the levels of the tetrasubstituted congeners depended on whether the chlorine dioxide was added before or after chlorine. Oxygen bleaching reduced 2378-TCDD from 4.6 to 0.4 ppt when chlorine dioxide was added first and from 1.8 to 0.4 ppt when chlorine was added first. The interaction was, in general, not observed for higher congeners, probably because they were less affected by changing the order of addition. This is another indication of a second mechanism of formation that is more important for higher congeners than lower ones.

Formation of 2378-TCDD and most of the tetrachlorinated furans was significantly decreased by adding chlorine before chlorine dioxide when no oxygen stage was present in the sequence. The effect depended on the degree of washing of the unbleached pulp and on the temperature of the chlorination stage. Reversing the order of addition proved to be of little value when the pulp was washed free of any residual black liquor before bleaching. Similarly, adding chlorine first was more effective in a low temperature chlorination than in a high temperature stage, principally because a beneficial effect of increasing temperature made reversing the order of addition redundant. A notable exception to the general beneficial effect of reversing the order of addition on tetrasubstituted congeners was the behavior of 2468-TCDF. This, together with previous observations of a lack of correlation with DBF content of the unbleached pulp, suggests that 2468-TCDF is not formed by chlorination of DBF. The formation of higher congeners is not inhibited by adding chlorine first.

Increasing the chlorination stage temperature from 30 to 60 degrees C decreased the amounts of 2378-TCDD, 2378-TCDF and several other chlorinated furans, most notably the 123467/123478 pair. The magnitude of the temperature effect was dependent on several other variables.

The effects of chlorination filtrate recycle were generally small and were statistically significant at a high confidence level only for 2 pentachlorinated furan isomers. Their levels were slightly increased by the recycled filtrate.

The effect of the black liquor in normally washed pulp was small and in most cases not statistically significant. The black liquor in the unbleached pulp increased TCDF if chlorine dioxide was added before chlorine but not if the reverse order was used.

ACKNOWLEDGMENTS

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TABLE 1. DIOXIN FORMATION IN (CDC) SEQUENCE

STAGE 2 CLO$_2$/ KAPPA	STAGE 3 CL$_2$/ KAPPA	STAGES 1+3 CHLORINE FACTOR	STAGE 3 EXIT pH	2378 TCDD	2378 TCDF	1278 TCDF
0.00	0.00	0.12	1.6	0.3	1.7	1.5
0.08	0.00	0.12	1.5	0.3	0.6	0.5
0.00	0.06	0.18	1.4	0.8	3.5	2.8
0.08	0.06	0.18	1.4	0.6	3.1	2.9
0.00	0.08	0.20	1.4	1.0	8.7	6.8
0.08	0.08	0.20	1.3	13.9	50.3	24.6
0.00	0.12	0.24	1.4	10.1	30.3	14.5
0.08	0.12	0.24	1.4	21.3	105.5	49.9
0.00	0.16	0.28	1.3	15.1	64.2	28.0
0.08	0.16	0.28	1.2	40.4	331.9	152.2

Note: Exit pH's For stages 1 and 2 were all in the range 1.4-1.5

TABLE 2: SUMMARY OF RESULTS OF MIXING STUDY

MIXING QUALITY	CONS. %	C-STAGE EXIT pH	E-STAGE KAPPA NO.	DIOXINS AND FURANS IN CHLORINATED PULP, PPT									
				TOTAL TCDD	TOTAL PeCDD	TOTAL HxCDD	TOTAL HpCDD	OCDD	TOTAL TCDF	TOTAL PeCDF	TOTAL HxCDF	TOTAL HpCDF	OCDF
GOOD	4	1.6	3.4	115	9	2	3	7	14363	684	82	25	19
		1.6	2.8	120	8	2	3	3	10408	452	161	17	2
POOR		1.6	4.4	73	8	3	5	7	9566	660	173	38	8
		1.5	4.0	88	6	2	2	6	10914	851	95	12	2
GOOD	6	1.7	3.4	132	9	4	11	14	10133	771	503	108	34
		1.5	3.0	126	8	2	2	5	13070	580	311	93	11
POOR		1.7	4.7	86	9	3	3	7	11083	1012	414	74	21
		1.5	4.1	89	6	2	2	3	8156	676	300	90	12
AVERAGE POORLY MIXED			4.3	84	7	2	3	6	9930	750	246	54	11
WELL MIXED			3.2	124	9	3	5	7	11993	617	284	60	16
AVERAGE 4% CONSISTENCY			3.6	99	8	2	3	6	11313	612	128	23	8
6% CONSISTENCY			3.8	109	8	3	5	7	10610	755	382	91	19

NOTES: 1. Unbleached pulp: Mill jackpine kraft; Kappa number 26.4; viscosity 28.2 cp. Spiked with DBD and DBF.

2. Chlorination conditions: 30 min. at 45 deg. C; 6.6% chlorine.

3. Good mixing: 180 sec. at 1800 rpm; coeff. of var. <3%.

4. Poor mixing: 13 sec. at 60 rpm; coeff. of var. 15-37%.

TABLE 3A: EFFECTS OF MIXING AND CONSISTENCY ON THE AMOUNTS OF INDIVIDUAL ISOMERS AND ISOMER GROUPS FORMED:

POLYCHLORINATED DIBENZODIOXINS

ISOMER	ISOMER NO.	GRAND MEAN	TREATMENT MEANS				STATISTICAL SIGNIFICANCE*	
			POOR MIXING	GOOD MIXING	4% CONS.	6% CONS.	MIX-ING	CONS.
1368 TCDD	1	0	0	1	0	0		
1379 TCDD	2	0	0	0	0	0		
1369 TCDD	3	0	0	0	0	0		
1247/1248/1378/1469 TCDD	4	0	0	0	0	0		
1246/1249 TCDD	5	0	0	0	0	0		
1268 TCDD	6	0	0	0	0	0		
1478 TCDD	7	0	0	0	0	0		
1279 TCDD	8	0	0	0	0	0		
1234/1236 1269 TCDD	9	0	0	0	0	0		
1237/1238 TCDD	10	0	0	0	0	0		
2378 TCDD	11	96	78	115	92	101	+++	+
1239 TCDD	12	0	0	0	0	0		
1278 TCDD	13	4	3	5	4	4	+++	
1267 TCDD	14	0	0	0	0	0		
1289 TCDD	15	0	0	0	0	0		

* statistical significance: blank: not significant
    +: possibly significant ($>90\%, <95\%$)
  ++: significant ($>95\%, <99\%$)
 +++: highly significant ($>95\%$)

TABLE 3B: EFFECTS OF MIXING AND CONSISTENCY ON THE AMOUNTS OF INDIVIDUAL ISOMERS AND ISOMER GROUPS FORMED:

POLYCHLORINATED DIBENZODIOXINS

ISOMER	ISOMER NO.	GRAND MEAN	TREATMENT MEANS *			
			POOR MIXING	GOOD MIXING	4% CONS.	6% CONS.
12468/12479 PeCDD	16	0	0	0	0	0
12469 PeCDD	17	0	0	0	0	0
12368 PeCDD	18	0	0	0	0	0
12478 PeCDD	19	0	0	0	0	0
12379 PeCDD	20	0	0	0	0	0
12369/12489 PeCDD	21	0	0	0	0	0
12346/12347 PeCDD	22	0	0	0	0	0
12378 PeCDD	23	6	6	6	6	6
12367 PeCDD	24	0	0	0	0	0
12389 PeCDD	25	0	0	0	0	0
124679/124689 HxCDD	26	0	0	0	0	0
123468 HxCDD	27	0	0	1	0	1
123469/123689 HxCDD	28	1	0	1	1	1
123478 HxCDD	29	0	0	0	0	0
123678 HxCDD	30	0	0	0	0	0
123467/123789 HxCDD	31	0	0	0	0	0
1234679 HpCDD	32	2	1	2	1	2
1234678 HpCDD	33	2	2	3	2	3
OCDD	34	7	6	7	6	7

* Neither mixing nor consistency had significant effects on the level of any isomer shown in this table.

TABLE 4: EFFECTS OF MIXING AND CONSISTENCY ON THE AMOUNTS OF INDIVIDUAL ISMOMERS AND ISOMER GROUPS FORMED:

TETRACHLORINATED DIBENZOFURANS

ISOMER	ISOMER NO.	GRAND MEAN	TREATMENT MEANS				STATISTICAL SIGNIFICANCE*	
			POOR MIXING	GOOD MIXING	4% CONS.	6% CONS.	MIX-ING	CONS.
1368 TCDF	35	0	0	0	0	0		
1378 TCDF	36	1	0	1	0	1		
1347/1379 TCDF	37	0	0	0	0	0		
1247/1468 TCDF	38	11	8	14	11	11	+++	
1367 TCDF	39	0	0	0	0	0		
1348 TCDF	40	11	10	13	12	11	++	
1248/1346 TCDF	41	230	218	243	248	213		
1237/1246 TCDF	42	0	0	0	0	0		
1268/1478/1369 TCDF	43	191	159	223	199	182	++	
1369 TCDF	44	0	0	0	0	0		
2468 TCDF	45	1	1	0	0	1		
1238/1467 TCDF	46	226	200	253	235	218		
1234/1236/2349 TCDF	47	0	0	0	0	0		
1278 TCDF	48	2926	2720	3132	3084	2768		
1349 TCDF	49	0	0	0	0	0		
2368 TCDF	50	59	43	74	62	56	+++	
1267/1279/1469 TCDF	51	93	77	108	99	87	++	
1249 TCDF	52	0	0	0	0	0		
2467 TCDF	53	0	0	0	0	0		
2347 TCDF	54	0	1	0	1	0		
2378 TCDF	55	6197	5617	6776	6322	6072		
1239/2348 TCDF	56	385	317	453	351	419	++	
1269 TCDF	57	0	0	0	0	0		
2346 TCDF	58	0	0	0	0	0		
2367 TCDF	59	288	230	347	300	276	+++	
3467 TCDF	60	0	0	0	0	0		
1289 TCDF	61	340	326	353	386	293		

* Statistical Significance: blank: not significant
           +: possibly significant (>90%,<95%)
          ++: significant (>95%, <99%)
       +++: highly significant (>95%)

TABLE 5: EFFECTS OF MIXING AND CONSISTENCY ON THE AMOUNTS OF INDIVIDUAL AND ISOMER GROUPS FORMED:

POLYCHLRINATED DIBENZOFURANS

ISOMER	ISOMER NO.	GRAND MEAN	TREATMENT MEANS				STATISTICAL SIGNIFICANCE*	
			POOR MIXING	GOOD MIXING	4% CONS.	6% CONS.	MIX-ING	CONS.
12468/13468 PeCDF	62	3	3	4	3	3		
23479 PeCDF	63	0	0	0	0	0		
12368/12478/13467/13478 PeCDF	64	74	79	70	70	79		
13479/23469 PeCDF	65	2	2	2	2	2		
12479 PeCDF	66	0	0	0	0	0		
12346/12347/12469/13469 PeCDF	67	9	8	11	9	10		
12348 PeCDF	68	20	22	17	18	21		
12378 PeCDF	69	203	224	181	183	222		
12367 PeCDF	70	4	4	3	4	4		
12379/23489 PeCDF	71	62	72	53	55	70	+	
12369/12489/13489/23478 PeCDF	72	218	252	185	196	240		
23467 PeCDF	73	71	66	75	56	86		
12349 PeCDF	74	0	0	0	0	0		
12389 PeCDF	75	17	17	16	16	17		
123468 HxCDF	76	1	1	2	1	1		
124678/134678/134679 HxCDF	77	8	7	9	5	11		+
124679 HxCDF	78	0	0	0	0	0		
124679 HxCDF	79	21	20	22	9	33		+++
123467/123478 HxCDF	80	149	145	152	72	225		+++
123479/123678 HxCDF	81	21	20	21	11	30		+
123469 HxCDF	82	0	0	0	0	0		
123679/123689 HxCDF	83	7	6	7	4	10		+
234678 HxCDF	84	4	3	4	3	5		
123789 HxCDF	85	5	5	6	3	8		
123489 HxCDF	86	39	37	41	20	58		++
1234678/1234689 HpCDF	87	14	13	16	6	22		+++
1234679 HpCDF	88	16	15	17	7	25		+++
1234789 HpCDF	89	27	26	28	10	43		+++
OCDF	90	13	11	16	8	19		++

* Statistical Significance: blank: not significant

+: possibly significant (>90%,<95%)

++: significant (>95%, <99%)

+++: significant (>99%)

++: highly significant (>95%)

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TABLE 6: SUMMARY OF RESULTS OF CHLORINATION VARIABLES STUDY

ClO2 DELAY	TEMP	C-STAGE FILTRATE RECYCLE	OXYGEN	BLACK LIQUOR CARRY OVER	C-STAGE EXIT pH	E-STAGE KAPPA NO.	2378 TCDD	1278 TCDF	2378 TCDF	12378 PeCDF	123467/123478 HxCDF	TOTAL TCDD	TOTAL HxCDD	TOTAL HpCDD	OCDD	TOTAL TCDF	TOTAL PeCDF	TOTAL HxCDF	TOTAL HpCDF	OCDF
-1	-1	-1	-1	-1	1.9	4.0	8.6	24.6	49.2	6.6	14.3	8.8	0.5	1.9	5.5	106.2	19.5	25.0	7.0	2.4
-1	-1	-1	-1	-1	1.9	4.4	3.3	6.0	11.9	1.5	9.2	3.4	0.5	1.5	4.9	33.7	5.9	14.9	7.0	1.6
-1	1	-1	-1	-1	2.0	3.7	1.6	6.4	6.9	3.8	3.9	1.8	0.7	2.2	5.2	28.9	12.2	7.2	1.8	0.5
-1	1	-1	-1	1	1.8	5.3	0.6	4.9	5.7	3.3	7.8	0.7	0.5	2.1	9.1	26.1	9.9	13.1	4.4	1.0
-1	-1	1	-1	-1	1.5	3.9	4.3	11.0	21.0	6.8	13.7	4.5	0.5	1.3	3.6	58.4	19.7	24.0	4.9	1.2
-1	-1	1	-1	-1	1.4	5.0	1.6	6.5	8.0	5.7	14.2	1.7	0.5	1.2	3.5	33.1	17.3	24.1	6.8	1.8
-1	1	1	-1	1	1.6	4.7	4.0	10.6	14.6	5.2	7.1	4.2	0.6	2.1	5.2	48.9	17.6	13.4	4.6	2.4
-1	1	1	-1	-1	1.8	5.0	1.9	9.4	11.1	8.3	5.7	2.1	0.6	1.7	6.5	45.1	24.0	11.2	1.5	0.5
-1	-1	-1	1	-1	2.1	2.5	0.7	1.8	2.9	0.6	5.0	1.0	0.6	1.8	4.3	9.1	2.8	8.1	4.3	2.5
-1	-1	-1	1	-1	1.9	3.3	0.3	1.5	1.5	1.8	7.0	0.3	0.4	1.0	3.8	10.3	5.9	11.7	3.1	0.9
-1	1	-1	1	1	2.2	3.4	0.2	5.6	5.2	1.8	2.4	0.3	0.5	1.4	5.4	16.6	6.6	4.1	2.4	1.2
-1	1	-1	1	-1	2.0	3.4	0.4	3.1	3.0	2.5	8.1	0.6	0.5	1.4	4.9	17.0	7.8	12.9	5.4	1.5
-1	-1	1	1	1	1.8	3.0	0.2	2.1	2.3	2.5	7.1	0.4	0.6	1.3	5.0	12.6	7.2	11.9	3.1	0.8
-1	-1	1	1	-1	1.9	3.1	0.4	3.5	3.7	2.4	3.8	0.8	0.8	2.3	7.5	17.6	8.0	6.7	1.9	0.6
-1	1	1	1	-1	1.9	3.0	0.5	2.9	2.7	1.5	3.6	0.6	0.4	1.6	6.6	13.1	5.1	6.3	2.3	0.9
-1	1	1	1	1	2.0	3.6	0.4	1.6	2.2	1.7	6.4	0.6	0.6	2.3	9.2	12.9	5.8	11.3	3.5	0.6

DIOXINS AND FURANS IN CHLORINATED PULP, PPT

AVERAGES	C-STAGE EXIT pH	E-STAGE KAPPA NO.	2378 TCDD	1278 TCDF	2378 TCDF	12378 PeCDF	123467/123478 HxCDF	TOTAL TCDD	TOTAL HxCDD	TOTAL HpCDD	OCDD	TOTAL TCDF	TOTAL PeCDF	TOTAL HxCDF	TOTAL HpCDF	OCDF
ClO2 FIRST:	1.8	3.5	2.5	8.1	13.1	3.6	7.1	2.7	0.6	1.7	5.1	36.7	11.3	12.5	3.8	1.5
Cl2 FIRST:	1.8	4.1	1.1	4.6	5.9	3.4	7.8	1.3	0.5	1.7	6.2	24.5	10.6	13.2	4.2	1.1
LOW TEMP:	1.8	3.6	2.4	7.1	12.6	3.5	9.3	2.6	0.6	1.5	4.7	35.1	10.8	15.8	4.8	1.5
HIGH TEMP:	1.9	4.0	1.2	5.6	6.4	3.5	5.6	1.4	0.5	1.8	6.5	26.1	11.1	9.9	3.2	1.1
- RECYCLE:	1.9	3.7	1.9	6.7	10.8	2.7	7.2	2.1	0.5	1.6	5.4	31.0	8.8	12.1	4.4	1.5
+ RECYCLE:	1.7	3.9	1.7	5.9	8.2	4.3	7.7	1.9	0.6	1.7	5.9	30.2	13.1	13.6	3.6	1.1
- OXYGEN:	1.7	4.5	3.2	9.9	16.1	5.1	9.5	3.4	0.5	1.7	5.4	47.5	15.8	16.6	4.8	1.4
+ OXYGEN:	1.9	3.2	0.4	2.8	2.9	1.8	5.4	0.6	0.6	1.6	5.8	13.7	6.1	9.1	3.3	1.1
- BLACK LIQ:	1.9	3.6	1.6	5.5	7.9	3.4	6.6	1.8	0.6	1.7	5.4	27.9	10.7	11.4	3.6	1.2
+ BLACK LIQ:	1.8	4.0	2.0	7.2	11.1	3.6	8.3	2.1	0.5	1.7	5.8	33.3	11.2	14.3	4.4	1.4

NOTES:
1. Unbleached pulp: Mill jackpine kraft; averge kappa number 34; average viscosity 28mPa·s.
2. ClO2 was added either 15 sec before Cl2 (DELAY=-1) or 15 sec after (DELA=1).
3. Temperature was either 30 (TEMP=-1) or 60 (TEMP=1) degrees C.
4. The liquid entering the chlorination stage included either 30% recycled chlorination filtrate (RECYCLE=1) or no recycled chlorination filtrate (RECYCLE=-1).
5. The pulp entering the chlorination stage was either untreated (OXYGEN=-1) or partially delignified in an oxygen stage (OXYGEN=1, average degree of delignification 40%).
6. The brownstock was either thoroughly washed (CARRYOVER=-1) or contained carryover typical of normal mill washing (CARRYOVER=1).

TABLE 7: C-STAGE FACTORIAL EXPERIMENT MEANS FOR SIGNIFICANT EFFECTS[*]

ISOMER	ISOMER NO.	GRAND MEAN	ClO_2 FIRST	Cl_2 FIRST	TEMPERATURE LOW	TEMPERATURE HIGH	RECYCLE −	RECYCLE +	OXYGEN −	OXYGEN +	BLACK LIQUOR −	BLACK LIQUOR +
2378 TCDD	11	1.8	2.5	1.1	2.4	1.2			3.2	0.4		
OCDD	34	5.6	5.1	6.2	4.7	6.5						
1248/1346 TCDF	41	1.1							1.5	0.6		
2468 TCDF	45	9.0					7.6	10.5	12.4	5.7		
1278 TCDF	48	6.3	8.1	4.6					9.9	2.8		
2368 TCDF	50	0.3	0.4	0.3					0.5	0.2		
1267/1279/1469 TCDF	51	0.2	0.3	0.1					0.3	0.1		
2347 TCDF	54	0.3			0.3	0.2			0.4	0.1		
2378 TCDF	55	9.5	13.1	5.9	12.6	6.4			16.1	2.9		
1239/2348 TCDF	56	1.5	1.8	1.1	2.0	0.9			2.6	0.4		
2346 TCDF	58	0.2	0.2	0.1	0.2	0.1			0.2	0.1		
2367 TCDF	59	0.5	0.6	0.3	0.6	0.3			0.8	0.2		
1289 TCDF	61	1.8	2.4	1.3					2.9	0.7		
12468/13468 PeCDF	62	0.8					0.6	0.9	1.0	0.5	0.1	0.2
12467/13467/13478 PeCDF	64	1.4							2.1	0.8		
12346/12347/12469/13469/23468 PeCDF	67	0.8					0.7	1.0	1.2	0.4		
12378 PeCDF	69	3.5					2.7	4.3	5.1	1.8		
12379/23489 PeCDF	71	0.9							1.3	0.5		
12369/12489/23478 PeCDF	72	1.2							1.7	0.7		
23467 PeCDF	73	2.1					1.6	2.5	3.0	1.2		
123468 HxCDF	76	0.2					0.2	0.2	0.3	0.1		
124678/134679 HxCDF	77	0.5			0.6	0.4			0.7	0.3		
124689 HxCDF	79	1.1			1.4	0.9			1.4	0.8		
123467/123478 HxCDF	80	7.5			9.3	5.6			9.5	5.4		
123479/123678 HxCDF	81	1.0			1.2	0.8			1.4	0.7		
123679/123689 HxCDF	83	0.3			0.3	0.2	0.3	0.4	0.4	0.2		
123789 HxCDF	85	0.2					0.2	0.3	0.3	0.2		
123489 HxCDF	86	2.0			2.5	1.6			2.7	1.4		
1234789 HpCDF	89	1.6			2.0	1.3						
TOTAL TCDD		2.0	2.7	1.3	2.6	1.4						
TOTAL TCDF		30.6	36.7	24.5	35.1	26.1	8.8	13.1	47.5	13.7		
TOTAL PeCDF		10.9							15.8	6.1		
TOTAL HxCDF		12.9			15.8	9.9			16.6	9.1		
TOTAL HpCDF		4.0										
OCDF		1.3										

[*] All treatment means shown represent effects that are statistically significant (=>90% confidence)

TABLE 8A: STATISTICALLY SIGNIFICANT EFFECTS AND 2-VARIABLE INTERACTIONS FROM C-STAGE FACTORIAL EXPERIMENT[*]

ISOMER NUMBER	GRAND MEAN	REP.	A	B	C	D	E	AB	AC	AD	AE	BC	BD	BE	CD	CE
1	0.2															
11	1.8	++	++	+		+++				++	+	++	+			
26	0.1												+			
28	0.2															
31	0.2	++						+								
32	0.8															
33	0.9														++	
34	5.6		+	+++										+	+++	
41	1.1					++					++					
45	9.0	+			+	+++										
48	6.3		++			+++				+	++	+				
50	0.3		++			+++				+++	+	++				
51	0.2		++			+++				+			++			
54	0.3	++	+++	+++		+++		+++		++	++	++	+++			+
55	9.5	+	+++	++		+++		++		++	++	++	++			+
56	1.5		++	+++		+++		++		++	+++	++	+++			++
58	0.2		+	+			++			+			+			
59	0.5	++	+++	++		+++		++		+++	++	++	+++			++

[*] statistical significance:
- blank: not significant
- +: possibly significant (>90%, <95%)
- ++: significant (>95%, <99%)
- +++: highly significant (>95%)

A: ClO$_2$ Delay   B: Temperature   C: Recycle   D: Oxygen   E: Black Liquor

TABLE 8B: STATISTICALLY SIGNIFICANT EFFECTS AND 2-VARIABLE INTERATIONS FROM ANALYSIS OF C-STAGE FACTORIAL EXPERIMENT*

ISOMER NUMBER	GRAND MEAN	REP.	A	B	C	D	E	AB	AC	AD	AE	BC	BD	BE	CD	CE
61	1.8		+			+++					+					
62	0.8				++	+++				++						
64	1.4					+++										
67	0.8				++	+++				++	+					
68	0.2	++														
69	3.5				+	+++										
71	0.9					+++										
72	1.2					+++										
73	2.1				+	+++				++						
76	0.2				++	+++				++						
77	0.5			++		+++				+						
79	1.1			+		++							++			
80	7.5	+		++		++							++			
81	1.0	+		+	+	+++										
83	0.3	++		+	+	+++		+								
85	0.2			++	+	++										
86	2.0			+		++										
87	1.1												+			
88	1.3												+			
89	1.6			+									+			
90	1.3															
TCDD	2.0	++	++	+		+++				++	+	++	+			
HXCDD	0.5	+							+				+	++		
HpDD	1.7														++	
OCDD	5.6															
TCDF	30.6		++	+		+++		++		++	++	+	++			++
PeCDF	10.9				+	+++										
HXCDF	12.9			++		++							+			
HpCDF	4.0												+			
OCDF	1.3												+			

* Statistical significance: blank: not significant
     +: possibly significant (>90%,<95%)
     ++: significant (>95%, <99%)
     ++: significant (>99%)
     +++: highly significant (>95%)

A: ClO_2 Delay   B: Temperature   C: Recycle   D: Oxygen   E: Black Liquor
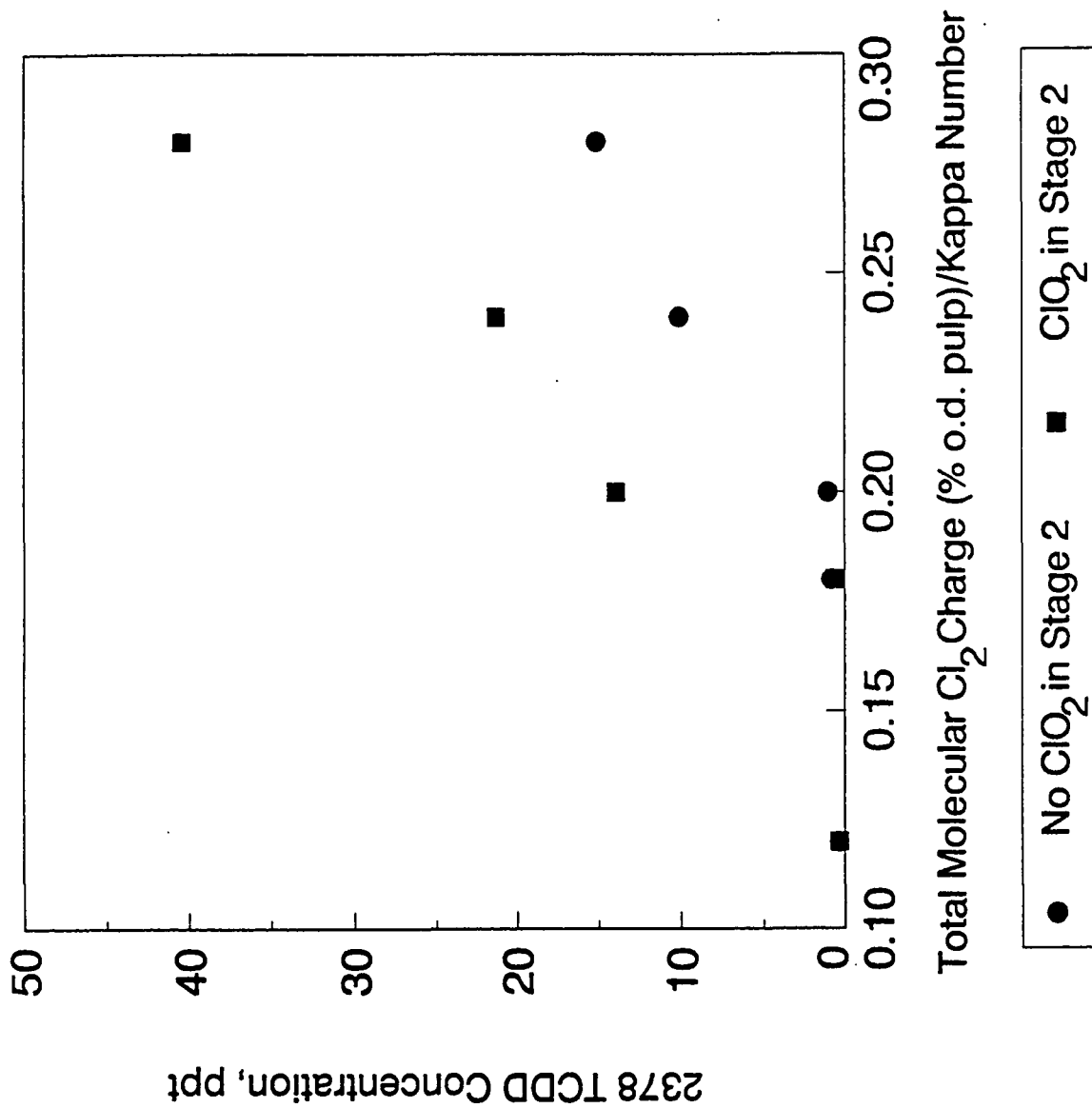
Figure 1: Formation of 2378-TCDD in CDC Sequence

Y-axis: 2378 TCDD Concentration, ppt (50, 40, 30, 20, 10, 0)

X-axis: Total Molecular Cl$_2$ Charge (% o.d. pulp)/Kappa Number (0.10, 0.15, 0.20, 0.25, 0.30)

Legend:
● No ClO$_2$ in Stage 2
■ ClO$_2$ in Stage 2

$$D_{mixed} = D_{av}$$

$$D_{unmixed} = \frac{D_{hi} + D_{lo}}{2} > D_{av}$$
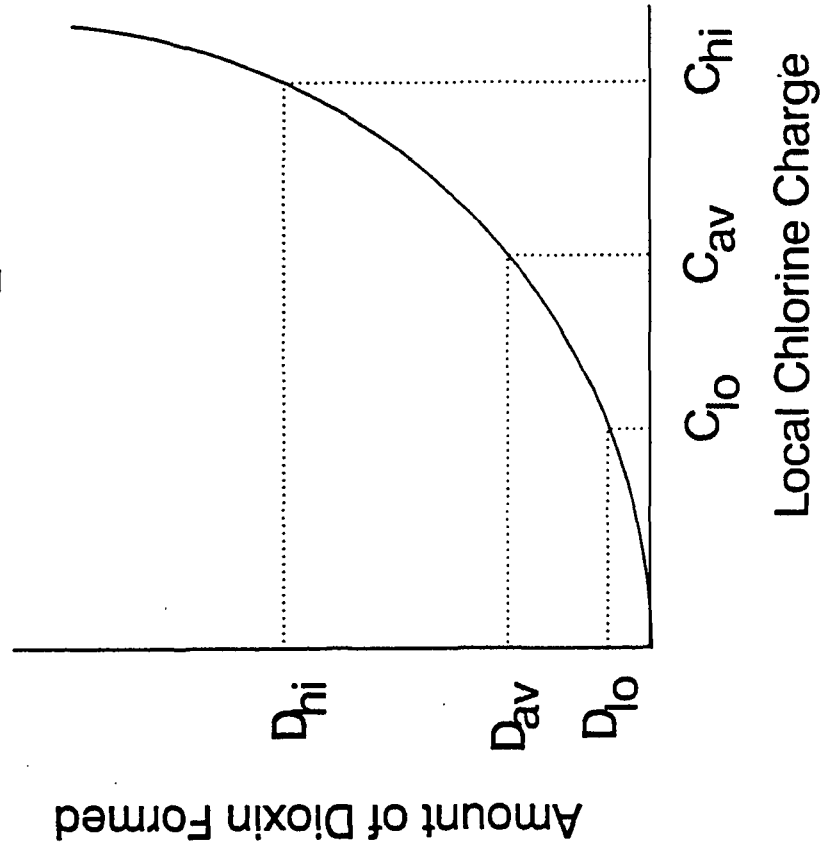
Figure 2a: Hypothetical dioxin - chlorine charge relationships and the corresponding predicted effects of poor mixing.

$$D_{mixed} = D_{av}$$

$$D_{unmixed} = \frac{D_{hi} + D_{lo}}{2} < D_{av}$$
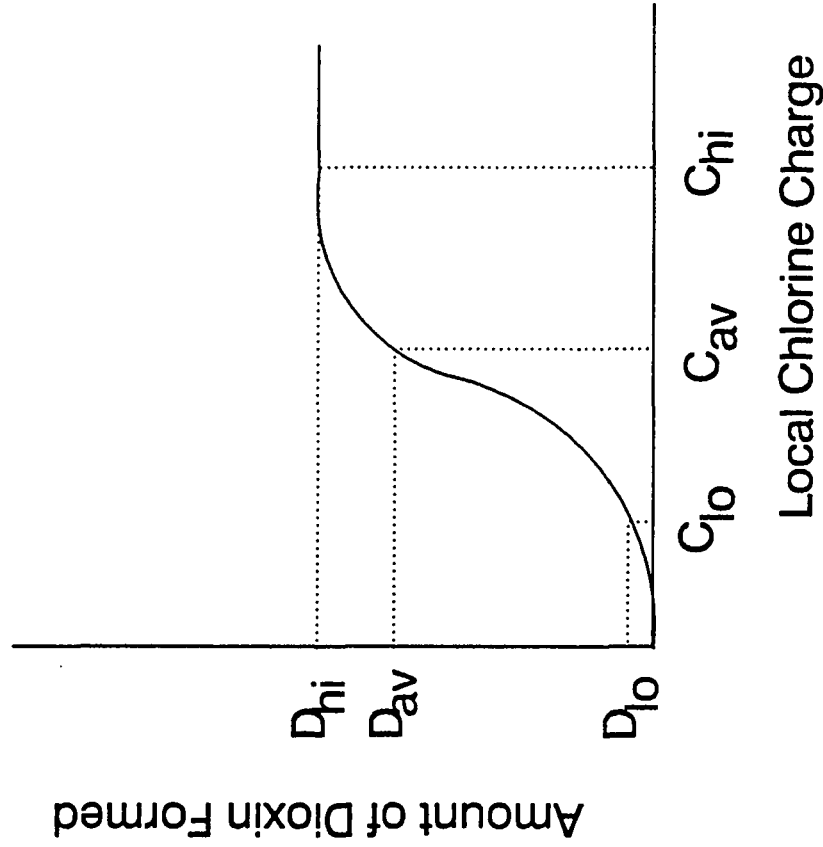
Figure 2b: Hypothetical dioxin - chlorine charge relationships and the corresponding predicted effects of poor mixing.
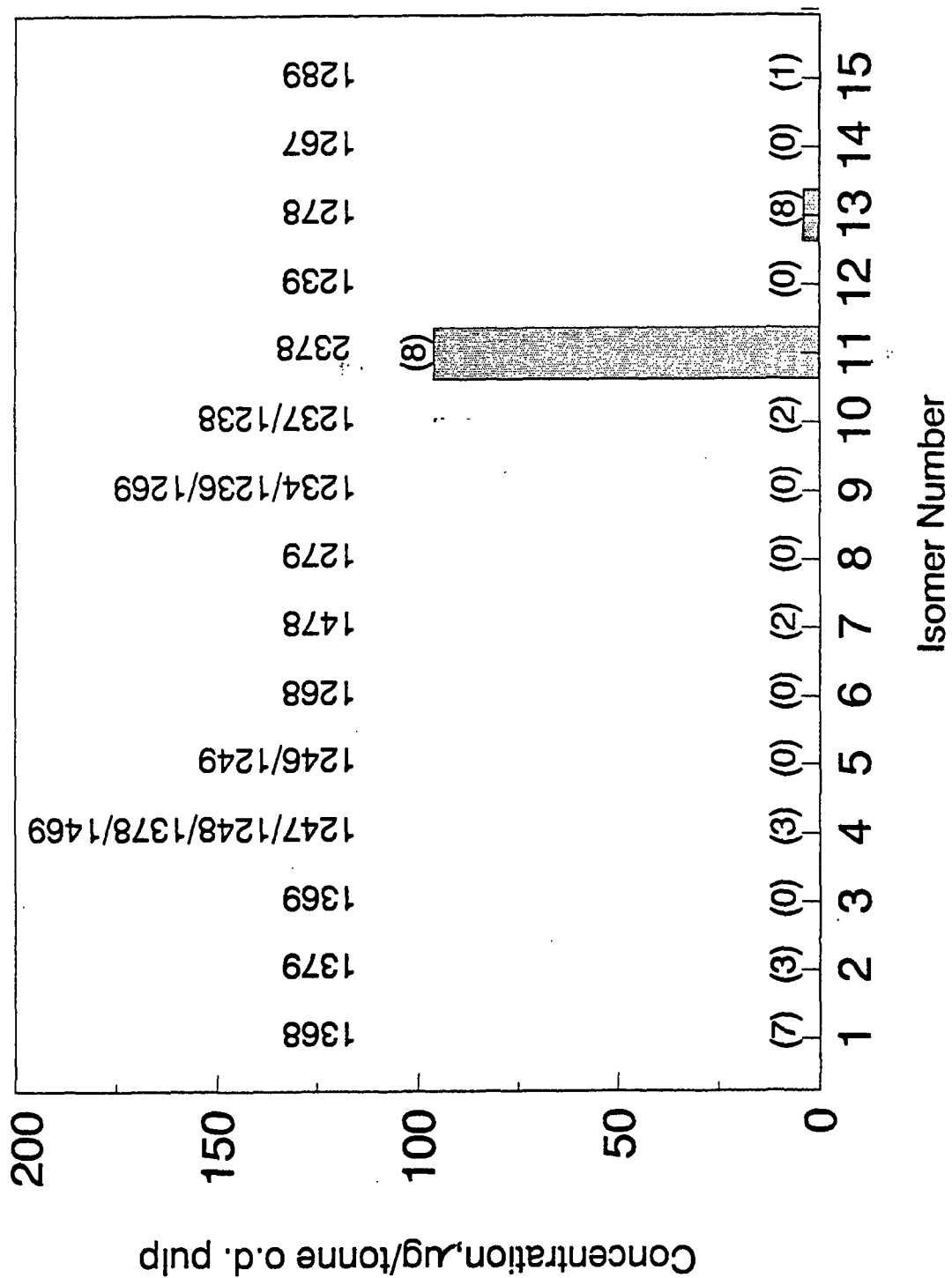
Figure 3: Average TCDD concentrations in chlorinated pulps of mixing study. Averages less than 1 μg/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.
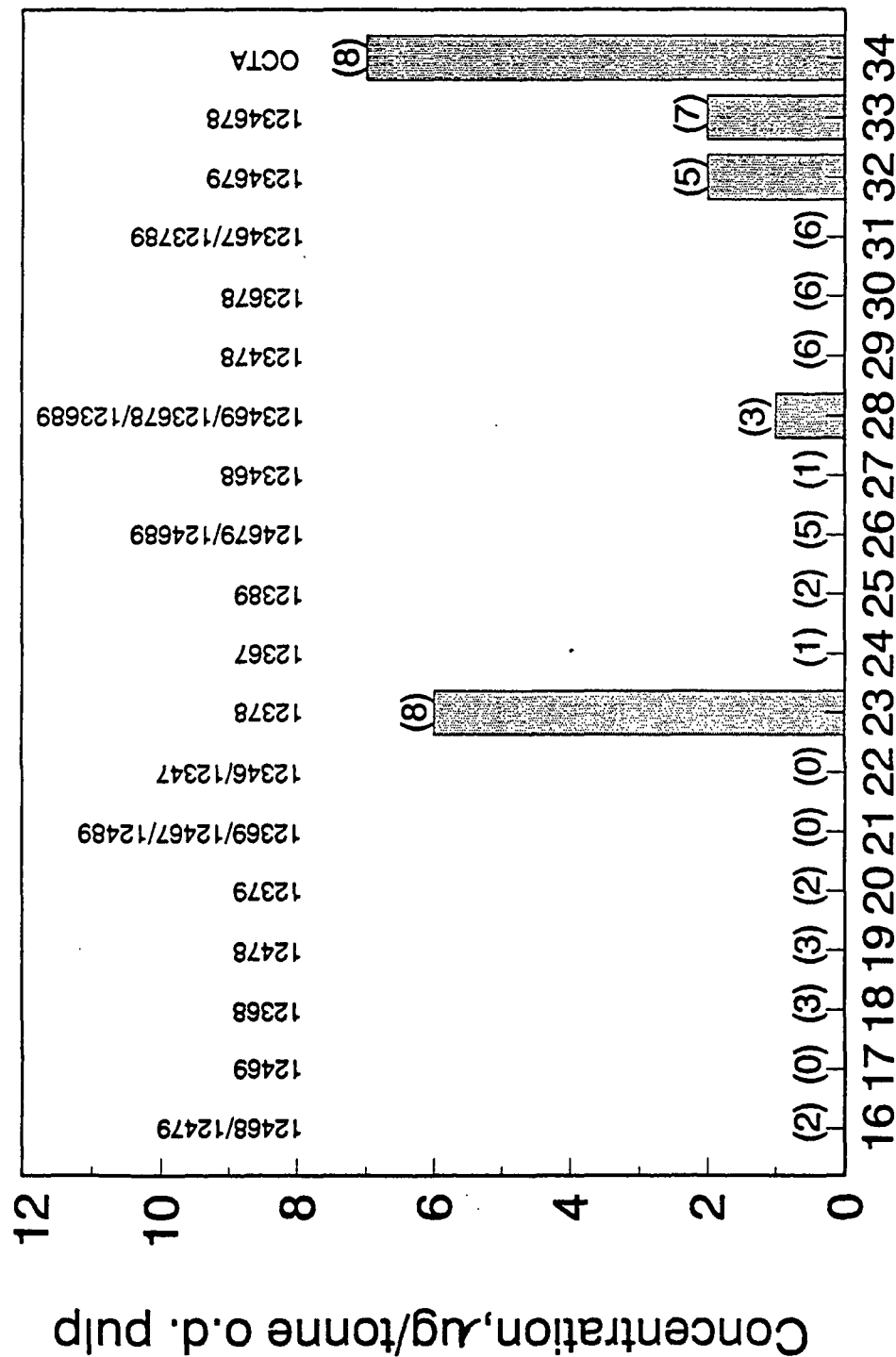
Figure 4: Average penta-, hexa-, hepta and octa- CDD concentrations in chlorinated pulps of mixing study. Averages less than 1 μg/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.
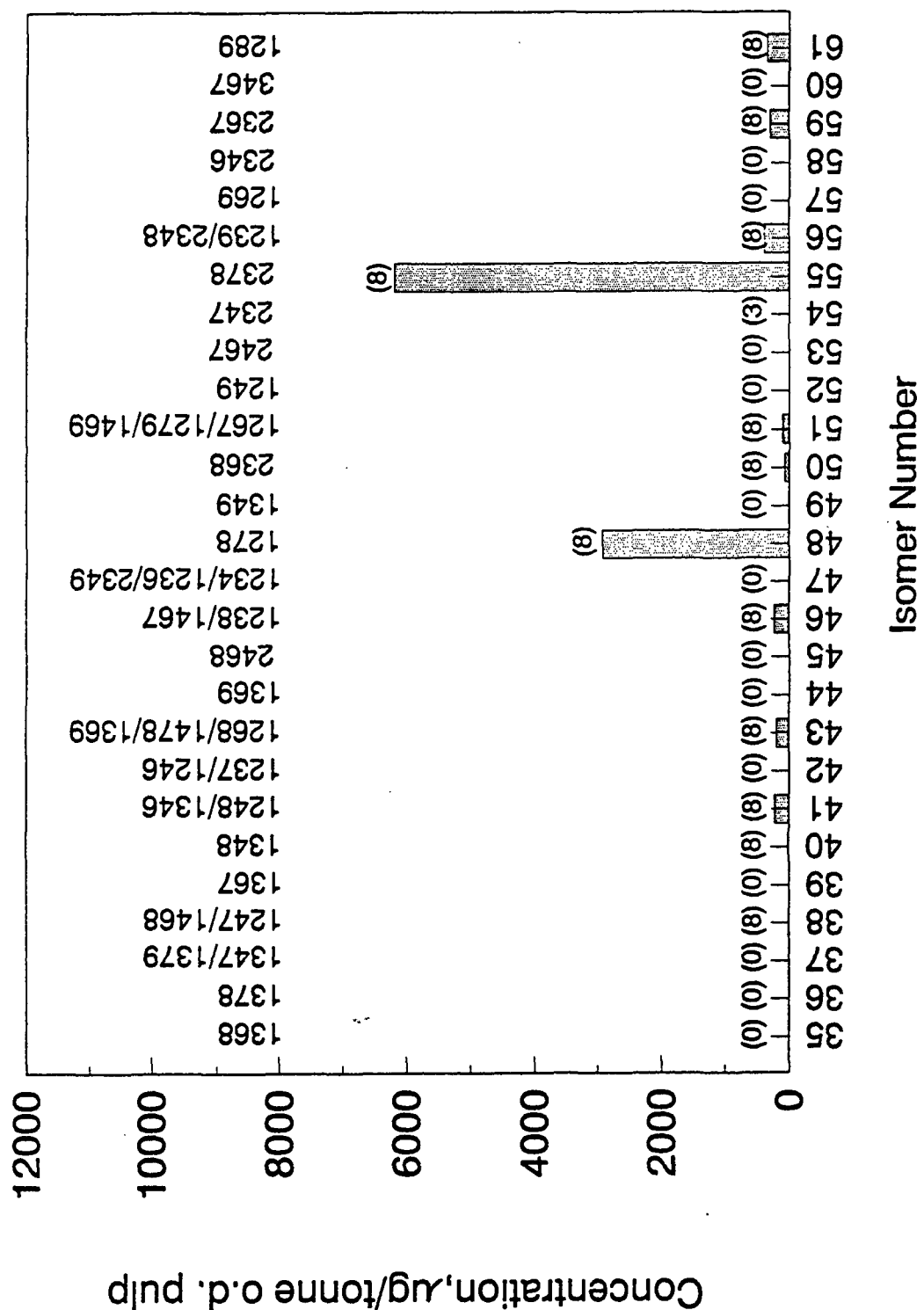
Figure 5: Average TCDF concentrations in chlorinated pulps of mixing study. Averages less than 50µg/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.
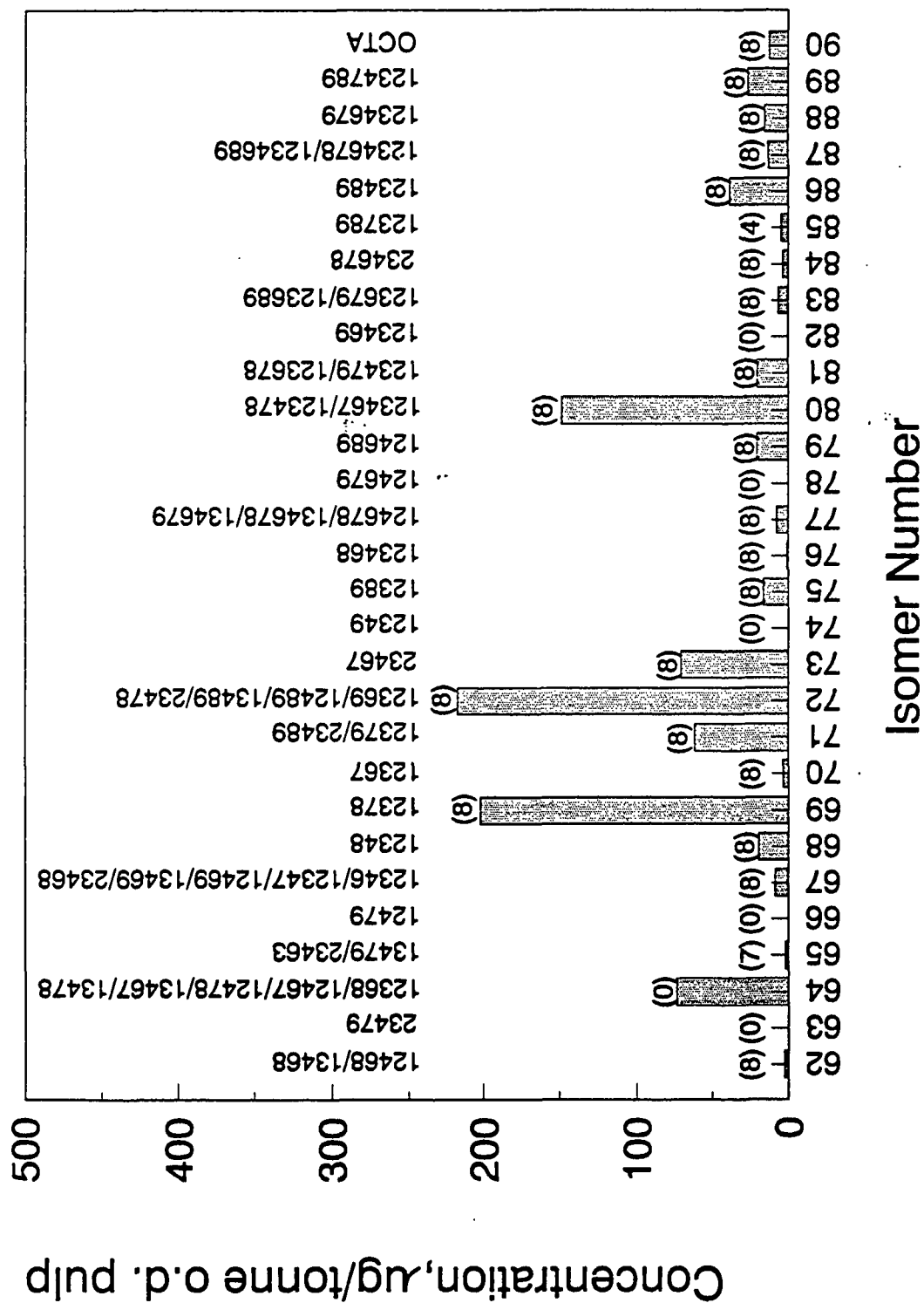
Figure 6: Average penta-, hexa-, hepta- and octa- CDF concentrations in chlorinated pulps of mixing study. Averages less than 1 µg/tonne not shown. No. of samples (out of 8) in which isomer was detected shown in parentheses.

PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION

OF BLEACHED PULP

PART 2: EFFECTS OF MIXING AND CONSISTENCY ON
AOX FORMATION DURING SOFTWOOD KRAFT PULP CHLORINATION

RESEARCH REVIEW

April 2, 1991

Amy R. Malcolm

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

PART 2: EFFECTS OF MIXING AND CONSISTENCY ON AOX FORMATION DURING SOFTWOOD KRAFT PULP CHLORINATION

The relationship between mixing quality and AOX formation is an important concern for the paper industry. The first part of this project developed a technique necessary to quantify good versus poor mixing. This was accomplished through injecting a dye tracer into a mixing pulp slurry, and measuring UV absorbance of liquid phase samples. The coefficient of variation of these measurements defined mixing quality.

After defining conditions for good and poor mixing, a set of chlorination-extraction experiments evaluated mixing and consistency effects on AOX levels. Individual C-stage and E-stage effluent samples were collected and these AOX results were compared to the equivalent combined effluent samples. A second set of chlorinations were designed to analyze mixing effects over a range of chlorine charges.

In summary, the effect of mixing quality on AOX formation was found to be dependent on the chlorine charge to the pulp. AOX formation was promoted by good mixing at high kappa factor, but was decreased by good mixing at low kappa factor. Further work to firmly establish equations for mixing quality versus AOX levels will provide insights as to the mill's need to control mixing quality with respect to AOX formation.

INTRODUCTION

Due to growing concerns about the environmental effects of chlorinated organic compounds (AOX), investigating the mechanisms of AOX formation has become a priority for the paper industry. Today's mill faces increasing regulation with respect to the allowable amount of AOX released. Mounting pressures are forcing the industry to devise alternative methods of furnishing a quality product while keeping waste effluents at acceptable levels. Mixing quality is an important aspect of the chlorination process and one where several questions have been raised in regard to AOX levels. Therefore, this study will focus on the production of AOX during the chlorination stage of the bleaching process with the emphasis on mixing quality and its relationship to AOX levels.

EXPERIMENTAL APPROACH

The role of mixing quality in AOX generation was addressed in three sets of experiments. The first step was to quantify the use of phenolphthalein (PPN) as a dye tracer in order to standardize poor and good mixing conditions during bleaching. The next set of experiments consisted of chlorination-extraction sequences on softwood kraft pulp and compared two different consistencies (4% and 6%) at poor and good mixing. The final set of bleaching experiments were also chlorination-extractions which varied the chlorine charge, or kappa factor, for poor and good mixing. Unless otherwise noted all experiments were conducted in the Quantum Technologies high-shear mixer. The chlorination stage effluents, extraction stage effluents and the total combined effluent samples for each bleach were analyzed for AOX content.

RESULTS AND DISCUSSION

Defining Mixing Conditions

The dye tracer experiments were designed to simulate a chlorination stage as closely as possible by using the Quantum Technologies high-shear mixer. Two variables to be examined were actual injection and mix time, and the rotor speed during mixing. A buffered PPN solution was injected into a buffered pulp slurry and mixed for a specified time and specified rotor speed. When mixing was complete, the reactor was opened and 25-30 random samples were withdrawn by syringe from the pulp slurry. Light absorbance was measured on each sample at 552 nm. The coefficient of variation of the resulting absorbance measurements was as taken an inverse measure of mixing efficiency. A homogeneous PPN solution was repeatedly measured to establish a coefficient of variation for control purposes.

Poor mixing was subsequently defined as an injection and initial total mix time of 11-13 seconds with the rotor shaft turning at 60 rpm. The coefficient of variation was 15-37% at 4% consistency and 15% at 7.7% consistency. An injection and initial total mix time of 180 seconds at 1800 rpm was considered good mixing, and gave a coefficient of variation equal to the control experiments (2-3%).

EFFECT OF MIXING AND CONSISTENCY ON AOX FORMATION

Experimental Design

To establish the effects of mixing and consistency on AOX formation a set of chlorination-extraction experiments were conducted in the Quantum Technologies high-shear mixer. These experiments utilized the two mixing extremes designated in the dye tracer experiments.

Each mixing condition was run at 4 and 6% consistency and replicated. The specific conditions for the chlorination-extractions are shown in Table 1. Effluent samples were collected individually from each bleach stage. A total combined effluent sample for each bleach was also analyzed. Kappa number, viscosity and AOX results are shown in Table 2.

AOX Sample Treatment Comparison

For the 4% consistency trials it was necessary to run two separate chlorination stages to obtain sufficient pulp to run the extraction stage. For these experiments, C-stage effluent samples were collected from both chlorinations and analyzed for AOX individually. Also, a combined C-stage effluent sample was analyzed. Since there was no significant discrepancy between the two results, these numbers were averaged and reported as C-stage average AOX in Table 2.

Two different techniques were used to analyze the E-stage effluents. For each extraction an effluent sample was collected and left untreated. Another sample was collected from the same extraction and acidified to pH 2.0 with 4N H_2SO_4. The AOX analysis demonstrated that the acidification did not affect AOX results. Therefore, the E-stage average AOX column in Table 2. represents the average of treated and untreated effluent samples for each extraction.

For each bleach two different combined effluent samples were prepared. Each contained equal portions of the C-stage effluent and the E-stage effluent. One combined sample (CM1) was left untreated and analyzed for AOX. The other combined sample (CM2) was sealed and heated at 60° C for 1 hour. The AOX results are presented in the columns headed CM1 and CM2 in Table 2. The CM2 results are slightly lower than the CM1 results and this could be attributed to a small amount of volatilization when the seal of the sample was broken.

The calculated average column is a simple mean of the average C-stage AOX and average E-stage AOX, in mg/l. Since the CM1 sample was made by combining C- and E- effluents in equal proportions, it can be compared to the calculated AOX values for a combined effluent sample. Because these numbers compare favorably, it can be concluded that there is no reaction occurring when independent C-stage and E-stage effluents are combined. Therefore, for future work, it can be said with confidence that a combined, untreated effluent laboratory sample simulates effluent discharged from the mill process.

The raw AOX data from Table 2 was converted to kg/mt and summarized in Table 3. The conversion factors used to correct the raw AOX values account for the oven dried grams of pulp, % consistency, % dilution and % thickened for each bleach stage. The total AOX released during bleaching is given by the sum of the C- and E-stage releases. It may also be estimated from the AOX content of the combined effluents CM1 and CM2. The 3 sets of measurements corroborate one another, taking into account the volatilization referred to above.

Consistency Effect on AOX Formation

Results hint that a higher consistency may produce higher AOX, but the differences could also be attributed to experimental variation. Statistically no link could be established between consistency and AOX formation.

Mixing Effect on AOX Formation

Kappa and viscosity measurements were run on E stage pulp from all bleaches. Good mixing shows overall lower kappa and viscosity numbers (Table 4).

Poor mixing gave 20% lower total AOX and 5% less delignification. At this high kappa factor, making the mixing poorer concentrates the added chlorine in "pockets". Within these pockets conversion of precursors to AOX is complete and excess chlorine remains. Outside of them, AOX precursors remain unconverted. The net result is inefficient conversion to AOX when the mixing is poor. Delignification is also inefficient, but in regions of low chlorine concentration delignification is less hindered by lack of chlorine than is AOX formation. This behavior is to be expected in situations where AOX increases linearly (or nonlinearly in a concave upwards fashion) with increasing chlorine concentration, since delignification is know to be more efficient (albeit less complete) at low chlorine concentration than when the chlorine concentration is high. Linear dependencies of AOX on kappa factor have been reported in the literature.

EFFECT OF CHLORINE CHARGE ON MIXING

Experimental Setup

A second set of mixing experiments was designed in order to better understand AOX formation during good and poor mixing at different kappa factors. Kappa factor is defined as the actual chlorine charge to the pulp divided by the pulp's kappa number. This set of experiments involved 10 separate bleaches with kappa factor as the variable. The kappa factors were 0.10, 0.14, 0.18 and 0.22 and each factor was applied using good and poor mixing conditions. The 0.10 kappa factor experiment was duplicated. Complete bleaching conditions are shown in Table 5.

Analysis of AOX Data

The AOX data for these experiments have been converted to kg/mt as in the previous set of experiments. Since the relationship between C-stage, E-stage and combined effluents were established in the prior set of bleaches, only the combined effluents were analyzed for this set (Table 6).

The more interesting aspects of this data set are represented graphically in Figure 1. AOX generation increases with kappa factor for both poor and good mixing. However the slope of the regression line is drastically different for each mix condition. When using a kappa factor of 0.15 or less, poor mixing produced higher AOX levels than good mixing. Concentrating the chlorine in pockets, where the chlorine concentration nevertheless remained low enough (because of the low kappa factor) so that it was all consumed, resulted in efficient local AOX generation which was not compensated for by the limitation placed on AOX precursor conversion by low chlorine concentration elsewhere. This requires as AOX-chlorine concentration relationship that is nonlinear in the concave upwards sense (less AOX formed per unit increase in chlorine concentration at low chlorine concentrations), in apparent contradiction to linear relationships that have been reported in the literature. A possible explanation may be that the literature correlations were developed, at least in part, by progressively replacing chlorine with chlorine dioxide rather than simply reducing the amount of chlorine added.

When the kappa factor is over 0.15 the results change dramatically. There is now an excess of chlorine in the poorly mixed pulp pockets which has essentially no lignin to react with and therefore remains as residual Cl_2. This is supported by looking at the residual Cl_2 data (Table 6). For poor mixing at kappa factors larger than 0.15 there is a distinct Cl_2 residual which is not evident for good mixing. Therefore, in good mixing, all of the Cl_2 has reacted with the pulp, producing higher AOX levels. Poor mixing on the other hand does not allow all the chlorine to react and thereby produces lower AOX levels for the same kappa factor.

Chlorine charge affects kappa number as well as AOX production. A higher chlorine charge allows more delignification and thereby lowers the kappa number. Figure 2 shows that for a given kappa number good mixing generates lower AOX values than poor mixing. However, the lower AOX values for good mixing can be explained by the fact that a lower chlorine charge was used to produce the same kappa number. A lower chlorine charge will naturally produce lower AOX values. Therefore, good mixing can achieve a desired kappa number with a lower kappa factor and lower AOX generation as compared to poor mixing.

EXPERIMENTAL DETAILS

Dye Tracer Experiments

All dye tracer experiments were designed to simulate chlorination stages using the Quantum Technologies high-shear mixer. A bleached softwood sulfite pulp was used for these experiments along with PPN as the dye tracer. 120 oven dried (o.d.) grams of pulp and 231 o.d. grams of pulp were used for the 4% and 7.7% experiments, respectively. This kept the volume in the reactor constant at about 3 liters. The pulp slurries were buffered at pH 10 with sodium carbonate-bicarbonate. The 1 liter volume of PPN solution injected into the slurry was chosen because it represents a standard chlorination injection volume.

Absorbance measurements were read on a Perkin-Elmer UV visible spectrometer. Sample volume was 0.5 ml and a buffer solution was used in the reference cell. All absorbencies were measured at 552 nm.

Consistency Effect Experiments

A mill unbleached kraft softwood pulp that had been spiked with minute traces of the dioxin precursors DBD and DBF was used in these experiments. This may be expected to have no effect on AOX results. All bleaching stages were run in the Quantum Technologies high-shear mixer. Specific bleaching conditions are in Table 1. No mixing occurred after the initial injection of Cl_2. No chlorine dioxide was used. All conditions were duplicated. Due to limitations on the concentration of Cl_2 water, the 7.7% consistency had to be lowered to 6% consistency. A visual inspection of both the 4% and 6% chlorinations confirmed a distinct difference of mixing quality. Effluent samples were collected directly out of each stage for AOX analysis. The pulp was thickened after the C-stage to 20% consistency. Pulp samples were also collected and analyzed for kappa number and viscosity.

Kappa Factor Effect Experiments

A different mill softwood kraft pulp than used in the previous experiment was provided for these experiments. All the chlorination stages were run in the Quantum Technologies mixer. The extraction stages were done in sealed Kapak bags in a heated water bath due to pulp limitations. Specific conditions for the bleaches are in Table 5. C-stage effluent samples were collected directly out of the C-stage at 4% consistency, after which the pulp was thickened to 20%. The E-stage pulp was diluted to 4% consistency and then an effluent sample for analysis was collected. Pulp samples were also collected and analyzed for kappa number and viscosity.

Test Methods

The AOX analysis for the effluent samples were done according to EPA method 9020. Kappa and Viscosity measurements were done according to TAPPI standards T236 CM-35, and T230 om-89, respectively.

CONCLUSIONS

The results from the first set of experiments, at 0.25 kappa factor, suggested high AOX production during good mixing and low AOX production during poor mixing. The results also show that no reaction takes place when C and E-stage effluents are combined.

Data from the second set of experiments, in which kappa factor was varied, show that at kappa factors less than 0.15, AOX levels for poor mixing were higher than AOX levels for

good mixing. Above 0.15 kappa factor, the good mixing AOX levels surpassed poor mixing AOX levels. Also, at a given kappa number, a lower chlorine charge was possible with good mixing, thereby producing lower AOX levels.

TABLE 1: CONDITIONS FOR MIXING AND CONSISTENCY STUDY

Starting Kappa number	26.4
Starting Viscosity, mPa-s	28.2

MIXING CONDITIONS

	GOOD	POOR
Shaft Speed - rpm	1800	60
Total Injection Time - sec.	180	13

OTHER CHLORINATION STAGE CONDITIONS

Chlorine Charge	6.6% on pulp
Temperature	45° C
Reaction Time	30 minutes
Consistency	4%, 6%

EXTRACTION STAGE CONDITIONS

NaOH Charge	3.63% on pulp
Temperature	70° C
Reaction Time	1 hour
Consistency	7%

TABLE 2: SUMMARY OF AOX CONCENTRATIONS (MG/L)

MIX QUALITY	CONS (%)	C-STAGE (AVG)	E-STAGE (AVG)	C AND E STAGE (AVG)	CM1[1] UNTRTD	CM2[2] HEATED
good	4	171	106	138	138	132
		173	95	134	127	126
poor	4	136	85	110	115	112
		128	82	105	98	93
good	6	182	116	149	149	125
		170	94	132	128	128
poor	6	142	96	119	122	116
		111	76	93	94	88

[1] C and E stage effluent combined in equal proportions.
[2] C and E stage effluent combined in equal proportions, and heat treated at 60° C for one hour.

TABLE 3: SUMMARY OF AOX DATA CONVERTED TO SIMULATE MILL RELEASE CONDITIONS (KG/MT)

MIX QUALITY	CONS (%)	C-STAGE	E-STAGE	SUMMED C AND E STAGE	CM1[1] UNTRTD	CM2[2] HEATED
good	4	3.42	1.40	4.82	4.81	4.61
		3.46	1.26	4.72	4.43	4.40
poor	4	2.72	1.13	3.85	4.01	3.91
		2.56	1.08	3.64	3.43	3.25
good	6	3.64	1.53	5.17	5.20	4.36
		3.40	1.25	4.65	4.47	4.47
poor	6	2.84	1.27	4.11	4.26	4.05
		2.22	1.01	3.23	3.26	3.06

[1] C and E stage effluent combined in equal proportions corrected for carryover and consistency difference.

[2] C and E stage effluent combined in equal proportions, and heat treated at 60° C for one hour. Corrected for carryover and consistency difference.

TABLE 4: KAPPA NUMBER AND VISCOSITY DATA FOR MIXING AND
CONSISTENCY EXPERIMENTS

Mixing	Cons. %	Kappa No.	Visc. (cp)
Good	4	3.4	8.1
Good	4	2.8	8.7
Poor	4	4.4	12.0
Poor	4	4.0	11.6
Good	6	3.4	8.4
Good	6	3.0	9.7
Poor	6	4.7	11.6
Poor	6	4.1	13.0

TABLE 5: EXPERIMENTAL CONDITIONS FOR VARIABLE KAPPA FACTOR EXPERIMENTS

Starting Kappa number	27.9
Starting Viscosity, mPa-s	31.1

MIXING CONDITIONS

	GOOD	POOR
Shaft Speed - rpm	1800	60
Total Injection Time - sec.	180	13

OTHER CHLORINATION STAGE CONDITIONS

Kappa Factor	0.10, 0.14, 0.18, 0.22
Temperature	45° C
Reaction Time	30 minutes
Consistency	4%

EXTRACTION STAGE CONDITIONS
(Kapak bags in heated water bath)

NaOH Charge	$0.55 * Cl_2$ charge
Temperature	70° C
Reaction Time	1 hour
Consistency	10%

TABLE 6: SUMMARY OF RESULTS FROM KAPPA FACTOR EXPERIMENTS

| VARIABLES | | C STAGE | | E STAGE | | TOTAL AOX RELEASED |
Mixing	Kappa Factor	pH	Res, g/l	pH	Kappa Avg	kg/ton
poor	0.10	2.1	0.04	11.4	13.9	1.94
poor	0.10	1.5	0.01	10.4	15.0	1.82
poor	0.14	2.0	0.01	11.2	14.5	2.50
poor	0.18	2.0	0.31	11.5	11.7	3.10
poor	0.22	1.1	0.70	11.6	7.4	3.76
good	0.10	2.0	0.00	10.1	14.0	0.85
good	0.10	1.3	0.00	10.5	13.0	1.28
good	0.14	2.0	0.01	10.4	9.7	1.29
good	0.18	1.2	0.00	10.9	5.1	4.27
good	0.22	1.8	0.00	11.3	4.4	5.08

FIGURE 1: KAPPA FACTOR VS AOX
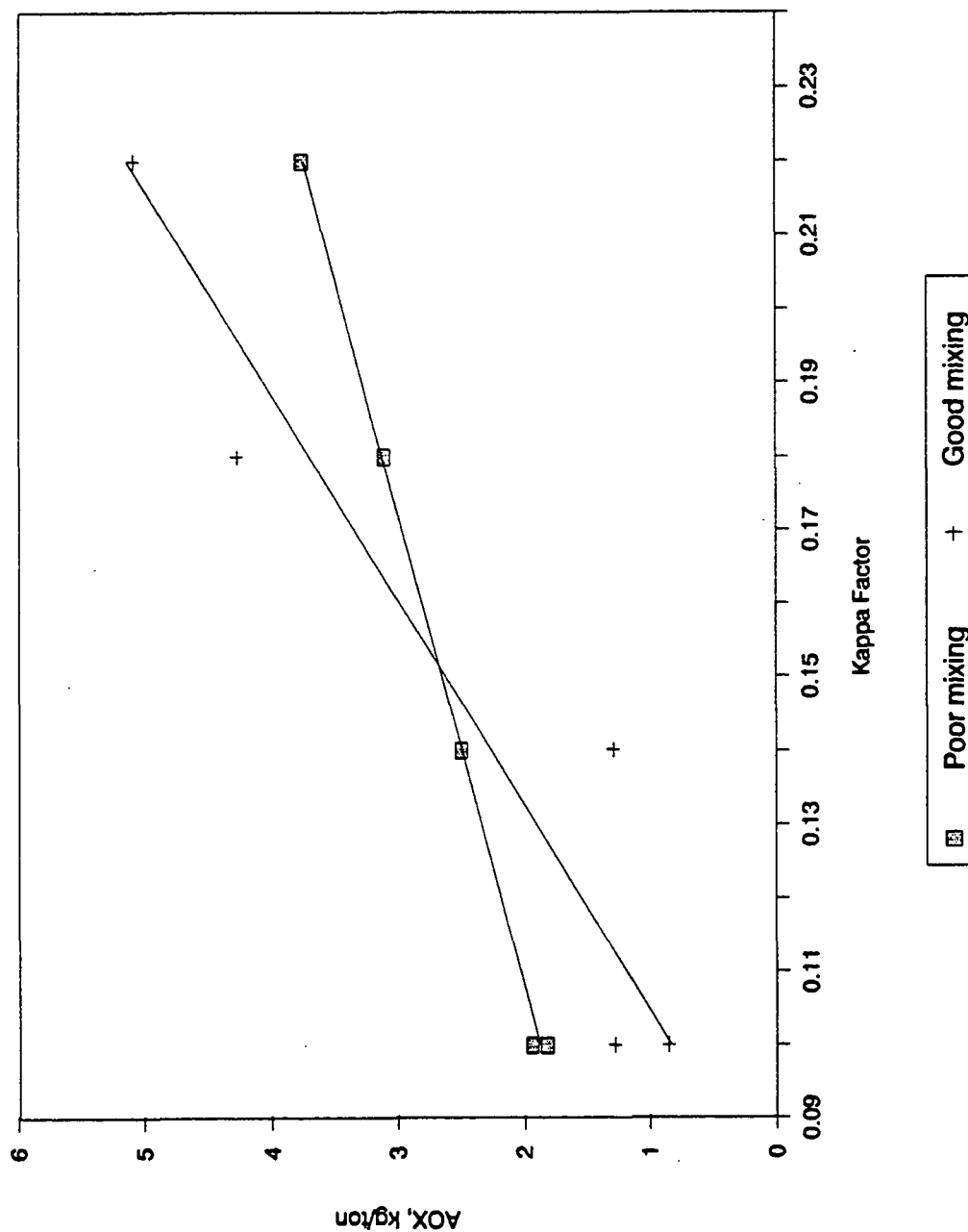
FIGURE 2: KAPPA NUMBER VS AOX
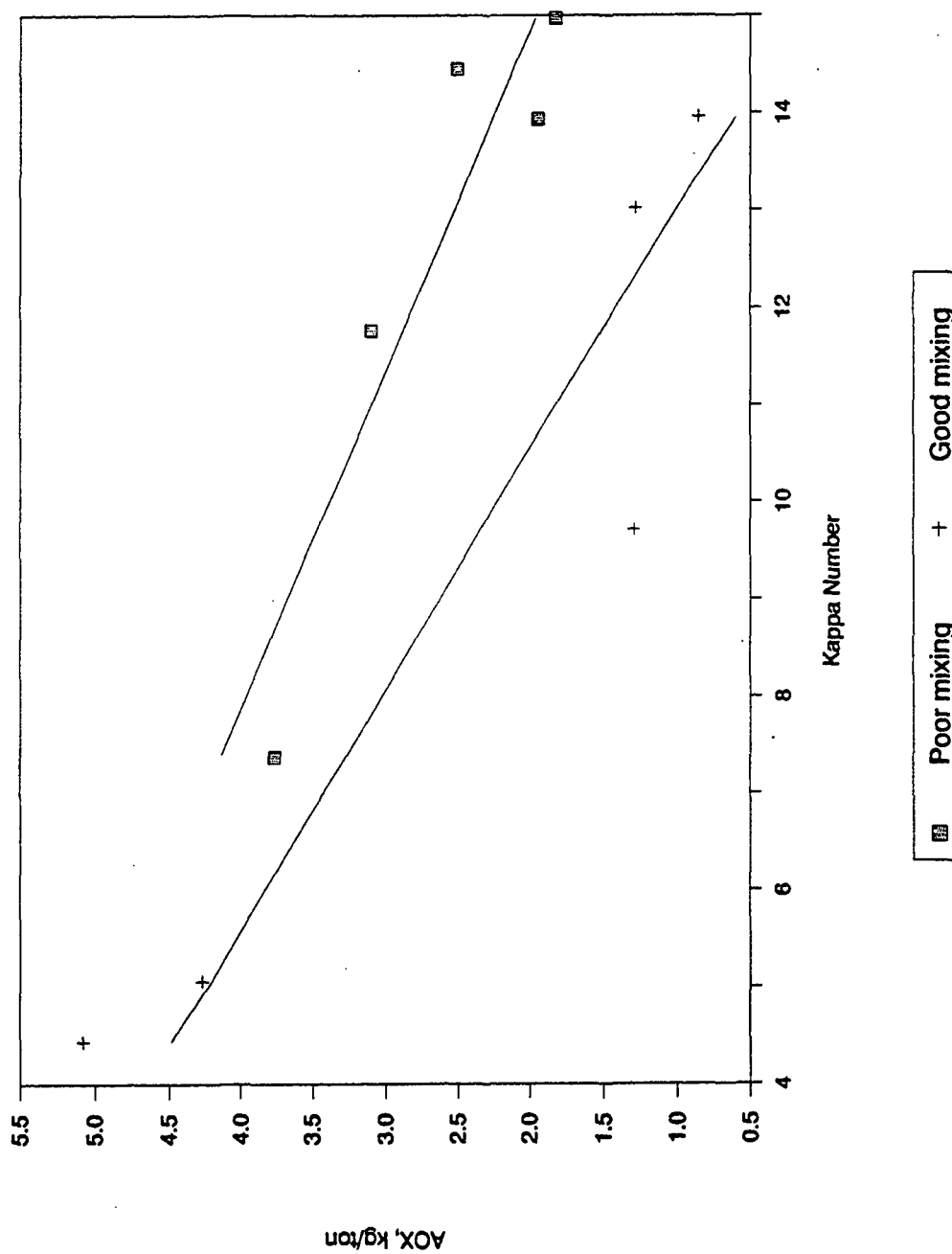
PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION

OF BLEACHED PULP

PART 3: PRETREATMENTS TO IMPROVE OXYGEN
BLEACHING SELECTIVITY

RESEARCH REVIEW

April 2, 1991

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SUMMARY

Treatment of unbleached kraft pulp with NO_2 leads to formation of acidic functional groups. Experiments suggest that NO_2-treatment enhanced hydrophilic properties of the residual lignin by introduction of both carboxylate (RCOOH) and nitrophenolic groups leading to improved delignification in subsequent alkaline oxygen bleaching. These results are similar to the observations of Samuelson et al.[1] for NO_2-treatment of softwood lignin (Indulin AT, Westvaco Corp.). Nitration of lignin has also been reported to decrease hot-alkali stability of some covalent bonds in lignin.[2,3] Both processes may play significant roles in the observed improvement in selectivity for deliginification over carbohydrate degradation during oxygen bleaching. The objective of our research is to clarify these issues.

1. INTRODUCTION

Pretreatment of kraft pulp before oxygen bleaching has been shown to maintain pulp viscosity during delignification to a given kappa number. Whether this occurs simply by an acceleration in delignification rate or is enhanced by protection from carbohydrate degradation remains unclear. One of the objectives of this research is to differentiate between these two processes by characterizing the changes in residual lignin induced by pretreatment.

Lindeberg and Walding[4] have shown that the influence of added nitrolignin on kappa number and viscosity is negligible in oxygen bleaching. The presence of nitrolignin in oxygen bleaching of softwood kraft pulp decreased both carbohydrate depolymerization and delignification so that these effects tended to cancel each other with no improvement in selectivity. Past experiments at IPST have supported these observations.[5] Experiments using 4-nitroguaiacol also showed no effect on carbohydrate protection during oxygen bleaching.[6]

It is hypothesized that the residual lignin is changed by pretreatment and is thereby activated for delignification during oxygen bleaching. If the rate of reaction between caustic or oxygen and residual lignin is enhanced by pretreatment, caustic would be consumed before significant carbohydrate degradation occurs.

The strategy for experimental work is to characterize changes in residual lignin induced by nitrogen dioxide pretreatment with an emphasis on functional group analysis, particularly hydrophilic group content. By relating changes in residual lignin to the observed changes in selectivity, alternative pretreatment schemes which are likely to induce these changes could be proposed.

During the current reporting period, new information has been obtained on the effect of NO_2 on acid group content of unbleached pulp and on soluble reaction products. In addition, a significant part of our effort has been devoted to the familiarization of new personnel with the required techniques, as well as re-establishing, improving and validating experimental techniques for NO_2 pretreatment and oxygen bleaching.

2. RESULTS AND DISCUSSION

2.1 Nitrogen dioxide pretreatment of kraft pulp

To understand the effect of pretreatments on oxygen bleaching, the reliability of the pretreatment reaction must be determined. If this is not done, it is difficult to ascribe results to a known change in the pulp before oxygen bleaching. The pretreated pulp must be well characterized and the degree of application of the pretreatment agent must be established. Tests which follow the fate of the reagent will indicate the degree of control in the pretreatment reaction.

When NO_2 was passed through a basic solution (0.1 M NaOH), it was readily hydrolysed into an equal molar solution of nitric acid and nitrous acid. After application of NO_2 to the pulp, the gas phase over the pulp was withdrawn through a standardized NaOH solution and the NaOH solution was then titrated to determine unreacted NO_2. No residual NO_2 was detected and the degree of application was considered to be identical to the amount of NO_2 determined gravimetrically before application. There are two possible fates of the applied NO_2; hydrolysis by the water in the pulp forming oxides which do not react further or reaction with the pulp itself.

After each application of NO_2, cold water was added to dilute the pulp to 6% consistency. The pulp was filtered and the filtrate or pretreatment liquor was analyzed for acid content and soluble organic material. Figure 1 shows a linear increase in both acid content and organic material versus application of NO_2.

It was desirable to identify the soluble organic material which existed in the pretreatment liquor as this would give insight into possible mechanistic pathways. Andersson and Samuelson[7] have reported that the principal nitro compounds present in pretreatment liquors are 4-nitroguaiacol and 5-nitrovanillin. To confirm this, the pretreatment liquor at 10% application of NO_2 was extracted with CH_2Cl_2 and after removal of solvent, the yellow residue was subjected to thin layer chromatography (TLC). By comparison with available pure 4-nitroguaiacol and 5-nitrovanillin, the residue was shown not to contain these nitro compounds as primary components. One major component was detected in the residue by thin layer chromatography and the slow elution rate indicated that it may be dinitroguaiacol. To test if 4,6-dinitroguaiacol was the primary soluble organic compound in the residue, 4-nitroguaiacol was further nitrated in a solution of glacial acetic acid and nitric acid and the TLC elution rate of the product compared to the pretreatment residue. It was found to be similar.

Further evidence that dinitroguaiacol was the primary component in the pretreatment residue was supplied by the UV/VIS spectrum of the pretreatment liquor at various pH levels. A solution of the nitrated 4-nitroguaiacol in nitric acid closely matched the pretreatment liquor's spectrum and exhibited similar shifts in absorbance versus pH. Finally, gas

chromatography-mass spectrometry was used to confirm that the primary component of the pretreatment residue was 4,6-dinitroguaiacol (mass 214: B, figure 2). In addition, no components having masses corresponding to 4-nitroguaiacol (mass 169) or 5-nitrovanillin (mass 197) were detected. It is worth noting that the early work of Gustafsson and Andersen[8] determined that dinitroguaiacol was the primary product formed when wood flour or lignin models were treated with nitric acid in ether. The results of recent experiments agree with this earlier work rather than Andersson and Samuelson's[7] conclusions.

2.2 Effect of nitrogen dioxide on carboxylate content of residual lignin

Accelerated delignification during oxygen bleaching after NO_2 treatment can very probably be attributed to NO_2-induced changes in the chemical structure of the lignin that remains in the pulp. The structural change responsible may be confined to the introduction of a specific fuctional group type, or may be the result of the introduction of several types. One of our objectives is to determine the effects of introducing specific group types, as well as combinations of various types. Currently, we are focusing on the role of carboxyl groups. To determine carboxylate content, pulps were equilibrated in an acid solution and then titrated with standardized NaOH. As shown in figure 3, the pH and conductance of the pulp suspension were measured during the titration. The carboxylate content is measured from the region of the titration curve where the pulp acts to buffer the ionic strength of the solution thereby maintaining constant conductance.[9,10] In addition, if the 1st derivative of the pH titration curve is calculated and a smoothed curve plotted through the points, the curve shown in figure 4 is obtained. As shown in figure 5, this curve is reproducible and exhibits a systematic change upon level of NO_2 addition. One possible interpretation of these curves is that the pretreatment changes the spectrum of ionizable groups of the residual lignin. For example, nitration of the aromatic ring would lower the pKa of free hydroxyl groups thereby allowing ionization during the titration. The carboxylate contents of the NO_2 treated pulps determined from the titration curves are about 50% greater than that of the untreated pulp, but these results may include the aforementioned nitrophenolic hydroxyl groups. The broadening of the second endpoint's transition in the conductometric titration of the NO_2 treated pulps may be an additional indication that nitrophenolic groups are being ionized during the titration. In future experiments we will block phenolic hydroxyl groups by methylation with diazomethane. Since diazomethane also methylates carboxylate groups, the pulp must be saponified to free the carboxylate groups leaving only hydroxyl groups blocked. Only after this modification can the carboxylate determinations be considered accurate. The possibility of quantifying functional groups within certain pKa ranges is indicated by the data.

In further experiments, other chemical treatments will be used to introduce carboxyl groups before oxygen bleaching, and the carboxylate content correlated with oxygen bleachability. This will be followed by similar experiments designed to assess the role of other functional group types (phenolic hydroxyl, α-carbonyl, etc.).

2.3 Oxygen bleaching of pretreated and nonpretreated kraft pulp

The initial two oxygen bleaching trials were of unpretreated samples at caustic levels of 1%, 2%, and 4%. The third and fourth bleaching experiments involved NO_2 pretreated samples at 2%, 4%, and 8% NO_2 along with unpretreated samples, with caustic levels of 1%, 2%, and 4%, for a total of 12 samples in each trial. Table 1 lists kappa numbers and viscosities which resulted for the unpretreated samples over the four bleaching trials.

When the data in table 1 is plotted as viscosity versus kappa number, the final states of the pulps describe a line as shown in figure 6. For this particular pulp, the bleaching reaction is defined uniquely by this curve. This plot can be used as a measure of selectivity for delignification over carbohydrate degradation. Variations between trials arise from temperature and oxygen pressure differences, particularly in the initial runs where we had not yet optimized control of the experimental system. Nevertheless, because the treatments to be compared are, in general, all included within each trial (the bomb accommodates twelve samples), averaging over runs may be used to highlight the differences between treatments (combinations of levels of NO_2 application in the pretreatment and caustic application in the oxygen stage). Table 2 shows how the average CED viscosity was affected by the level of NO_2 pretreatment and the data is then plotted in figure 7. Similarly, average kappa numbers after oxygen bleaching are listed in table 3 and are plotted in figure 8.

Table 1. Oxygen bleaching of unpreteated kraft pulp. Initial Kappa number 39.4 and initial 0.5% CED viscosity of 40.8 centipoise. All samples with 0.1% Mg++ ion present.

	NaOH	Trial 1	Trial 2	Trial 3	Trial 4
Kappa No.	1%	33.4	31.6	32.9	34.0
Viscosity (cp)		33.8	32.5	33.2	33.7
Kappa No.	2%	25.9	22.7	29.0	29.2
Viscosity (cp)		31.5	25.1	29.6	28.5
Kappa No.	4%	14.2	14.5	17.6	19.5
Viscosity (cp)		17.7	17.5	18.9	22.2

Table 2. Average 0.5% CED viscosity in centipoise after oxygen bleaching. All samples with 0.1% Mg++ ion present.

NaOH	0% NO_2	2% NO_2	4% NO_2	8% NO_2
1%	33.3	33.7	32.6	32.6
2%	28.7	30.4	31.8	31.0
4%	19.1	23.1	26.3	26.8

Table 3. Average kappa number after oxygen bleaching. All samples with 0.1% Mg++ ion present.

NaOH	0% NO_2	2% NO_2	4% NO_2	8% NO_2
1%	33.0	28.8	27.6	27.7
2%	26.7	21.5	21.4	19.8
4%	16.5	16.3	16.5	16.2

Viscosity versus kappa number plots can be now be made from the data in table 2 and table 3 to show how NO_2 affects delignification rates for oxygen bleaching (figure 9).

3. CONCLUSION

Pretreatment of softwood kraft pulp with nitrogen dioxide before oxygen bleaching was shown to enhance delignification while maintaining viscosity. The primary soluble reaction product after pretreatment was identified as 4,6-dinitroguaiacol. The number of acid groups in the residual lignin was also increased significantly by pretreatment; however, these acidic groups may be carboxylate or phenolic hydroxyls which are made more acidic by nitration of the aromatic ring. The ease with which dinitroguaiacol was formed indicates that partial nitration of the residual lignin is probable. Indeed, if NO_2 was bubbled through a 0.1 M NaOH solution, the resulting mixture of nitrogen oxides at high pH would nitrate 4-nitroguaiacol. Reactions in basic media of this type have not been investigated and their role in oxygen bleaching is unknown. Techniques to quantify hydrophilic functional groups are being developed which will clarify their role in selectivity enhancement resulting from pretreatment.

4. EXPERIMENTAL

4.1 Nitrogen dioxide pretreatment

The procedure for pretreatment of kraft pulp with nitrogen dioxide followed the original technique reported by Samuelson et al.[11] except that the amount of pulp was adjusted to give an exact percentage of NO_2 application. In general, 43 to 45 od grams of pulp was used for each pretreatment reaction. The softwood kraft pulp (loblolly) was fluffed and the consistency determined to be 33.3% before addition of NO_2.

4.2 Carboxylate determination

Conductometric titrations were performed at half the scale of the procedures reported by Pu and Sarkanen.[10] A Markson Electromark Analyzer was used for conductivity measurements with the meter standardized with 0.100 M KCl before the titration. A Corning model 150 ion analyzer was used for pH measurements with the meter calibrated at pH 7.00 and pH 10.00 using standard buffer solutions. A slow flow of nitrogen gas was bubbled through the suspension during the titration to reduce effects from carbon dioxide absorption.

4.3 Oxygen bleaching

Pulp samples were allowed to air dry to between 75% and 85% consistency and caustic/$MgSO_4$ solution was then added to give the desired level of application with a final consistency of 26% before oxygen bleaching. The impregnation solution was dispersed in the pulp by compressing the pulp sample several times so that the impregnation solution was released and reabsorbed by the sample. The sample was fluffed by hand and placed in a small perforated pvc cup which was then stacked in a 2.2 liter pressure vessel. After charging to 70 psig oxygen at room temperature, the pressure vessel was lowered into an oil bath at 120° C. After 70 minutes in the oil bath, the vessel was withdrawn and the oxygen displaced with nitrogen while the vessel was cooled. The final temperature during bleaching was generally 105° C for about 30 minutes. Oxygen pressures were 105 to 110 psig during this period.

After bleaching, samples were washed with 200 ml of distilled water at which time a pH reading was taken. The sample was filtered, resuspended in 1 liter of distilled water and filtered again on a coarse fritted glass funnel. The pulp pad was allowed to air dry for later testing.

4.4 Kappa number, viscosity, gas chromatography and mass spectrometry

Kappa number tests were at 1/10 the scale of the T236 standard method and had an average repeatability of 1.7%. CED viscosity tests were by standard method T230 with repeatability generally less than 4%. Gas chromatography/mass spectrometry (GC/MS) was performed on a Hewlett Parkard HP5985B GC/MS system using a nonpolar column and a 50-275° C , 5° C/min temperature program.

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UV Absorbance of Pretreatment Liquors
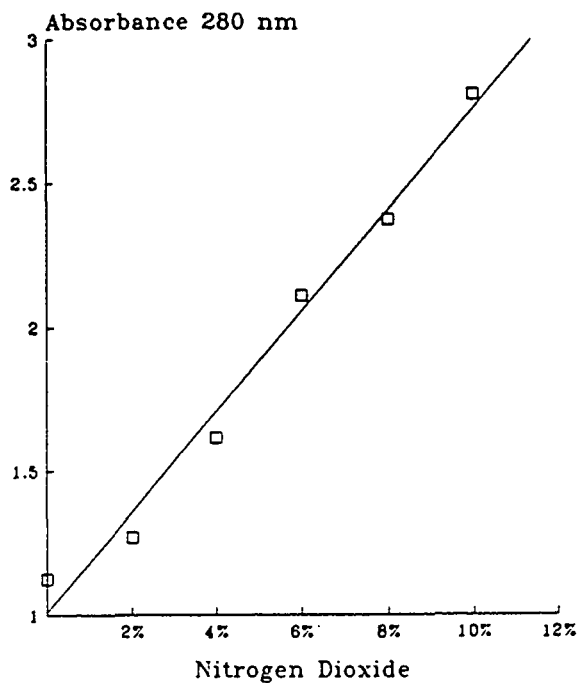
Acid Content of Pretreatment Liquors
50ml Aliquot
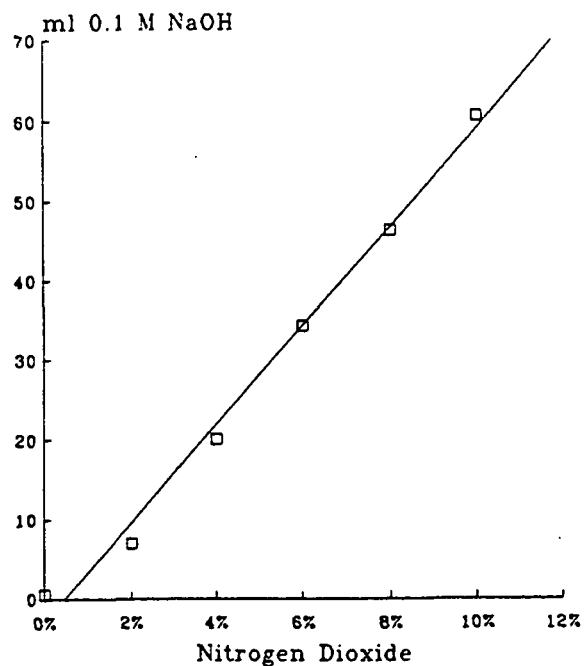
Figure 1. Analysis of NO_2 pretreatment liquors showing a linear increase in both absorbance at 280 nm and acidity.
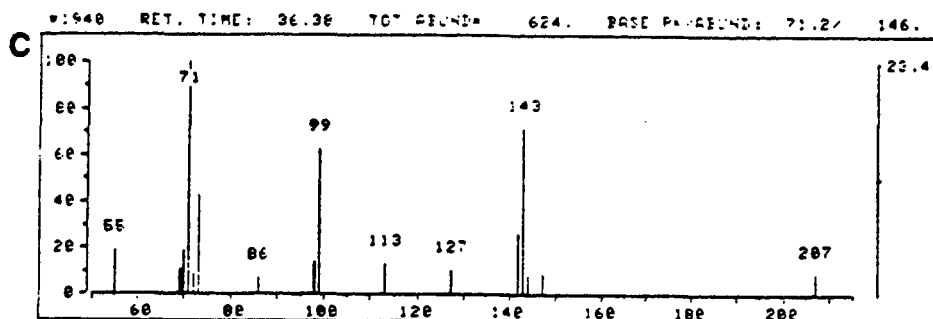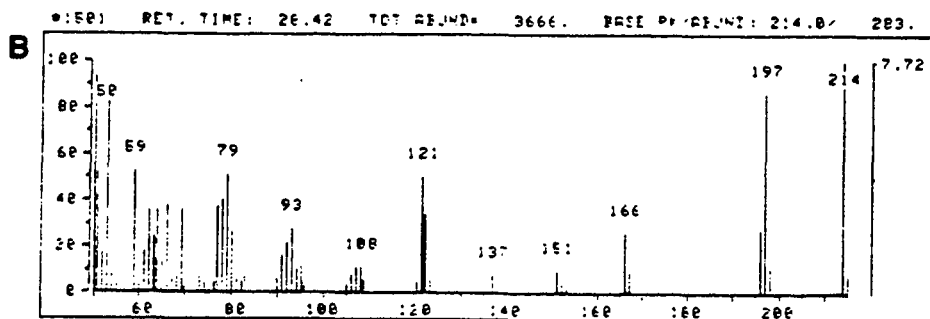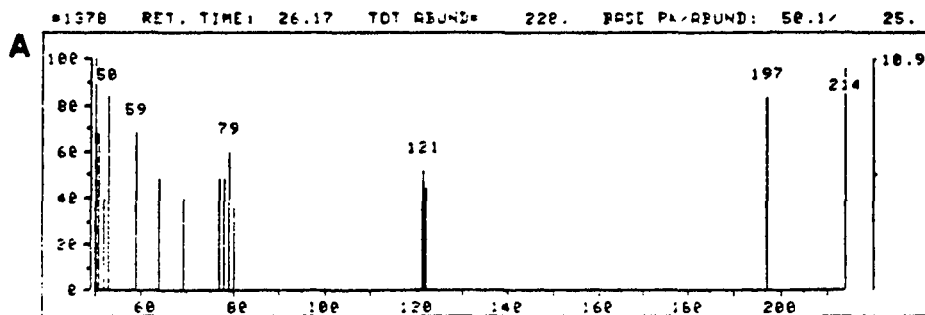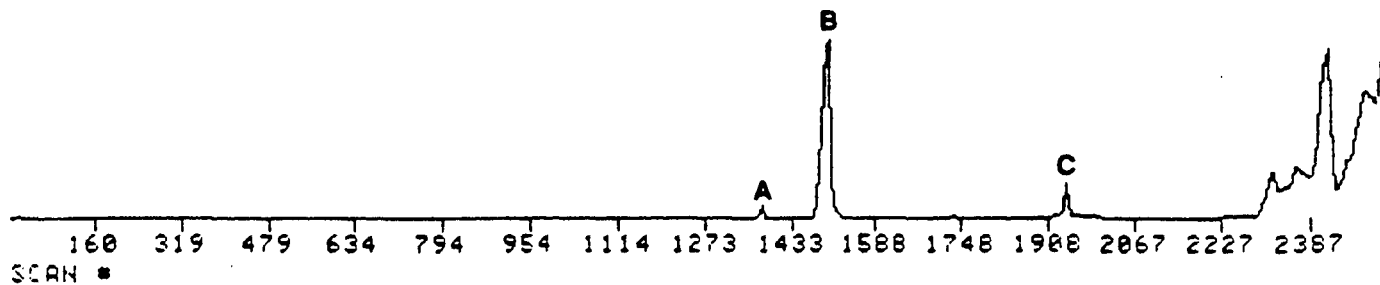
Figure 2. Gas chromatography/mass spectral analysis of 10% NO_2 pretreatment residue: A) unknown; B) component identified as 4,6-dinitroguaiacol; C) unknown.

Conductometric Titration
of Untreated Kraft Pulp
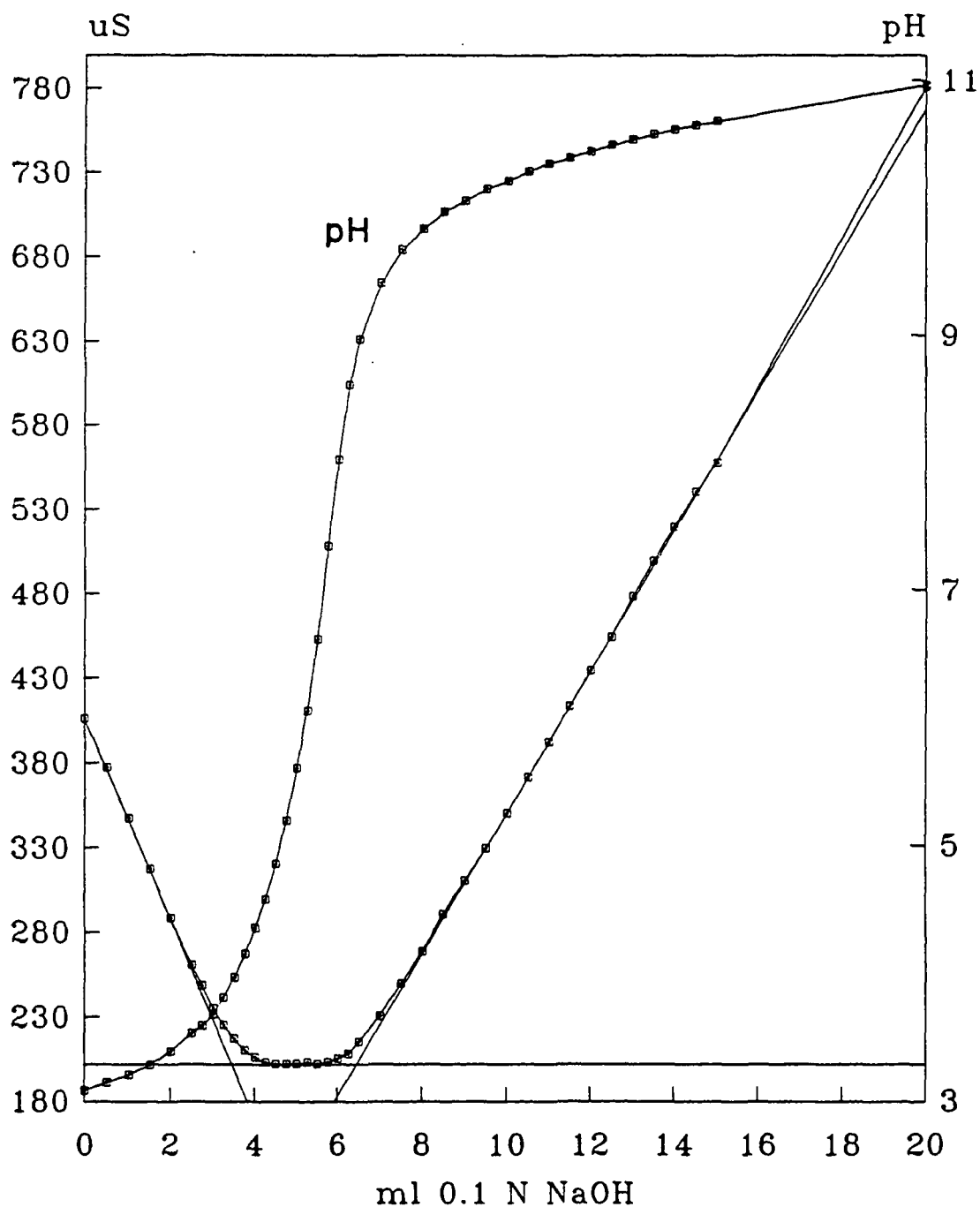
Figure 3. Conductometric titration of kraft pulp. Pulp (3.07 od grams) was acid washed and suspended in 450 ml 0.001 M NaCl. 3.00 ml 0.1 M HCl added before titration.

Conductometric Titration
of Untreated Kraft Pulp
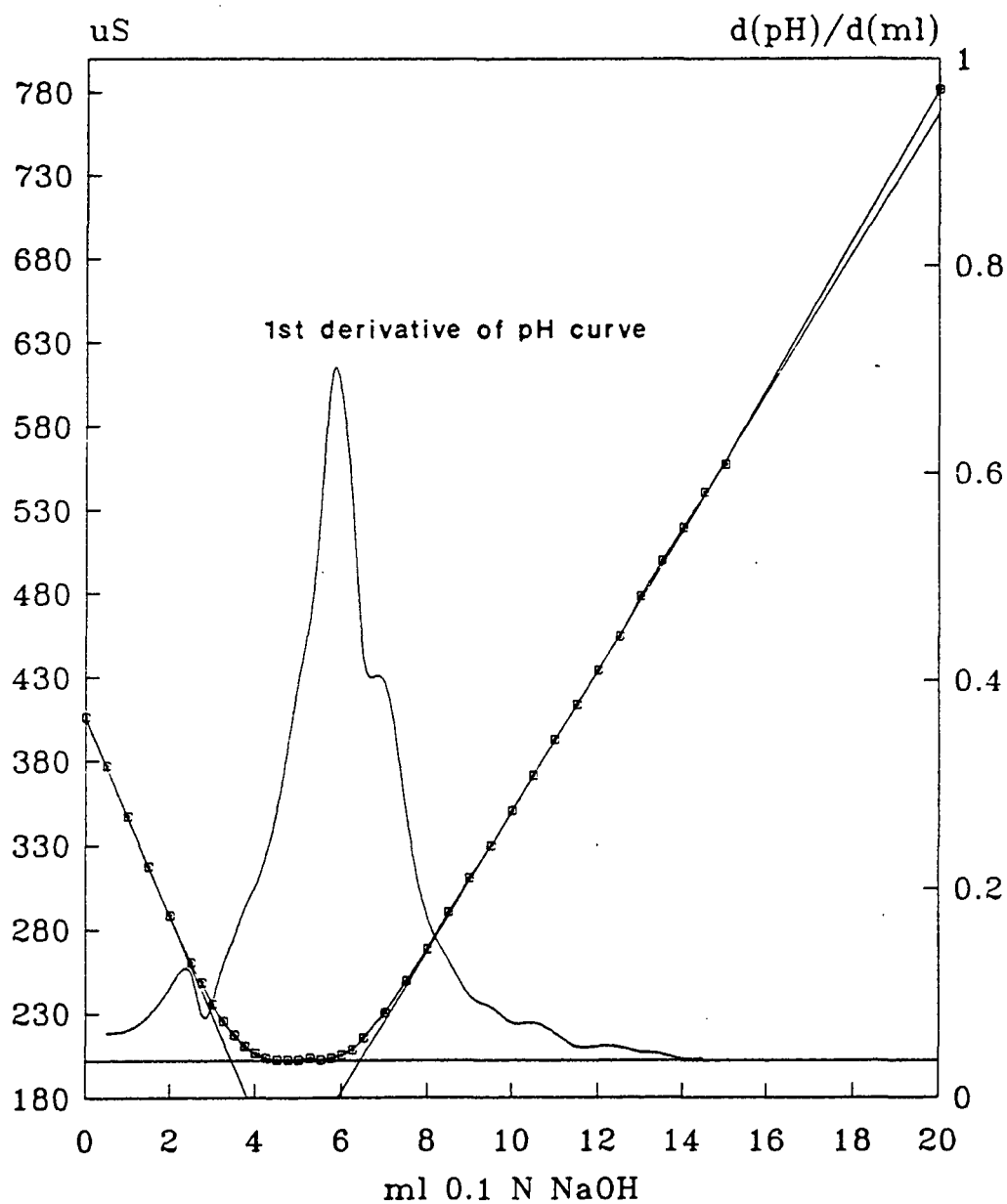
Figure 4. Calculation of 1st derivative of pH curve shown in figure 3. Smoothed curve fitted to calculated points.
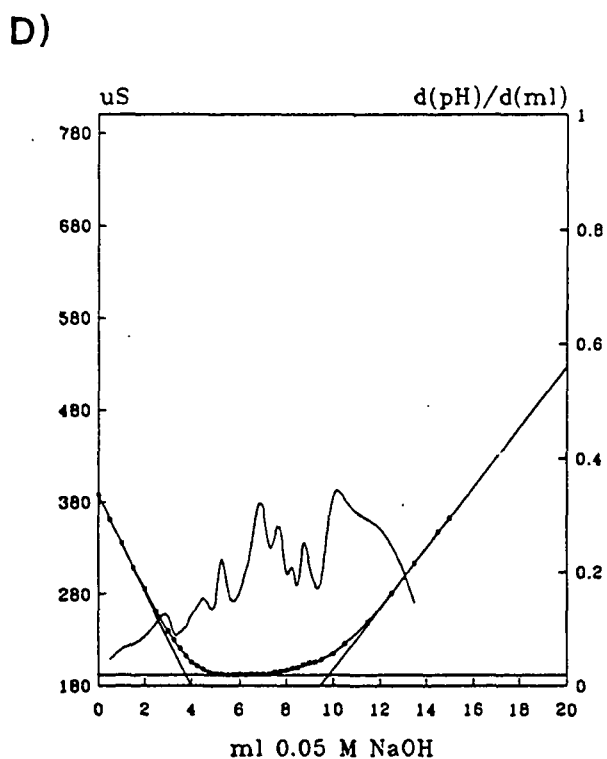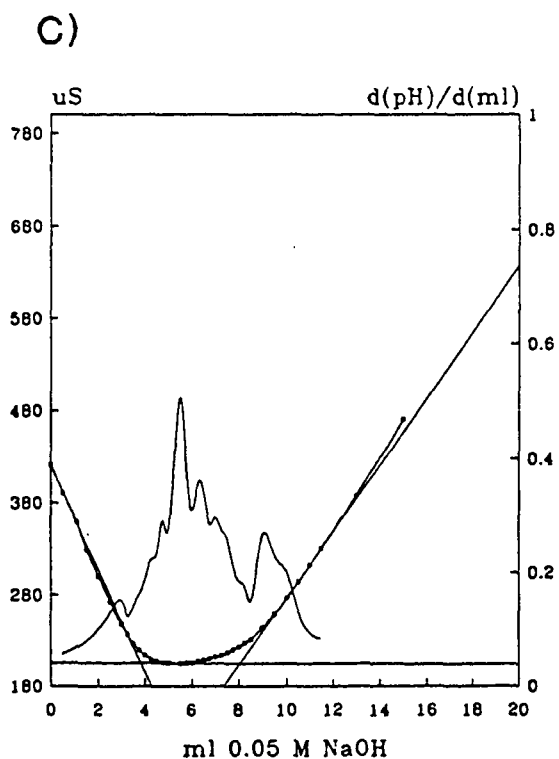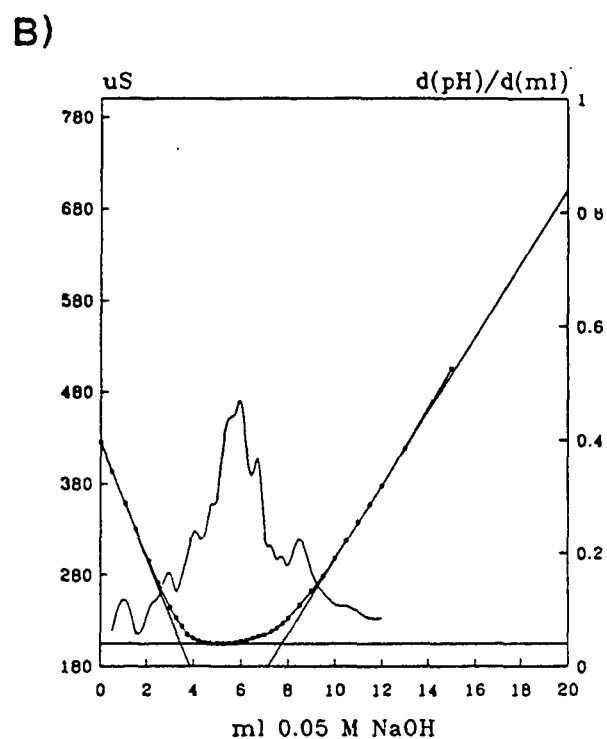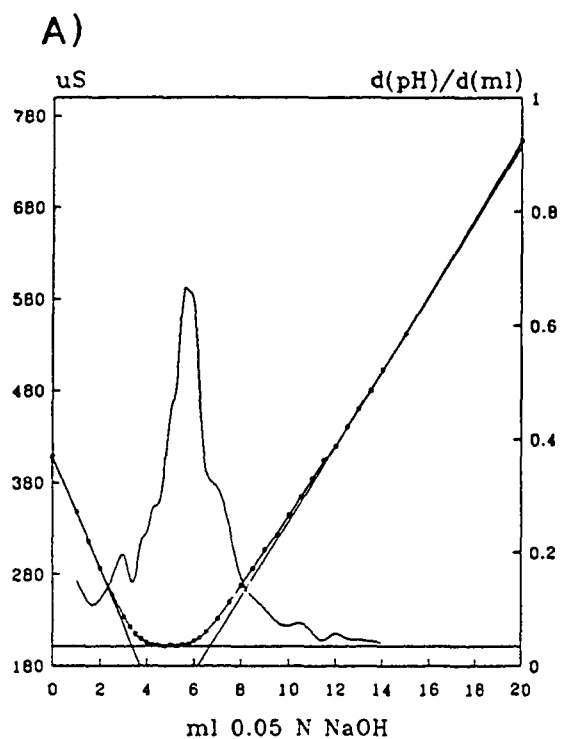
Figure 5. Conductometric titrations of NO_2 pretreated pulps:
A) 0% NO_2; B) 2% NO_2; C) 4% NO_2; D) 8% NO_2.

Figure 6. Viscosity versus kappa number plot for oxygen bleaching of unpretreated kraft pulp over four bleaching trials.
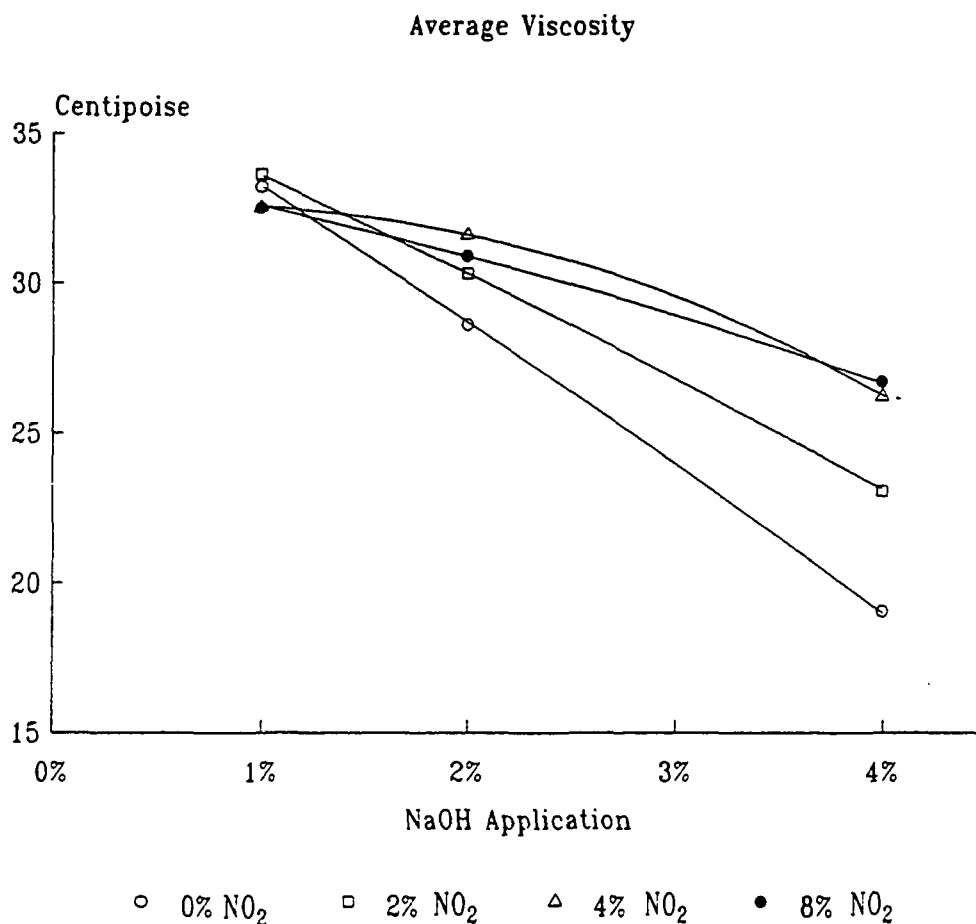
Figure 7. Average 0.5% CED viscosity versus caustic level during oxygen bleaching. (All samples with 0.1% Mg++ ion application.)

Average Kappa Number
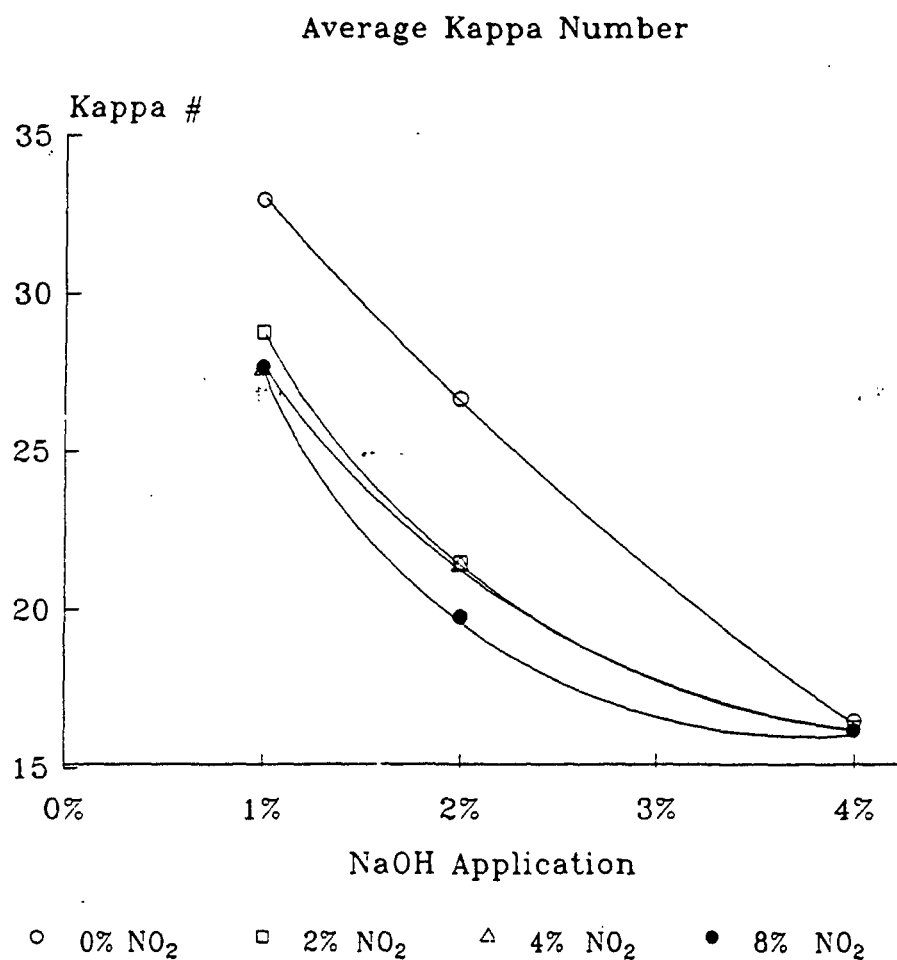
Figure 8. Average kappa number versus caustic level during oxygen
bleaching. (All samples with 0.1% Mg++ ion
application.)

Viscosity/Kappa # Plots for Nitrogen Dioxide Pretreatment
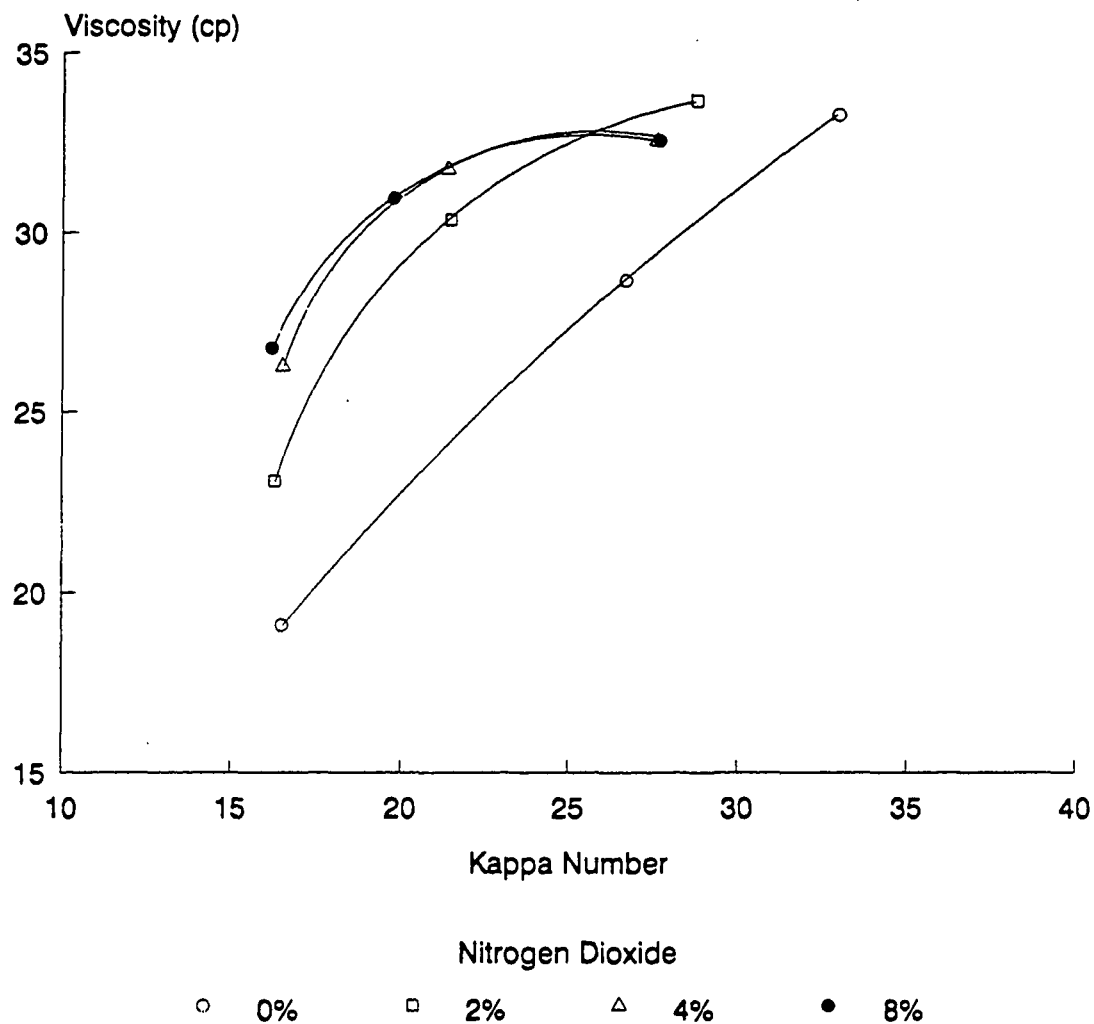
Figure 9. Average viscosity versus average kappa number plots for NO$_2$ pretreated kraft pulp. (All samples with 0.1% Mg++ ion application.)

OXYGEN BLEACHING OF INCOMPLETELY WASHED

HARDWOOD SULFITE PULP

Prepared for presentation at AIChE Annual Meeting, Chicago, IL
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RESEARCH REVIEW

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OXYGEN BLEACHING OF INCOMPLETELY WASHED
HARDWOOD SULFITE PULP

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OXYGEN BLEACHING OF INCOMPLETELY WASHED
HARDWOOD SULFITE PULP

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SUMMARY

A laboratory bleaching study was done to evaluate the potential benefits of installing oxygen delignification at a tissue grade sulfite pulp mill. The oxygen stage would be placed between the unbleached pulp washers and the screen room, to avoid having to install thickening equipment. This means that relatively large amounts of knots, fiber bundles and spent pulping liquor would enter the oxygen reactor with the pulp. After screening, the oxygen delignified pulp would go to an existing hypochlorite stage.

The results, in the form of interpolated values, are summarized in Table 1. Delignification was strongly retarded by the presence of spent pulping liquor, and alkali consumption was increased. At a given level of spent liquor carryover, yield loss was proportional to the amount of lignin removed. There was, however, a compensating beneficial effect on the amount of screen rejects in the pulp. Most of the rejects entering the reactor are converted to usable pulp by reaction with oxygen and alkali. Because the rejects are normally discarded, the yield of screen accepts emerging from the reactor, expressed as a percentage of the amount of accepts entering it, is more meaningful than the total yield. These values approach, or even exceed, 100%.

Table 1. Summary of results.[a]

Carryover of spent pulping liquor solids to O-stage, lb/o.d.t.	0	0	0	330	330	330	330
NaOH charged to O-stage, lb/o.d.t.	1.0	1.6	2.0	2.5	3.3	4.0	No O-stage
Rejects, % o.d. unbleached pulp	1.7	1.7	1.7	3.1	3.1	3.1	8.7
Accepts KMnO$_4$ No.	7.1	5.7	4.9	8.1	7.6	7.2	12.9
Oxygen stage total yield, % o.d. unbleached pulp	95.5	92.7	91.1	94.2	93.2	92.3	n.a.[d]
Oxygen stage accepts yield, % o.d. unbleached accepts	102.6	99.8	98.2	100.0	99.0	98.2	n.a.
Hypochlorite consumed to 80 brightness, % av. Cl$_2$[b]	n.d.[e]	2.4	n.d.	n.d.	3.4	n.d.	4.8
BOD, lb/ton O-stage		17.7			97.8		93.8[c]
H-stage[b]		4.4			5.5		12.3

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[a]Interpolated.
[b]Hypochlorite stages after thorough washing.
[c]BOD in unbleached pulp.
[d]n.a. = not applicable.
[e]n.d. = not determined.

When oxygen delignified pulp was subsequently screened, washed well, and bleached to 80 brightness, it consumed substantially less hypochlorite than pulp which had not been oxygen delignified. The savings ranged from 30 to 50%, depending on how much spent pulping liquor had been carried into the oxygen stage.

The hoped-for beneficial effect on BOD did not materialize. Most of the BOD that emerges from the bleach plant originates with spent pulping liquor carryover that enters it. The oxygen stage destroys part of this, but creates a similar amount by dissolving lignin and carbohydrate.

The oxygen stage reduced the unbeaten tensile index of the pulp, when this was measured after the hypochlorite stage. It had no detectable effect on the dirt count of the bleached pulp.

It was concluded that, at existing levels of spent pulping liquor carryover, installation of an oxygen stage could be expected to result in a 30% reduction in hypochlorite usage with almost no reduction in effective yield and a substantial reduction in the volume of screen rejects for disposal. The requirement for alkali would be 2.9% sodium hydroxide. Little or no beneficial effect on BOD would be seen.

It was also concluded that a substantial degree of oxygen stage inefficiency can be attributed to spent pulping liquor carryover. If washing before the oxygen stage were perfect, alkali consumption would be only 1.6% and hypochlorite consumption would decrease to 2.4% (from the present 10%). BOD production would decrease from more than 100 to about 25 lb/ton.

INTRODUCTION

Sulfite pulps, and especially those made from hardwoods, are readily delignified by oxygen and alkali at relatively low temperature and pressure. In view of this, the present study was conducted in cooperation with a sulfite pulp mill. Its purpose was to evaluate the potential benefits of installing a medium consistency oxygen stage ahead of an existing calcium hypochlorite bleaching stage. Effects on biochemical oxygen demand (BOD), chemical consumption, and rejects levels, were of interest.

The mill in question pulps a mixture of birch, maple, and other high density hardwoods in a calcium acid sulfite process. The pulp is washed to a level that corresponds to a carryover of 200-300 lbs of spent pulping liquor solids per ton pulp. It is then screened and bleached to a TAPPI brightness of 80 with calcium hypochlorite.

The medium consistency oxygen stage would be placed between the unbleached pulp washers and the screen room, to avoid having to install thickening equipment ahead of it. This means that relatively large amounts of knots, fiber bundles and spent pulping liquor would enter the oxygen reactor with the pulp. As well as placing heavy demands on the oxygen stage, this offers the possibilities that oxygen will decrease the amount of screen rejects (presently landfilled) and the BOD of the spent pulping liquor.

EXPERIMENTAL APPROACH

Unscreened, unbleached pulp taken from the last washer repulper was provided by the mill. Upon arrival at our laboratory, the liquor it contained was separated by centrifugation and reserved for controlled addition to some of the pulp samples before oxygen bleaching. The centrifuged pulp was then thoroughly washed to remove all dissolved solids.

Oxygen bleaching was done in a well-stirred, electrically heated reactor. Samples of the thoroughly washed unscreened pulp were oxygen delignified at three different alkali addition levels. At each level, two different methods of adding the alkali were used. In the first of these, the pulp was placed in the reactor and the temperature was raised linearly to its maximum value over a period of 15-20 minutes, after which the required amount of NaOH solution was injected into the reactor. In the second method, the caustic was thoroughly mixed with the pulp in a Hobart kitchen mixer before being transferred to the reactor. The principal differences between the two methods are that the second gives a slightly greater effective reaction time and thoroughly mixes the caustic with the pulp before it undergoes any heating.

In an otherwise identical but separate set of experiments, unscreened pulp samples were oxygen delignified in the presence of an amount of spent pulping liquor equivalent to that in the pulp coming off the final stage of unbleached pulp washing under worst-case conditions. This set of experiments was intended to more closely simulate the conditions that may be encountered in the mill, while the previous set was done to allow an assessment of the benefits of improved washing before the oxygen stage.

After oxygen bleaching, the pulp samples were washed and screened, and the degree of delignification achieved was determined by measuring both the kappa number and the K number of the screen accepts. Both are measurements of oxidant ($KMnO_4$) demand, and are directly related to the amount of lignin remaining in the pulp. For one set of oxygen stage conditions, the total amount of lignin removed was estimated by measuring the kappa number of unscreened samples after fiberizing them to make the lignin in the rejects accessible to permanganate. Yields, rejects contents, and pulp viscosity were determined for all samples, and samples of the effluents from selected oxygen bleaches were submitted for duplicate determinations of BOD.

After inspecting the results of these experiments, conditions judged to be optimum were selected and used to prepare additional oxygen bleached samples for hypochlorite bleaching. The resulting samples, from oxygen bleaches of both unwashed and washed pulps, were thoroughly washed and bleached at each of three levels of hypochlorite addition: 2, 4, and 8%. The results were used to select hypochlorite charges that were expected to give 80 brightness, and an additional set of bleaches was done with these charges. All of the "80 brightness" hypo stage effluents and all of the effluents from hypo stages conducted with 4% hypo were submitted for duplicate determinations of BOD.

TAPPI test methods were used throughout.

RESULTS

UNBLEACHED PULP SAMPLE

Analysis of the liquor separated from the unbleached pulp gave a dissolved solids content of 2.94%. At 15% consistency, this corresponds to a solids carryover of 330 lb per ton of pulp. In the following, the term "unwashed pulp" means thoroughly washed pulp to which this amount of spent liquor solids has been readded. It corresponds to pulp collected after mill washing under worst-case conditions.

The kappa number of the pulp after screening was 18.7 (calculated K no. 12.9). The unscreened pulp had an apparent kappa number of 21.9 (14.6 K), which, with increasing degree of fiberization in a Waring blender, increased toward an asymptotic limit of 28.2 (17.2 K) as a result of increased accessibility to permanganate. Screening on a 0.009-inch cut flat screen gave a rejects content of 8.7%. It follows from these data that the approximate lignin contents of the accepts and rejects are 3.1 and 21.4%, respectively.

The species composition of the pulp was 60-70% maple, 15-20% birch, and smaller amounts of ash, oak, elm, and beech.

The 0.5% cupriethylenediamine solution viscosity was 11.5 cp.

OXYGEN BLEACHING

Oxygen bleaching of unscreened pulp samples gave the data in Table 2. The pulp emerging from the oxygen stage still contained some screen rejects, which are less accessible to permanganate in the K number and kappa number tests than fibers. Direct measurement of either the K number or the kappa number would therefore have given a result that would not solely reflect lignin content. For this reason the oxygen bleached pulp was first screened before measuring these quantities.. Because the kappa number test is more accurate and precise than the K number test, kappa number was used as the primary indicator of the degree of delignification achieved. The K numbers of all pulps were also measured, and a regression equation relating the two was derived (Fig. 1 and Table 6).

K numbers calculated from the kappa numbers by means of this regression equation are included in Table 2 and plotted in Fig. 2. Regression analysis was also used to determine which of the observed effects were statistically significant and to derive equations enabling prediction of K number and yield. These equations are shown in Table 6 and plotted in Fig. 2 and 3, together with the experimental data. One apparently spurious result (Run 7) was omitted from the yield analysis.

It is apparent from Fig. 2 that delignification is strongly retarded by the spent liquor that accompanies the pulp into the oxygen stage. This may simply be due to consumption of alkali by the acids in the spent liquor, including the acids already present and those formed by oxidation of dissolved organics

during oxygen delignification. It is also apparent that adding the caustic in a Hobart mixer prior to putting the pulp into the reactor gives more extensive delignification than adding it to the pulp in the reactor after maximum temperature has been attained. This could be due either to the longer effective reaction time or to better mixing in the former case.

Table 2. Laboratory oxygen bleaching data.[a]

Run No.	Spent Pulping Liquor to O-stage lb solids/ o.d.t. pulp	NaOH % o.d.t.	Caustic Addition Method[b]	Exit pH	Accepts Kappa Number (measured)	Accepts KMnO$_4$ Number (calc'd)[c]	Accepts KMnO$_4$ Number (measured)	Total Yield, % o.d. Unbleached Pulp	Rejects, % o.d. Bleached Pulp	Accepts Viscosity (TAPPI T 230), cp
Unbl. Pulp					18.7	12.9		100.0	8.7	11.5
5	0	0.8	1	8.9	12.7	8.0	7.4	97.2	2.1	10.6
2	0	1.2	1	9.2	11.9	7.4	7.6	96.4	1.7	10.9
11	0	1.2	2	9.1	10.6	6.7	6.2	94.4	1.8	11.9
3	0	1.6	1	9.5	10.0	6.4	6.5	94.4	1.8	11.5
9	0	1.6	2	9.9	8.9	5.8	5.7	93.0	1.3	12.0
15	0	1.6	2	9.3	8.1	5.4	5.4	91.0	1.5	11.6
10	0	2.0	2	9.6	7.6	5.2	5.3	92.5	1.3	11.2
7	330	2.5	1	8.2	15.5	10.0	10.0	93.4	1.7	11.1
8	330	2.9	1	8.0	12.2	7.6	7.9	94.1	2.2	11.8
14	330	2.9	2	7.8	12.5	7.8	7.4	93.5	2.1	11.2
6	330	3.3	1	7.7	13.2	8.3	8.7	94.7	2.4	11.0
13	330	3.3	2	7.9	12.0	7.5	7.1	91.1	3.3	11.5
16	330	3.3	2	7.9	12.0	7.5	7.5	92.7	4.1	11.2
12	330	3.7	2	6.8	12.0	7.5	7.8	94.4	3.0	11.2

[a]Oxygen stage conditions: 12% consistency, 45 min at 160°F (71°C), total pressure 60 psig.
[b]1 = addition at temperature; 2 = addition before heating; see text for details.
[c]From regression equation derived in this study.

Figure 3 shows that, over the range of K numbers represented, there is an approximately linear relationship between the total yield of the oxygen stage and the K number of the accepts in the oxygen bleached pulp. Note, however,

that the yield plotted in Fig. 3 is the weight of unscreened pulp emerging from the oxygen stage expressed as a percentage of the unscreened pulp entering the stage. This is of less practical interest than the weight of accepts emerging from the stage expressed as a percentage of the weight of accepts entering it, because screen rejects are discarded in normal operation. Yields calculated in this way are plotted in Fig. 4, which shows that the effective yield of the oxygen stage can be greater than 100% because it converts rejects into usable pulp. The regression equation corresponding to Fig. 4 can be found in Table 6.

The total degree of delignification in the oxygen stage cannot be determined from the data in Table 2 because the oxygen bleached pulp was screened before determining its K no. and the K no. of the rejects therefore remains unknown. Furthermore, the K no. of the accepts in the bleached pulp cannot be directly compared with that of the accepts in the unbleached pulp because the oxygen stage converts rejects to accepts. These new accepts consist of fibers that may have a higher lignin content than fibers that entered the oxygen stage as accepts. As a result, the K no. of the bleached accepts is a weighted average of the K no. of the fibers that entered the stage as fibers and that of the fibers that were liberated from rejects by the oxygen stage. To obtain an estimate of the total degree of delignification in the oxygen stage, the unbleached pulp and two of the oxygen bleached pulps were specially treated to obtain K no.'s that could be related to the total lignin content.

The total lignin content of a pulp, including both the lignin in the rejects and the lignin in the fibers, can, in principle, be estimated by completely converting all of the rejects to separated fibers before measuring the K no. In practice, it can be estimated by fiberizing the whole pulp for various periods of time, measuring the K no. or kappa no., and extrapolating to infinite fiberization time by estimating the asymptotic limit by nonlinear regression. This also provides information on the ease of fiberization of the rejects. This was done for the unbleached pulp and two of the oxygen bleached pulps, with the results shown in Fig. 5.

The kappa number of the oxygen bleached pulp from run 3 after screening was 10.0 (calculated K no. 6.4). The unscreened oxygen bleached pulp had an apparent kappa number of about 12.4 (7.8 K), which, with increasing degree of fiberization in a Waring blender, increased toward an asymptotic limit of 16.1 (10.5 K). Thus the screened kappa number underestimated the whole pulp kappa number by 38%. Since the rejects content of this pulp was only 1.8%, it follows that the lignin content of the rejects is very high, about 57%. This, together with their slow rate of fiberization, suggests that they consist exclusively of highly lignified knot particles and are of little value. A similar analysis of the unbleached pulp, however, gave a rejects lignin content of only 21.4% and a fiberization rate about twice as high, showing that the rejects in the unbleached pulp are potentially of value. The oxygen stage effectively reclaims them.

The data of Fig. 5 also show that 45% of the total amount of lignin in the unbleached pulp was removed by the oxygen stage in run 3. The lignin content of the accepts in the oxygen bleached pulp was 46% lower than that of the accepts in the unbleached pulp. For the reasons stated above, this agreement is fortuitous.

HYPOCHLORITE BLEACHING

Samples prepared by duplicate oxygen bleaches of fully washed pulp (runs 9 and 15 of Table 2) were washed and bleached with various amounts of calcium hypochlorite and measurements were made of brightness, viscosity, unbeaten tensile index and dirt count. The same was done for pulps from duplicate oxygen bleaches done in the presence of spent pulping liquor in the amount prevailing at the time the sample was collected at the mill washer (runs 13 and 16 of Table 2). In addition, samples of thoroughly washed unbleached pulp were bleached with various amounts of hypochlorite. The results are tabulated in Table 3.

The brightness response of the various pulps is illustrated in Fig. 6. After washing, the unbleached pulp required 4.8% hypochlorite to reach 80 brightness. The oxygen bleached pulp that had been thoroughly washed prior to the oxygen stage required only 2.4% hypochlorite to reach the same brightness level, and the pulp bleached with oxygen in the presence of spent pulping liquor required 3.4%. Thus, oxygen bleaching significantly reduces the amount of chemical required in a subsequent hypochlorite stage.

The amount of hypochlorite needed to raise the brightness of the unbleached pulp to 80 in the laboratory (4.8%) was considerably less than in the mill (10%). This is probably due to the presence of spent pulping liquor carryover in the mill and its absence in the laboratory bleaches of thoroughly washed pulp. After oxygen bleaching of mill-washed pulp, the hypochlorite demand of the subsequently washed pulp was reduced by 30%, from 4.8 to 3.4%. If, as it seems reasonable to assume, the hypochlorite demand of the spent liquor solids is reduced by a similar amount, one might expect to require only 7% hypochlorite in the mill if oxygen bleaching were installed with no improvement in unbleached pulp washing.

Table 3. Laboratory hypochlorite bleaching data.

O-stage Run Number	Spent Pulping Liquor to O-stage lb Solids/ o.d.t. Pulp	NaOH in O-stage % o.d. Unbl. Pulp	O-stage Run No.	Accepts KMnO$_4$ No. Out of O-stage	Av. Cl$_2$ % on o.d. O-stage Pulp	Exit pH	TAPPI Brightness	Viscosity, cp	Tensile Index kN/m	Dirt Count
9	0	1.6	9	5.8	2.00	6.9	74.1	10.8	1.16	265
					3.00	6.3	85.6	9.6	1.24	366
					4.00	7.2	88.0	9.2	1.27	126
					8.00	7.7	90.4	6.6	1.25	198
15	0	1.6	15	5.4	2.00	6.2	73.2	10.1	1.22	235
					3.00	7.1	85.3	8.8	1.28	102
					4.00	7.2	87.5	8.9	1.33	90
					8.00	7.7	90.9	6.5	1.31	183
13	330	3.3	13	7.5	2.00	6.2	59.5	10.9	1.25	410
					3.75	6.8	81.6	8.8	1.39	402
					4.00	6.9	84.1	9.8	1.51	262
					8.00	7.3	89.0	7.0	1.47	135
16	330	3.3	16	7.5	2.00	7.1	59.0	10.5	1.31	405
					3.75	7.0	82.0	8.8	1.35	258
					4.00	6.6	84.0	9.0	1.37	310
					8.00	7.1	89.2	6.5	1.43	190
Unbl.	0				2.00	6.8	50.1	NA	NA	n.d.[a]
					4.00	6.8	72.9	NA	NA	n.d.[a]
					6.00	7.4	87.8	NA	NA	n.d.[a]
					10.00	7.3	89.1	6.2	1.75	185
					10.00	7.8	88.9	6.0	1.72	255

[a]n.d. = not determined.

The data of Table 3 also show that pulp viscosity was significantly decreased by hypochlorite bleaching and that the size of the decrease was independent of oxygen stage conditions.

Unbeaten tensile index increased with increasing hypochlorite charge and was higher for samples which had been oxygen bleached in the presence of spent pulping liquor than for those that were thoroughly washed before oxygen bleaching. Analysis of variance of the data showed that both effects were statistically significant. The tensile indices of all oxygen bleached samples were lower than those of samples bleached only with hypochlorite.

Dirt count was decreased by hypochlorite bleaching but was not significantly affected by oxygen stage conditions. There was no evidence for concluding that the oxygen stage affected dirt count.

BIOCHEMICAL OXYGEN DEMAND

Duplicate determinations of BOD in oxygen stage effluent and spent pulping liquor carryover gave the results in Table 4. Oxygen bleaching without additional washing produced an average of 98 lb BOD per ton of pulp; thorough washing before the oxygen stage reduced this to 18 lb. The pulp as collected from the mill washer contained 94 lb/ton. It thus appears that the oxygen stage creates about 18 lb BOD/ton by dissolving pulp components and simultaneously destroys about the same amount. The net result is that the oxygen stage has no effect on the BOD accompanying the pulp to the screen room.

Table 4. Biochemical oxygen demand of spent oxygen bleach liquors and spent pulping liquor carryover.

Stage	Spent Pulping Liquor to O-stage, lb Solids/ o.d.t. Pulp	Run No.	NaOH in O-stage, % o.d. Unbl. Pulp	Av. Cl₂, % o.d. on O-stage Pulp	B.O.D.		
					mg/L	lb/o.d.t. Pulp into Stage	Average lb/o.d.t.
Oxygen	0	9	1.6	—	460	17.5	
					452	17.2	
	0	15	1.6	—	482	18.3	
					467	17.7	17.7
	330	13	3.3	—	3060	116.3	
					2610	99.2	
	330	16	3.3	—	2410	91.6	
					2210	84.0	97.8
Spent pulping liquor carryover					7980	90.4	
					8580	97.2	93.8

Table 5 contains the corresponding data for hypochlorite bleaching after thoroughly washing the pulp. Thoroughly washing the pulp before a preceding oxygen stage caused the BOD generated in the hypochlorite stage to decrease from 5.5 to 4.4 lb/ton, a statistically significant effect. Omitting the oxygen stage and using excess hypochlorite caused the BOD generated in the hypochlorite stage to increase sharply, to 12.3 lb/ton. This indicates that the hypochlorite stage would generate less BOD after a preceding oxygen stage than without it, but the available data do not allow the size of the reduction to be accurately predicted, because a control simulating spent pulping liquor carryover into the hypochlorite stage was not done. A reasonable rough estimate would be a BOD reduction of 3 lb/ton if the oxygen stage were installed.

Table 5. Biochemical oxygen demand of spent hypochlorite bleach liquors.

Spent Pulping Liquor to O-stage lb Solids/ o.d.t.Pulp	O-stage Run No.	Av. Cl₂ % on o.d. O-stage Pulp	B.O.D.		
			mg/L	lb/o.d.t. Pulp into Stage	av. lb/o.d.t.
0	9	3	112	4.3	
			112	4.3	
0	9	4	121	4.6	
			81	3.1	
0	15	3	127	4.8	
			125	4.8	
0	15	4	146	5.5	
			101	3.8	4.40
330	13	3.75	137	5.2	
			151	5.7	
330	13	4	151	5.7	
			156	5.9	
330	16	3.75	142	5.4	
			106	4.0	
330	16	4	151	5.7	
			166	6.3	5.49
0	unbl.	10	323	12.3	
			323	12.3	12.3

Table 6. Regression equations derived from data of Table 2.

Dependent Variable	Equation	Multiple Correlation Coefficient R^2	Standard Error of Estimate s
K Number	$K = 3.73 + 0.0263 \text{ (Kappa)}^2$	0.96	0.27
K Number	$K = 10.74 - 0.508 \text{ (\% NaOH)} - 0.733 \text{ (Method)} - 1.70 \text{ (Wash) (NaOH)}$	0.86	0.53
Yield	$Y = 77.74 + 2.036 \text{ (K No.)} - 3.33 \text{ (Wash)}$	0.78	0.93
Accepts Yield	$Y' = 83.17 + 2.081 \text{ (K No.)} - 4.78 \text{ (Wash)}$	0.70	1.37

Variable definitions:

% NaOH = NaOH charge in oxygen stage, o.d. pulp basis.

Wash = 0 for pulp containing spent pulping liquor carryover.
1 for pulp washed free of spent pulping liquor.

Method = 1 when NaOH was added at maximum temperature.
2 when NaOH was mixed with pulp before heating.

CONCLUSIONS

1. Installation of a medium consistency oxygen bleaching stage between the unbleached pulp washers and the screen room in the mill in question would result in a reduction in laboratory flat screen accepts K number from 12.9 to 7.8 at the expense of 2.9% NaOH, based on o.d. unbleached, unscreened pulp. This assumes a carryover of spent pulping liquor into the oxygen stage of 330 lb total solids per ton of pulp. The yield of screen accepts emerging from the stage would be 99% of the flow of accepts entering it, this being the net result of pulp shrinkage and rejects fiberization. There would be little or no effect on BOD production. Hypochlorite consumption could be expected to decrease from 200 to about 140 lb/ton. Unbeaten tensile index would decrease slightly, while pulp viscosity and dirt count would be unaffected.

2. A substantial degree of oxygen stage inefficiency can be attributed to spent pulping liquor carryover into the oxygen stage. The extent of this inefficiency was determined by experiments in which the pulp was thoroughly washed to remove all spent pulping liquor solids before oxygen bleaching. Perfect washing and oxygen bleaching would give an accepts K number reduction from 12.9 to 5.8 at the expense of only 1.6% NaOH. The yield of accepts leaving the stage would be 100% of the flow of accepts entering it. BOD production would decrease from about 106 to about 26 lb/ton, the improvement being attributable to washing rather than to oxygen bleaching. Hypochlorite consumption would be expected to decrease from 200 to about 50 lb/ton.

ACKNOWLEDGMENTS
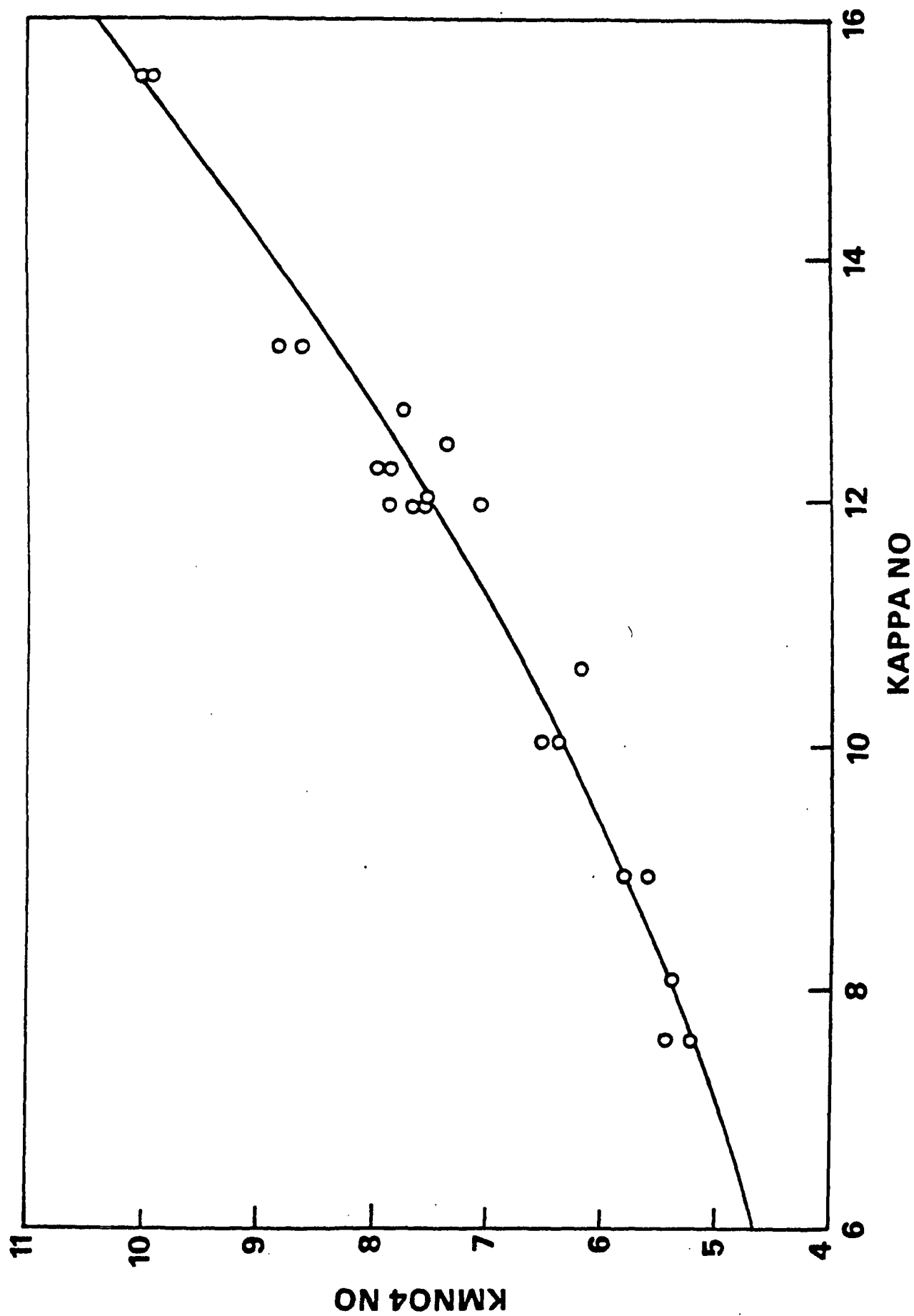
Figure 1. KMnO4 number vs. kappa number for oxygen bleached pulps.
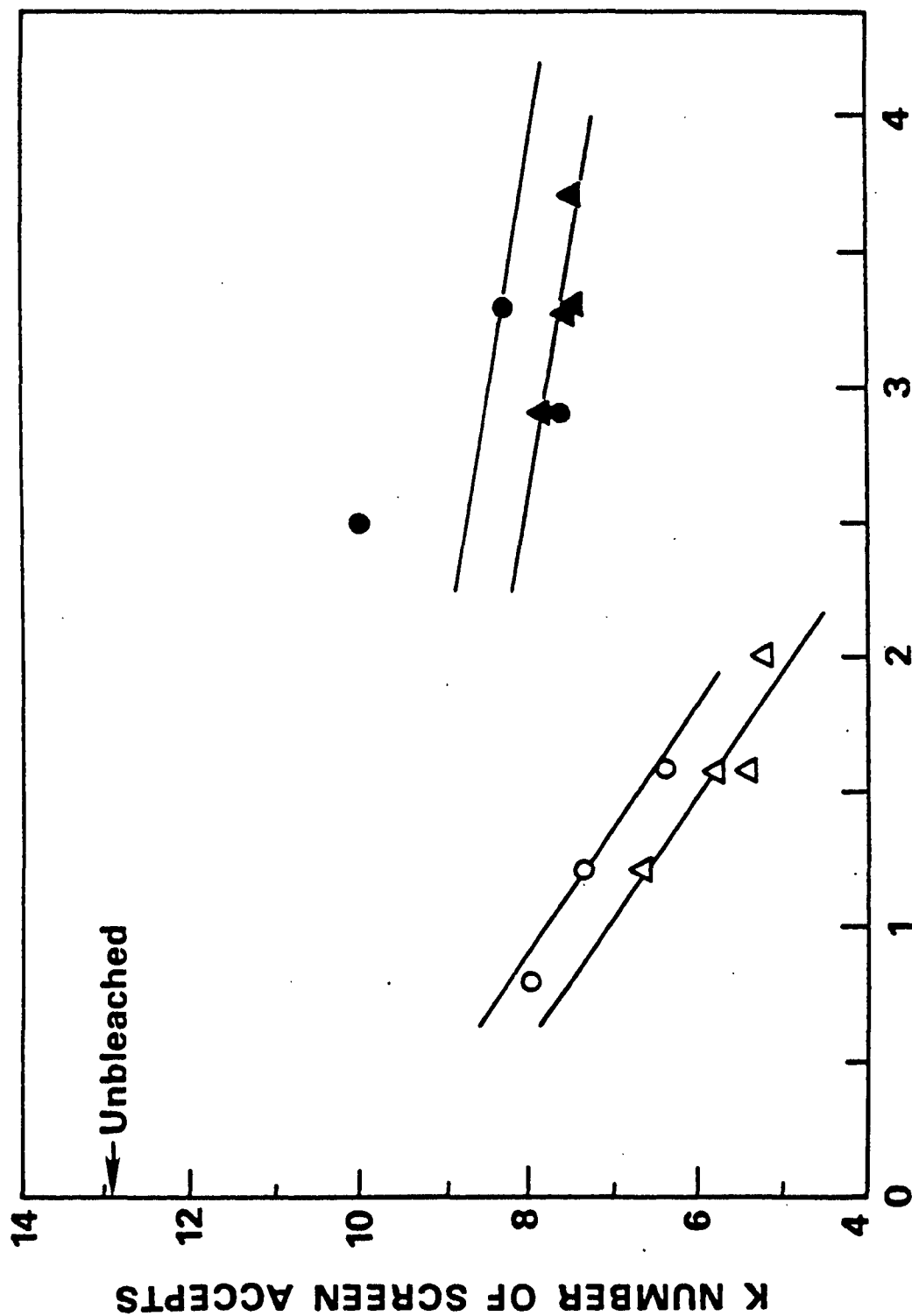
TOTAL NaOH APPLIED, % O.D. UNBL. UNSCR. PULP

K NUMBER OF SCREEN ACCEPTS

Figure 2. K number (calculated from kappa number) after oxygen bleaching vs. alkaline charge in oxygen stage for washed (open symbols) and unwashed (filled symbols) pulps. Caustic was added before heating (triangles) or when maximum temperature was reached (circles).
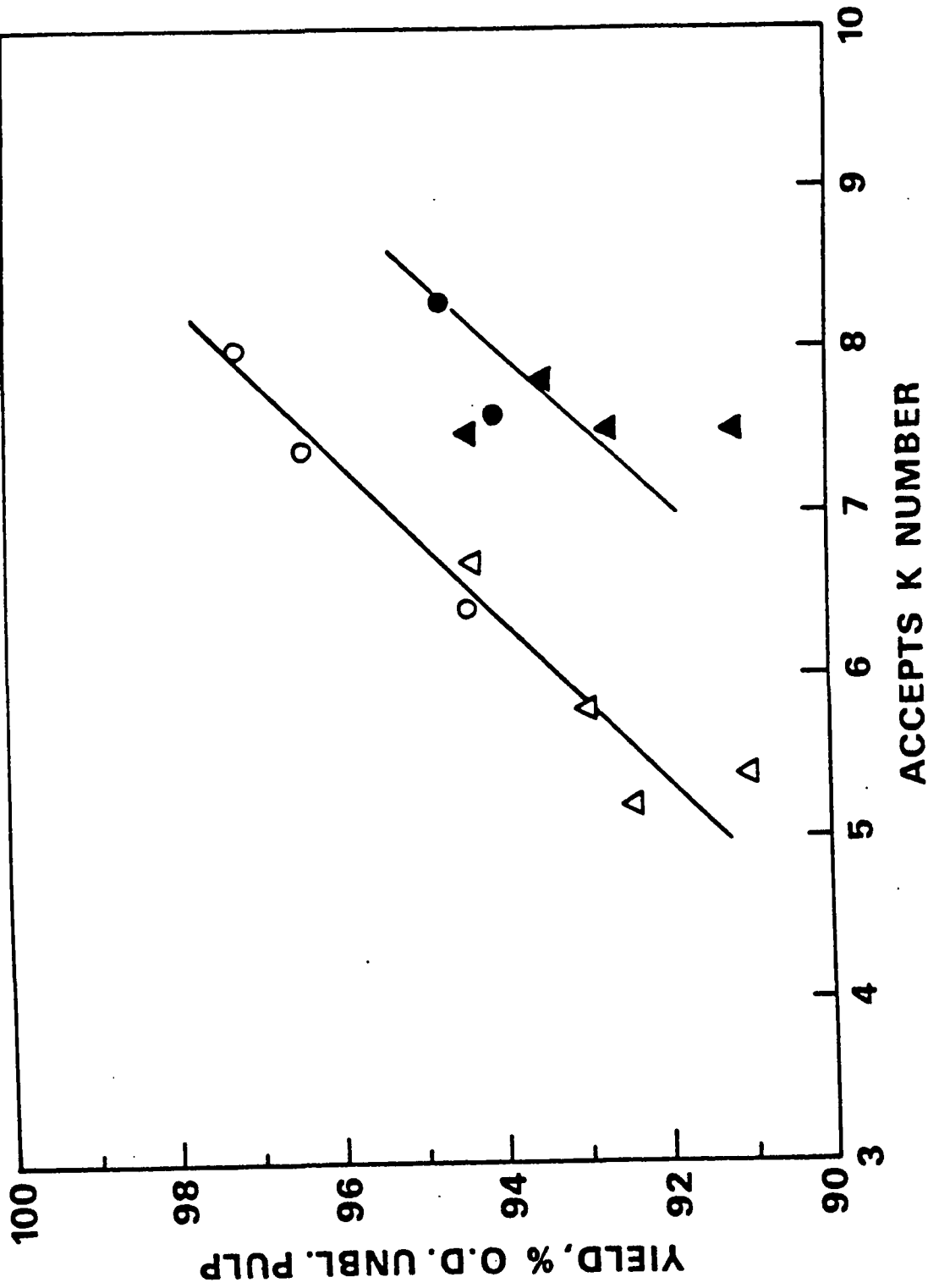
Figure 3. Unscreened oxygen stage yield vs. K no. of oxygen bleached pulp screen accepts (calculated from kappa no.). Symbols as in Fig. 2.
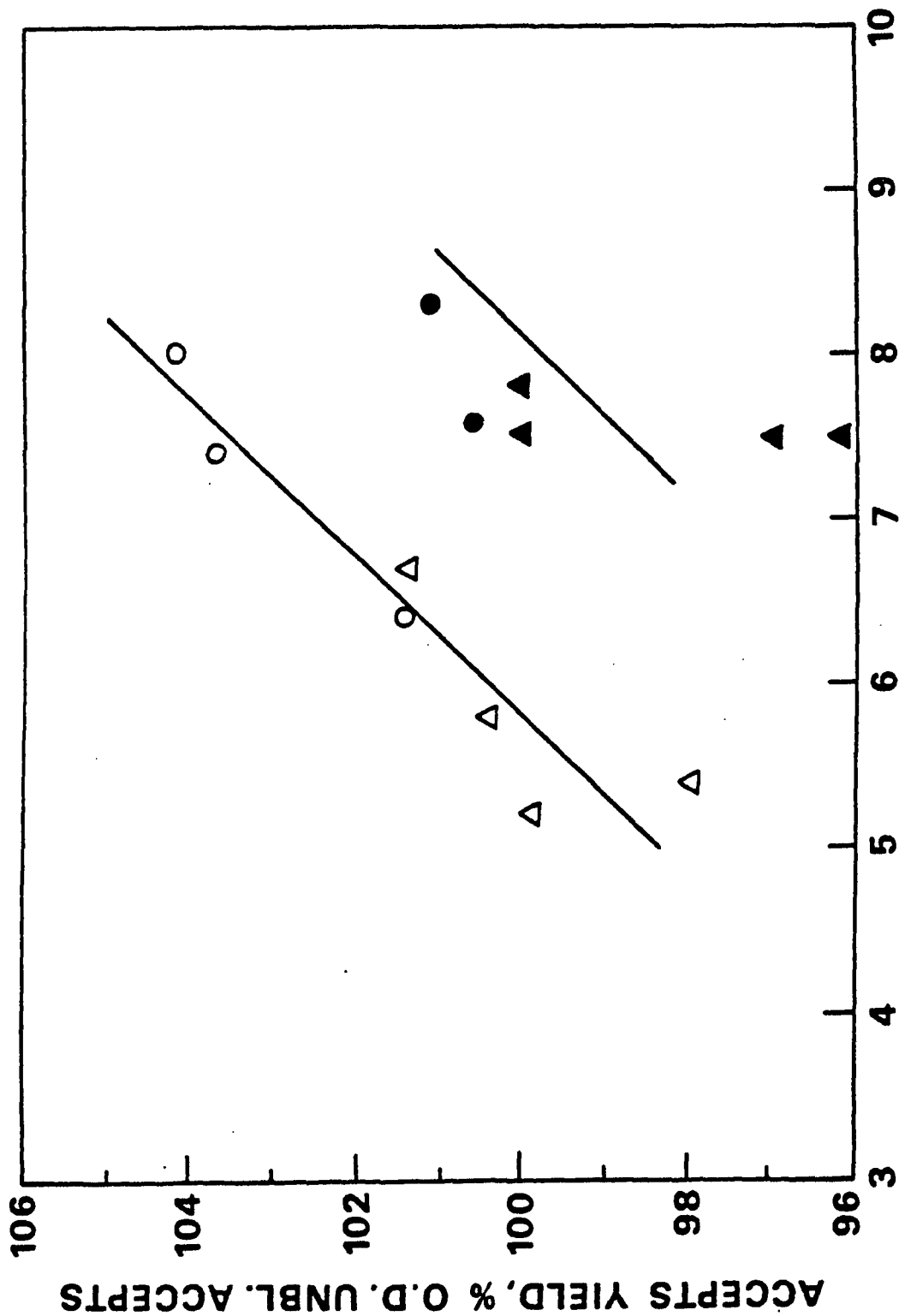
Figure 4. Yields of screen accepts after oxygen bleaching expressed as a percentage of the screen accepts in the pulp entering the oxygen stage vs. K no. (calculated from kappa number). Symbols as in Fig. 2.
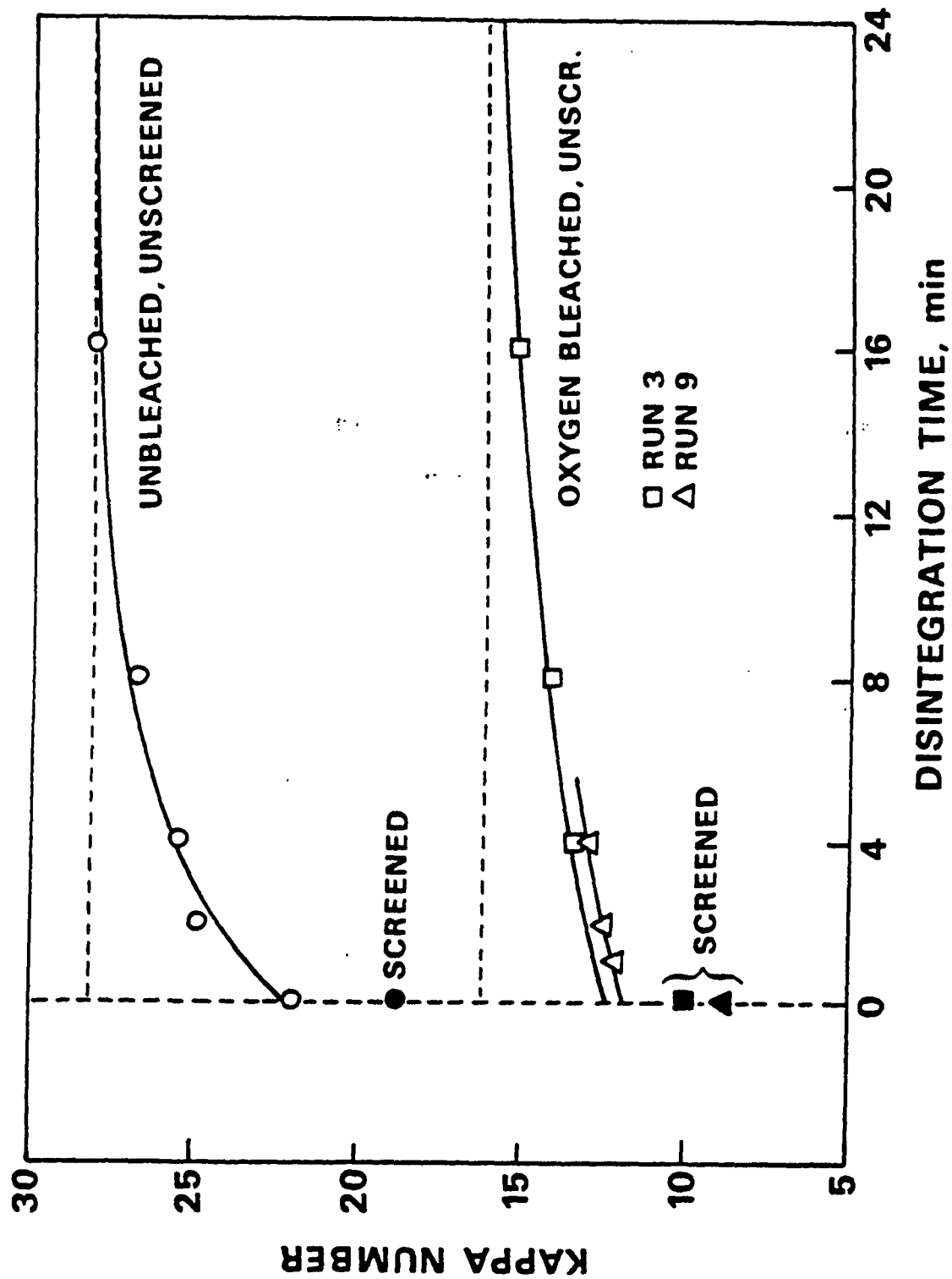
Figure 5. Kappa number of unscreened pulps vs. time in Waring blender.
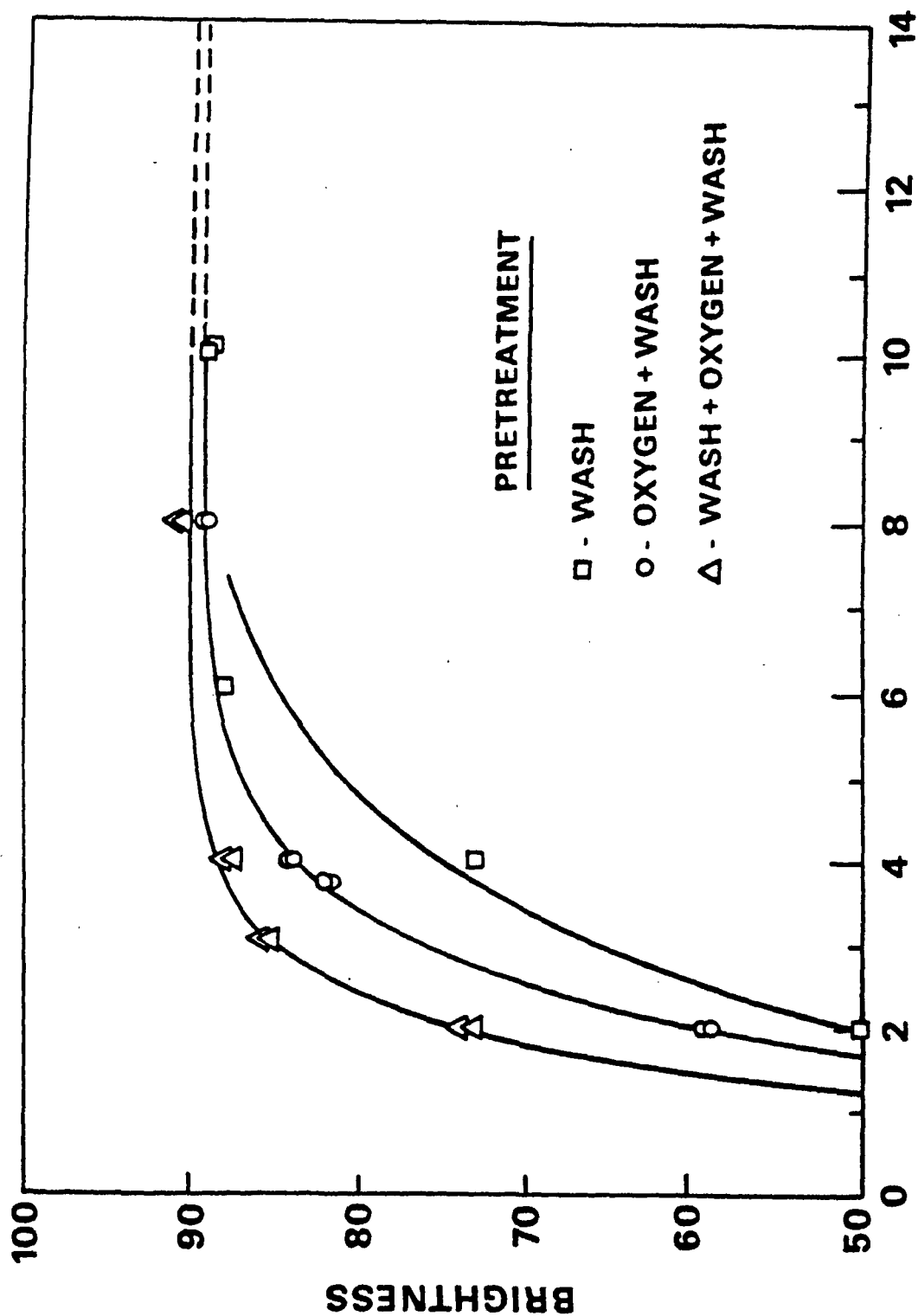
Figure 6. Pulp brightness vs. hypochlorite charge for unbleached pulp (squares) pulp oxygen bleached after thorough washing (triangles) and pulp oxygen bleached in presence of spent pulping liquor (circles). All three pulps were thoroughly washed before hypochlorite bleaching.

PROJECT 3699

EVALUATION OF COMMERCIALLY AVAILABLE

CONDUCTIVITY SENSORS

RESEARCH REVIEW

April 2, 1991

Charles E. Courchene

PROJECT SUMMARY FORM
FY 90-91

Project Title: EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY
SENSORS
(API/MTC FUNDED)

Division: Chemical and Biological Sciences
Project Code: (Funded)
Project No.: 3699
Project Staff: Charles Courchene, Lee Thames
FY 90-91 Budget: $55,000

OBJECTIVE:

To evaluate commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams.

EVALUATION OF COMMERCIALLY AVAILABLE
CONDUCTIVITY SENSORS

OBJECTIVE

To evaluate commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams.

INTRODUCTION

Conductivity is the measurement of the ability of a solution to conduct electric current. This ability is primarily determined by the concentration and species of electrolytes in the solution. The current that can be passed through the solution is measured at a known constant voltage. Conductance is then calculated based on cell dimensions and electrolyte concentration. The common unit of measure has been mhos/cm or micromhos/cm derived from the reciprocal of ohms or resistivity. The accepted unit of measure is now microSiemens/cm. One microSiemen is equal to one micromho.

Conductivity has been determined in several studies to be representative of the alkalinity of a process stream (1,2,3). One of these (2), conducted in IPST laboratories, established detailed relationships of the output of a four electrode sensor with alkali concentrations, organic salt concentration, and temperature. At high hydroxide concentration, the high ionic conductance of the hydroxide ion dominates and a relationship between pH and conductance can be developed. However, below a pH of approximately 12, the conductance of other ions must be considered and simple correlations cannot be obtained.

A recent study has investigated the quantification of factors affecting the conductivity of black liquor (4). Conductivity was found to be affected by Kappa number, liquor composition, dilution, temperature, and fibers. Several factors were found to interact with each other such as temperature and dilution. Effects of fiber concentration were stated to be sensor-dependent. Theoretical relationships were only partially successful in predicting liquor conductivity. Regression analysis was used to establish the final relationships between conductivity, total and effective alkali, and Kappa number.

Another study (5) investigated the response of a commercial conductivity sensor to kraft white liquor, weak white liquor, cooking liquor, and green liquor. The conductivity of white liquor was found to correlate well with effective alkali. For weak white liquor and green liquor, the correlation was found to include Na_2CO_3 in addition to NaOH and Na_2S. For cooking liquor the correlation also included lignin concentration. Temperature compensations were also determined in each case.

Conductivity is already used extensively in pulp mill processes. The major pulp mill areas where on-line conductivity measurement is made include:

1. White Liquor Alkalinity
2. Black Liquor Residual Alkali
3. Caustic Dilution and Hypochlorite Manufacture
4. Pulp Washing Efficiency
5. Evaporator Condensate Carry-over
6. Black Liquor Spill Reclamation

The disadvantages of on-line liquor conductivity measurements have been reported to be: (6)

1. Temperature of the liquor seriously affects solution conductivity. Temperature compensation is required.
2. Conductivity is affected by the presence of chloride ions and dissolved carbohydrates and lignin.
3. Systems with electrodes tend to foul readily.
4. High solution conductivity requires electrical isolation of pipe sections up and downstream of conductivity electrodes.
5. Electrodes can become polarized.

The major types of sensors in use have been identified as:

1. Two electrode
2. Four electrode
3. Electrodeless (or toroidal)
   a. Flow Through
   b. Insertion

The two electrode sensor measures the current generated in a solution between the electrodes. Using two electrodes results in polarization and fouling of the electrodes so that the applied voltage becomes non-linear and leads to inaccuracies. The four electrode sensor uses two electrodes for the current and a separate pair of electrodes to measure the voltage so that polarization and contamination are automatically compensated for.

The electrodeless sensor consists of a pair of wire wound metallic toroids which are isolated from the process stream by encasing them in an inert material. One coil will induce a current in the second toroid. Since these toroids are coupled by the process fluid the current induced in the second toroid is directly proportional to the conductivity.

For this study three sensor-transmitter combinations were acquired on loan from suppliers. These were:

1. Four electrode
2. Flow through electrodeless
3. Insertion electrodeless

The purpose of this study was to evaluate commercially available sensors so they were installed and utilized according to the manufacturer's recommendations.

Phase 1 of this project was designed to look at typical white liquor concentrations to include, $NaOH$, Na_2S, Na_2CO_3, Na_2SO_4, and $CaCO_3$. Flow velocity and temperature were also variables to be studied.

A test stand as shown in Figure 1 was designed and installed. This utilized the Institute's 1.8 cubic foot digester and liquor recirculation pump. A flow loop was constructed from the outlet of the pump and consists of the three sensors, a magnetic flow meter, temperature probe, and pressure transducers. All signals from the transmitters are a 4-20 mA output. This is converted to a 1-5 Vdc input for a data acquisition computer.

The flow is controlled by a variable speed drive on the pump and the temperature is manually controlled by the flow through an indirect steam heat exchanger. All piping is 1" diameter except for an enlargement in the line of 6" diameter to accomodate the insertion electrodeless sensor.
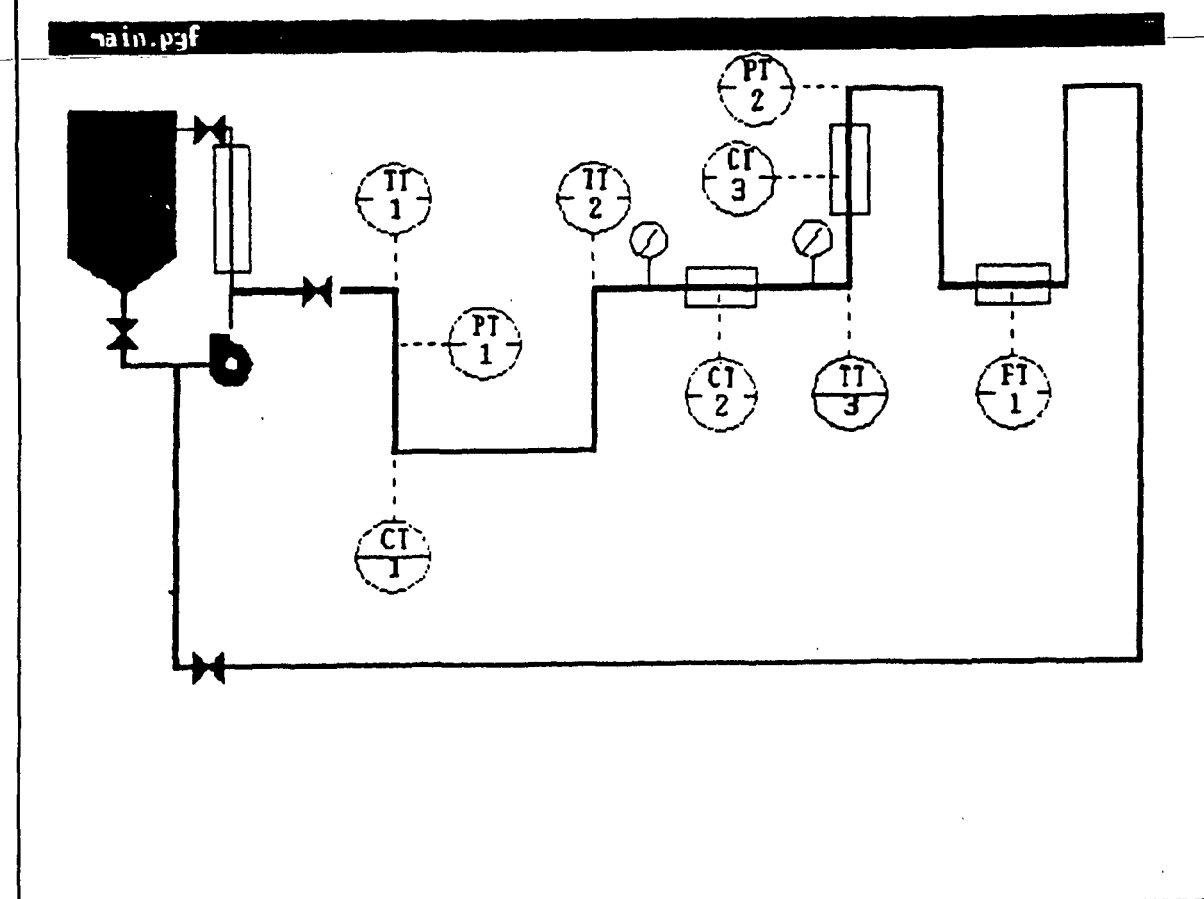
Figure 1

RESULTS

Temperature Compensation

Initial testing was done with solutions of NaOH to check the calibration of the instruments and the accuracy of the temperature compensation function. It was found that the three suppliers approach the temperature compensation differently.

The four electrode sensor-transmitter, referred to as COND1, comes equipped with an integral temperature probe in the tip. The temperature compensation is accomplished by internal electronics and is based on a KCl standard at 25°C. The transmitter does not allow any adjustment of the compensation function except for turning it off by disconnecting the temperature probe leads.

The flow through sensor-transmitter, COND2, also uses a temperature standard of 25°C. The transmitter is microprocessor-based and allows for adjustment of the slope of the temperature compensation curve as well as the cell constant. It comes from the factory with a slope of 2%/°C and a constant of 3.0 but it is recommended by the supplier that the user do an initial calibration in the actual process to more accurately determine a cell constant and slope.

The insertion electrodeless sensor-transmitter, COND3, comes with three preprogrammed curves to cover a range of uses. One curve is for NaOH solutions at 25°C, one is for NaOH at 100°C, and the third is for black liquor at 100°C. These are selectable by a code on the transmitter. This supplier makes the argument that better accuracy is obtained when using a reference temperature that is closer to the actual process temperature.

Testing With NaOH

For the initial testing, COND1 was operated with the temperature compensation as supplied. COND2 was operated with no temperature compensation so that a slope could be calculated. COND3 was operated with the 100°C compensation curve.

NaOH solutions of 56.6 g/l to 124 g/l as Na_2O were tested at temperatures from ambient to 100°C. Flow was varied up to 18 gpm and in this range there were no differences seen in the conductivity readings. For each sensor the conductivity was plotted vs. temperature at each NaOH concentration.

Fig. 2 shows the response of COND1. Even though this was operating with temperature compensation there is a slight positive slope to each line. At the highest concentration of 124 g/l the transmitter was out of the normal range and showed a much greater dependence on temperature. After seeing these results the supplier decided that a different sensor tip based on an NaOH standard at 25°C would be less sensitive to temperature. This new tip was received and installed for the white liquor testing. It was also acknowledged that in actual use the temperature of the process does not vary much and the temperature effect we saw over a wide range might not be as significant. For a process with changing temperature an external RTD temperature input could be used with a faster response or an uncompensated signal could be used and transformed to a reference temperature by an algorithm established by the user for the particular process.
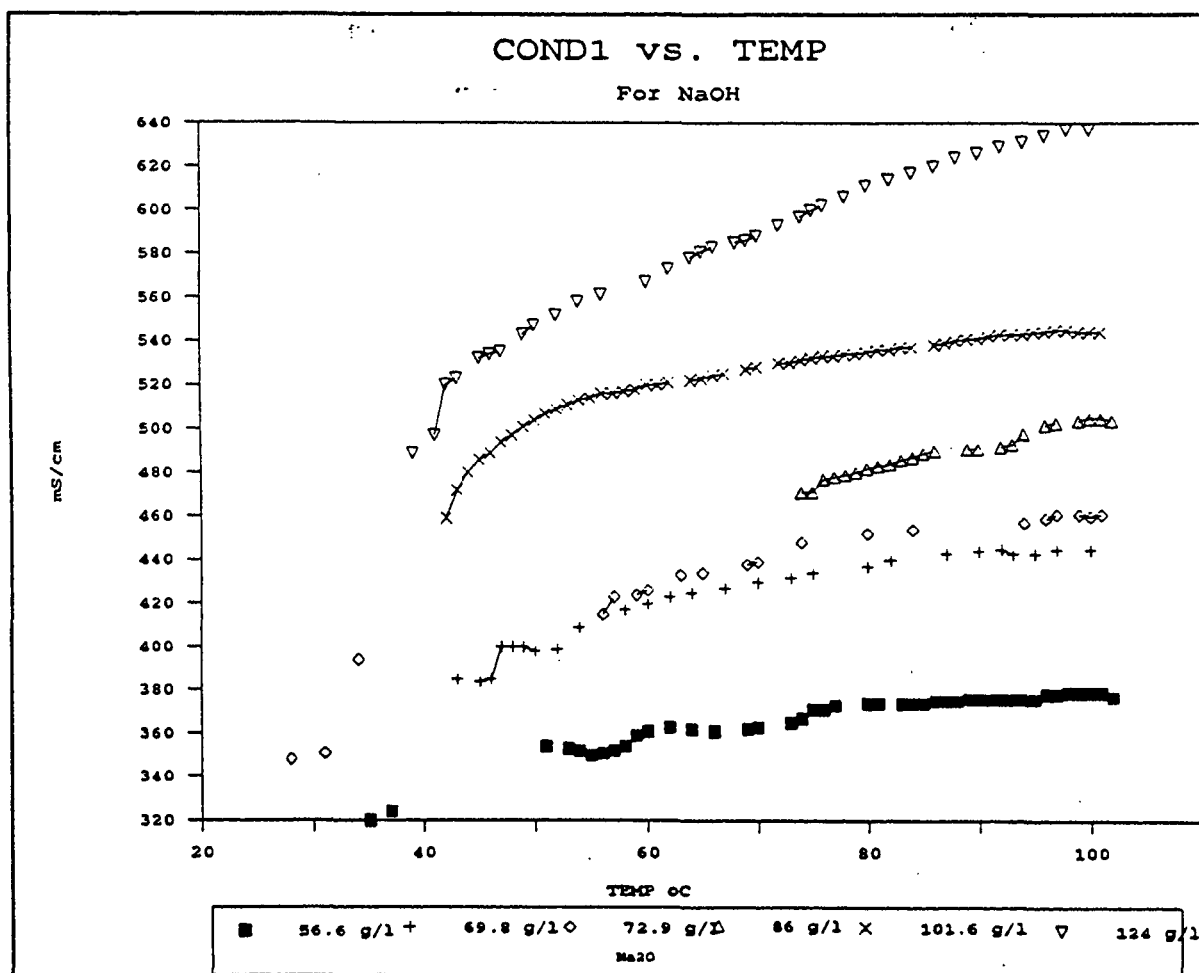
Figure 2

Fig. 3 shows the response of COND2 vs temperature. This was an uncompensated signal so it varied directly with temperature. From this data the slope was calculated to be 2.11 %/°C and this was put in the transmitter for the white liquor testing. Also the cell constant was determined to be 6.36 for conductivity of NaOH at 25°C and this was also put in the transmitter.

COND2 vs. TEMP
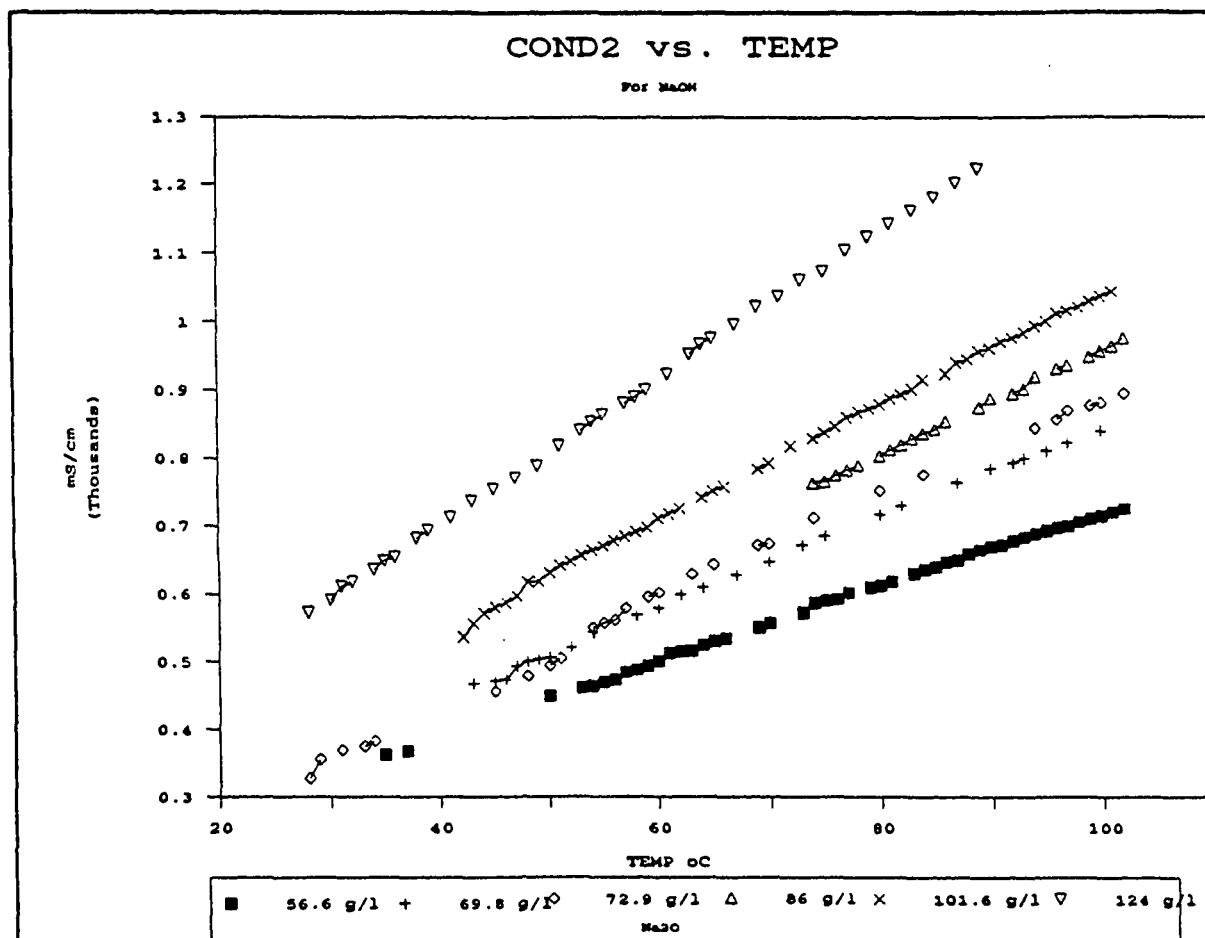
Figure 3

-183-

Fig. 4 shows the response of COND3 vs temperature. For each concentration there is a consistent slope in the line until about 60°C then a levelling off to a steady reading up to 100°C. At the highest concentration there was still some increase with temperature but this transmitter was also out of range at this concentration. The supplier's response was that this is an expected result since the 100°C compensation curve is specified to be good at temperatures above 64°C. For temperatures below this the 25°C curve should be used.
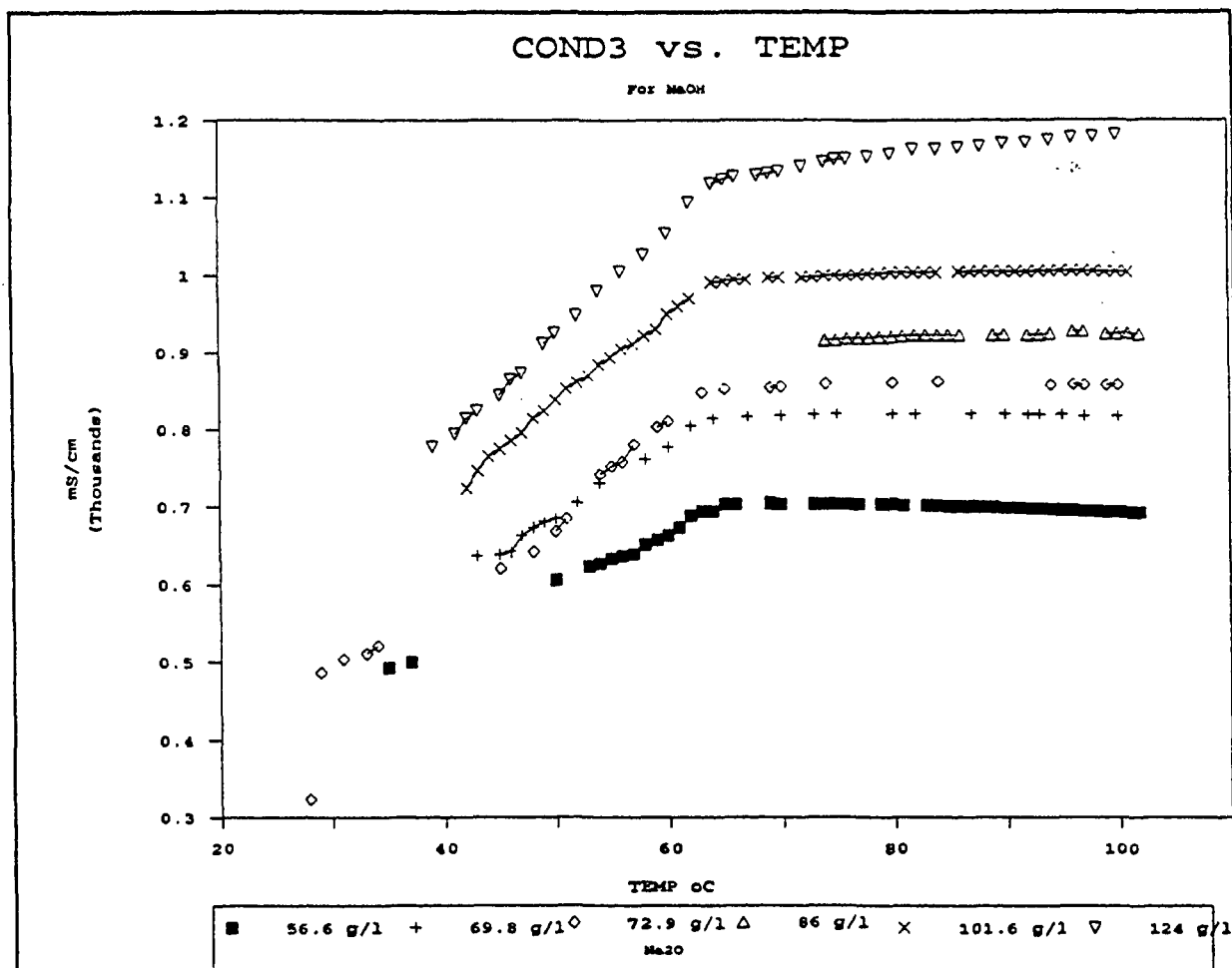
Figure 4

The conductivity values at 100°C were plotted against NaOH concentration as Na$_2$O as shown in Figure 5. A good correlation was obtained for each sensor.

CONDUCTIVITY vs. ALKALI

Values at 100 oC for NaOH
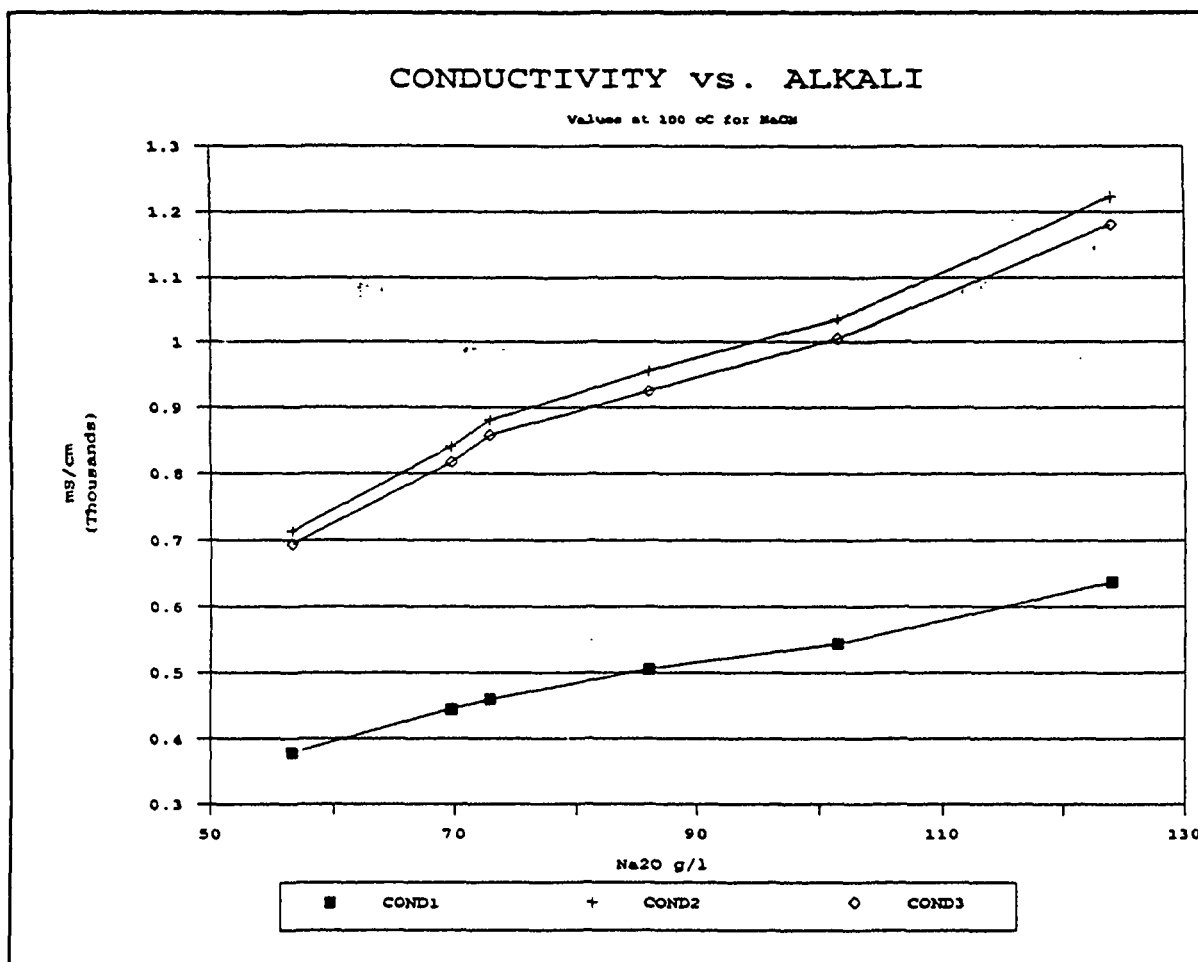
Figure 5

White Liquor Testing

Following the NaOH testing, white liquor testing was planned. A different circulating pump was installed to give flow rates up to 30 gpm. A 2^5 factorial was designed to study the effect of chemical concentration with a half replicate to be utilized. The temperature was to be varied from the range of 80-100°C and the flow from 5-30 gpm.

For this testing white liquor was made up from deionized water and technical grade salts of the species to be studied. The concentration of NaOH, Na_2S, and Na_2CO_3 was determined by the standard "ABC" test and the concentrations reported as g/l Na_2O. The Na_2SO_4 and $CaCO_3$ concentration was determined by quantitative measurement.

Testing is on-going and the results have not been completely analyzed. The results of Runs to date are shown in Table 1. Conductivity values were recorded for temperatures of 80, 90, and 100°C. It became apparent from the initial runs that the flow up to 30 gpm has no effect on the conductivity. Later runs were then done at one flow rate only.

At a given temperature all three sensors exhibited a steady response. As the temperature was raised, COND2 and COND3 maintained steady readings but COND1 showed a consistent increase with increasing temperature. In fact the temperature sensitivity was greater with the new tip in the white liquor than with the old tip in the NaOH. The slopes of the conductivity vs temperature lines for NaOH solutions ranged from 0.7-1.2 while for the white liquor the slopes range from 1.4-1.7.

Multiple regression analysis will be done on the data to determine the influence of each variable on the conductivity. It is expected that the conductivity can be strongly correlated with active alkali.

Future Work

Future work will be planned after the completion of the white liquor testing. This is expected to involve using black liquor solutions as well as monitoring the long term response of the sensors.
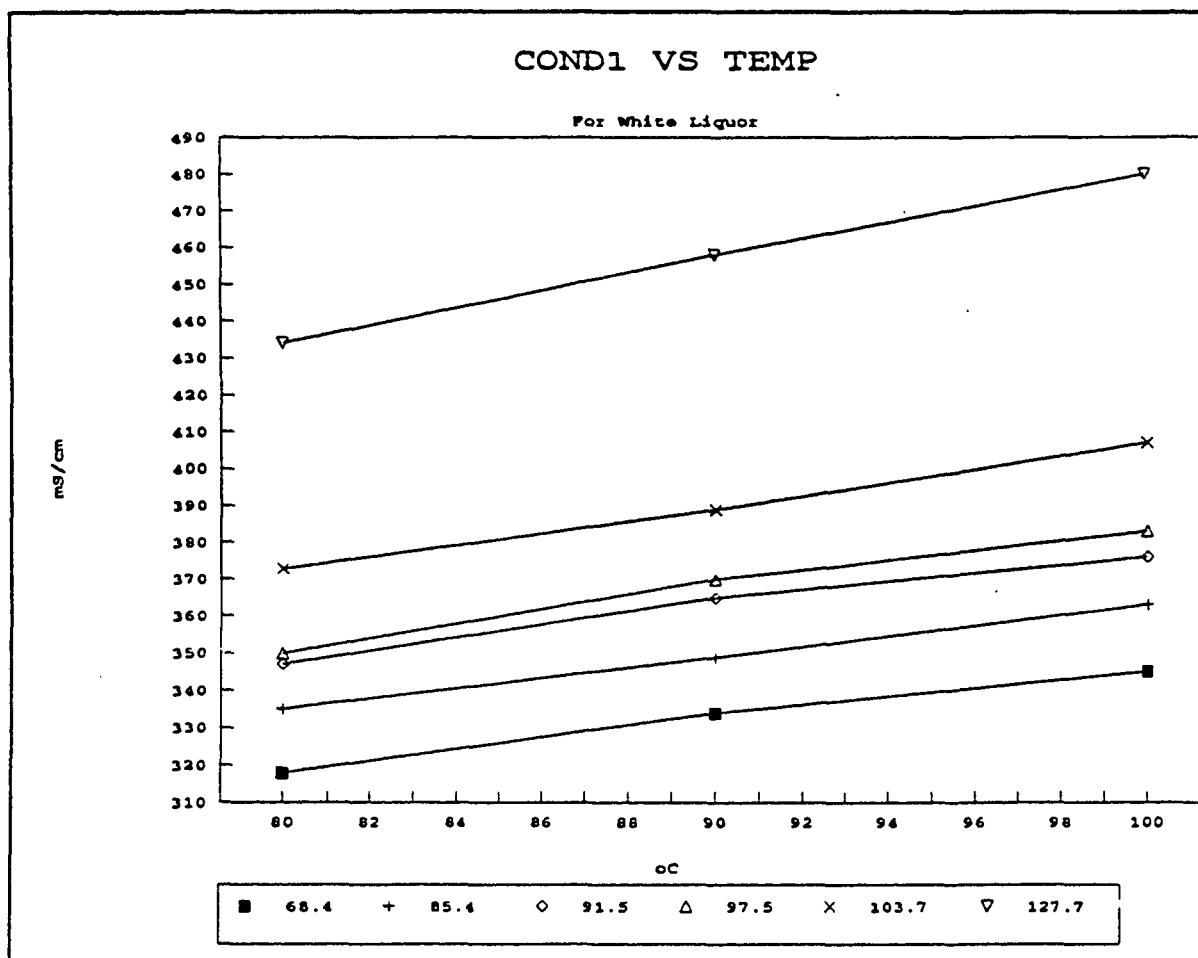
COND1 VS TEMP
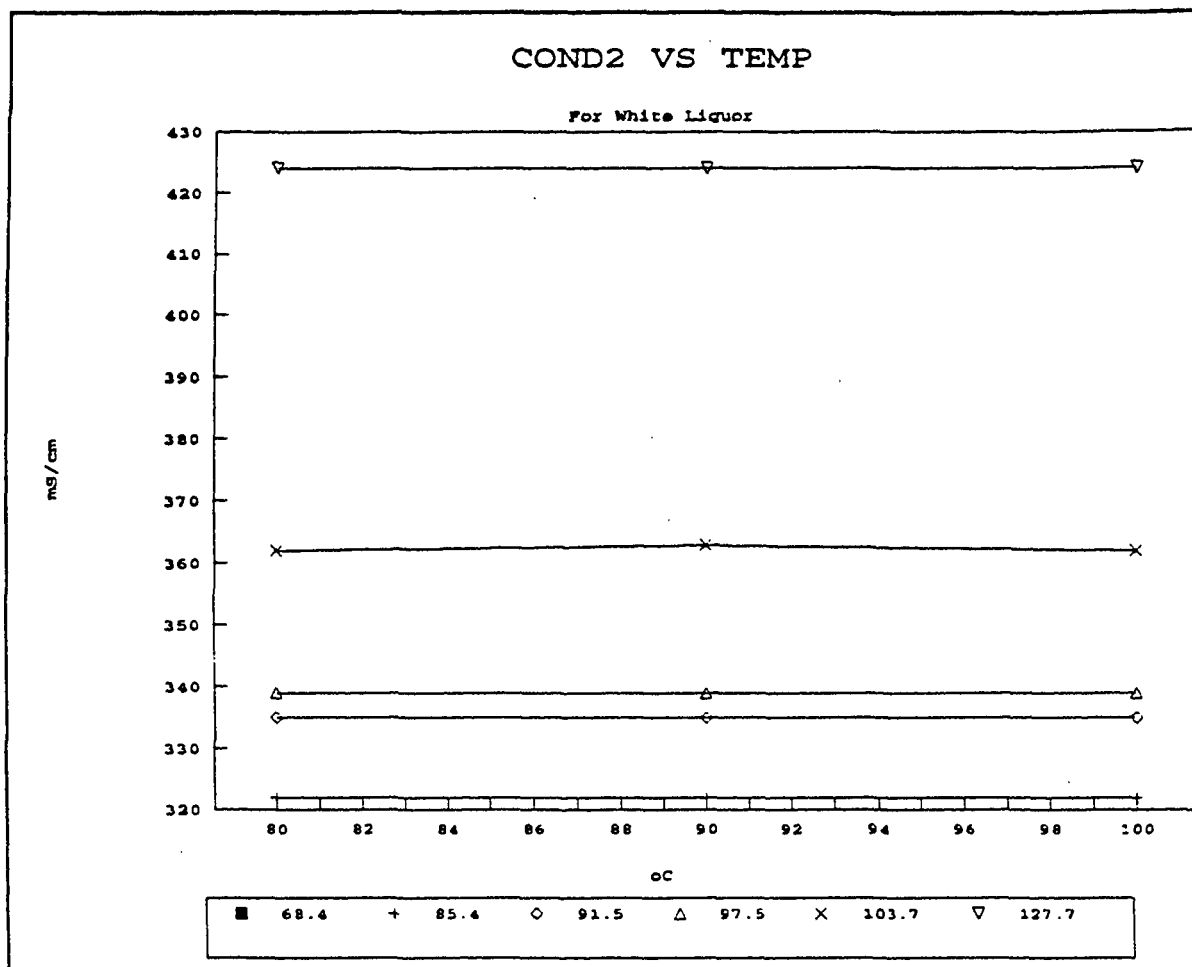
For White Liquor

Figure 6

COND2 VS TEMP

For White Liquor

Figure 7

COND3 VS TEMP

For White Liquor

Legend: ■ 68.4   + 85.4   ◇ 91.5   △ 97.5   × 103.7   ▽ 127.7

Figure 8
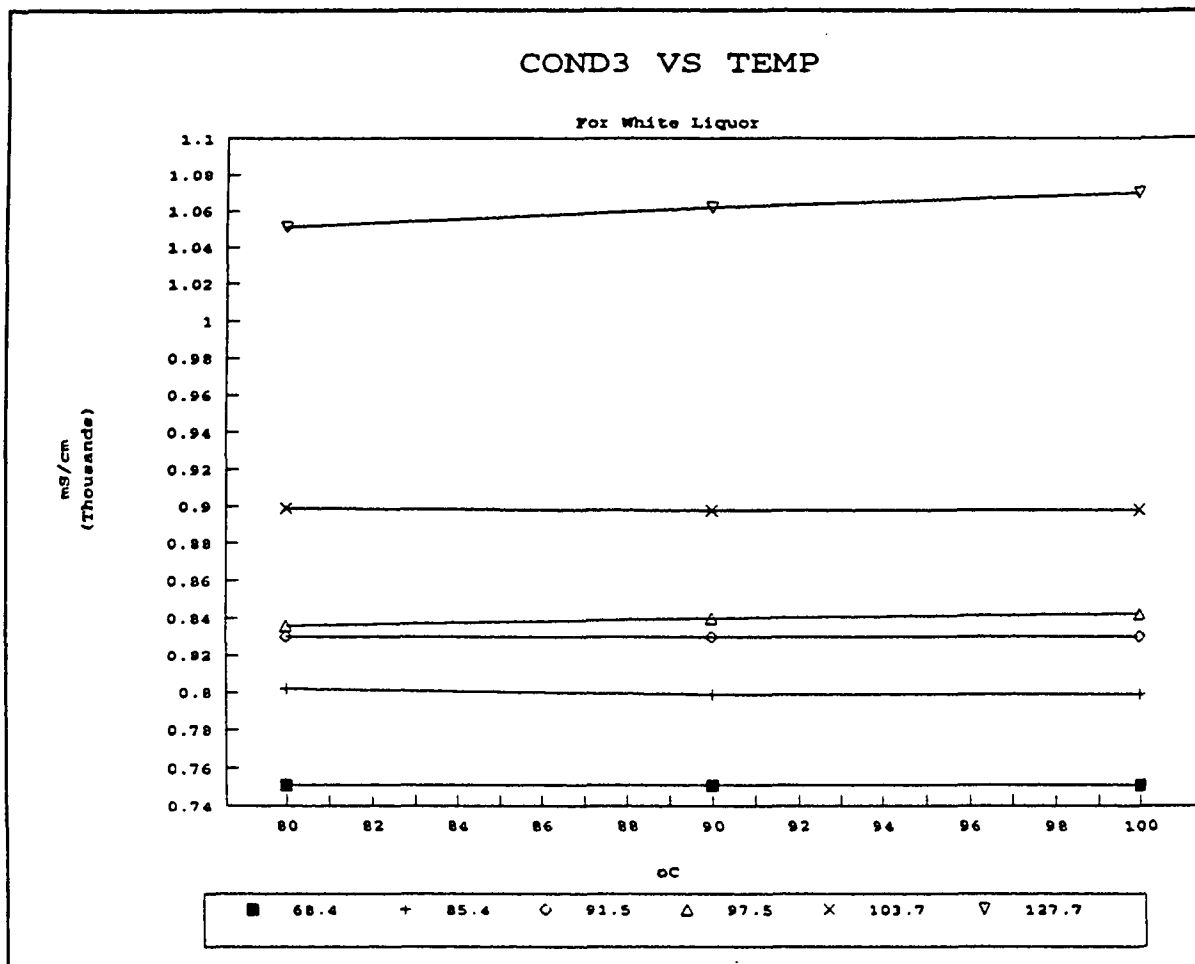
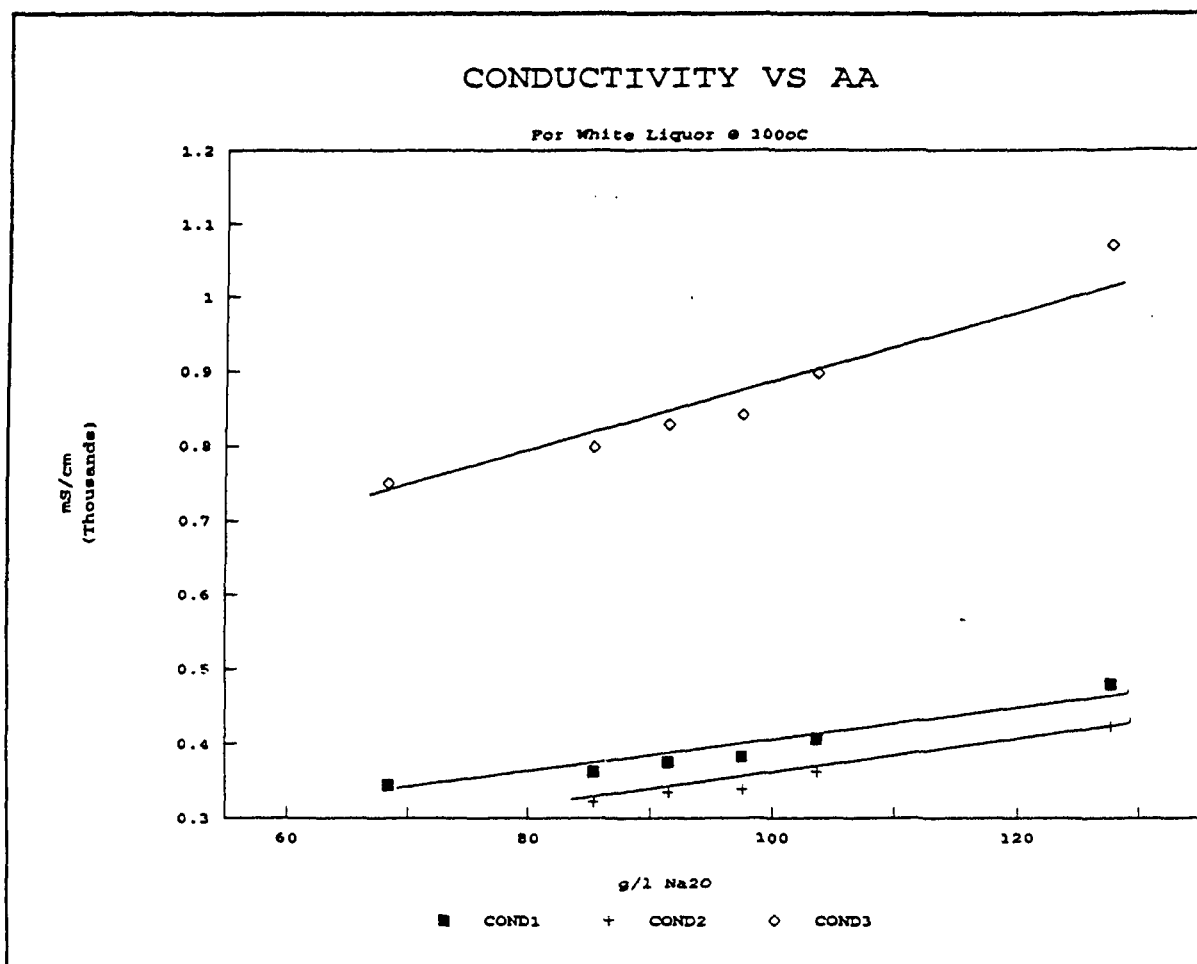CONDUCTIVITY VS AA

For White Liquor @ 100oC

Figure 9

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PROJECT 3716

ESTIMATING YIELD FOR THE PREDICTION OF END-USE

PROPERTIES IN SEMI-CHEMICAL PULPING

RESEARCH REVIEW

April 2, 1991

Clark P. Woitkovich

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

IPST GOAL:

To improve the control of semichemical pulping processes.

OBJECTIVE:

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

ESTIMATING YIELD FOR THE PREDICTION OF

END-USE PROPERTIES IN SEMI-CHEMICAL PULPING

OBJECTIVES:

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

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

INTRODUCTION:

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

$$\% \text{ Yield} = \frac{\text{weight of pulp X pulp consistency}}{\text{weight of wood X wood consistency}} \times 100$$

An accurate gravimetric determination of this quantity requires precise measurements of weight and consistency, a difficult task on an industrial-scale process line. In practice, yield is usually inferred indirectly from measurements of lignin content. Although lignin content can be quantified directly ("Klason" or acid-insoluble lignin; Tappi Method T222 om-88), the method is relatively laborious and time-consuming. A more typical approach to the estimation of yield is to estimate lignin content by determining pulp kappa number (Tappi Method T236 cm-85). Yield can then be estimated by referring to a predetermined laboratory correlation that relates yield to kappa number.

This approach can be relatively quick but suffers from two important limitations. First, any correlation between lignin content and yield is tenuous at best. This is because a measurement of lignin content ignores the other two principal constituents of pulp: cellulose and hemicellulose. If, for example, the selectivity of a pulping reaction were to be negatively altered, it is conceivable that a yield decrease could be accompanied by an actual increase in lignin content. For this reason, it becomes desirable to develop a method that is sensitive to not one, but all of the major chemical constituents found in wood pulp.

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

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

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

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

BACKGROUND

Near-infrared Spectroscopy

In near-infrared spectroscopy, a sample is sequentially irradiated with bands of light energy having an extremely narrow wavelength range (approximately 10 nanometers). During exposure to each individual band, the absorption of radiation is measured indirectly by detecting the amount of incident energy that has interacted with and reflected from the sample. Exposing a sample to a continuum of such bands results in absorption measurements that cover a wide spectral region (1100 to 2500 nm). A plot of absorption as a function of wavelength for a particular sample is called its absorption spectrum.

Near-infrared absorption spectra consist primarily of overlapping bands that result in broad spectral features from which it is difficult to derive structural information. The spectra, however, have been found to be very useful for quantitative analysis and the technique is widely employed as an analytical tool in a variety of industries. The appeal of NIRS lies in its fast analysis time with minimal sample preparation, its relatively compact and rugged design, and its recently emerged compatibility with fiber optic technologies. These attributes have rendered NIRS an ideal candidate for several on-line applications in the pulp and paper industry.

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

Ultraviolet-visible Luminescence Spectroscopy

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

The emitted radiation, or luminescence, is actually comprised of two different forms of emission: phosphorescence and fluorescence. Phosphorescence is distinguished from fluorescence by the long lived emission after extinction of the excitation source. Fluorescence generally occurs within 10^{-9} to 10^{-7} seconds of excitation while phosphorescence has a long lifetime varying from 10^{-6} to 10^{+2} seconds. Although the luminescence spectrometer used in this study offers the capability of detecting either phosphorescence or fluorescence, only the fluorescent behavior of pulps has been explored to date.

As in NIRS, UV-VIS fluorescence spectroscopy employs an excitation monochromator to sequentially irradiate a sample with bands of light energy having a narrow wavelength range.

Unlike the NIRS instrument, however, the fluorescence spectrometer is equipped with a second monochromator on the emission side of the sample. This optical arrangement provides the capability of acquiring three distinctly different types of spectral information.

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

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

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

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

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

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

EXPERIMENTAL APPROACH:

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

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

RESULTS AND DISCUSSION:

Near-infrared Spectroscopy

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

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

Because baseline shift can also be caused, at least in part, by a variety of sampling-related factors, the feature is virtually useless as a predictor of a specific sample characteristic. It therefore becomes desirable to compensate for baseline differences so that differences in other spectral features may be enhanced. A convenient way of accomplishing this is to mathematically transform raw spectral data into second derivative spectra. The second derivative inverts absorption maxima to minima and increases the apparent resolution in a spectrum.

Second derivative spectra obtained from the raw spectral data shown in Figure 1 are depicted in Figure 3. Single-sample variability appears significantly reduced in the transformed spectra while narrow-band differences between the two samples are enhanced.

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

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

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

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

Ultraviolet-Visible Fluorescence Spectroscopy

Figure 14 shows UV-VIS fluorescence excitation spectra acquired from two fluffed, air-dried pulps having different yield levels. In the acquisition of this data, fluorescence intensity was detected at a wavelength setting of 490 nm while the excitation wavelength was varied continually from 260 nm to 470 nm. Prominent differences are evident between the two spectra. The broad peak centered at 400 nm and the sharper feature at approximately 430 nm exhibit significantly decreased intensity in the lower yield sample.

As with the NIRS data, it is possible that the observed spectral differences are not entirely attributable to yield differences. Instrument variability, sample variability, and surface effects (such as particle size distribution) may be contributing. In light of this uncertainty, however, these preliminary results remain encouraging because of the magnitude of the observed differences.

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

CONCLUSIONS:

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

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

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

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

EXPERIMENTAL:

Sample Preparation

Chestnut oak chips were kindly supplied by the Willamette Industries pulp mill located Hawesville, Kentucky. Prior to use, the chips were hand-sorted to isolate approximately 900 grams of chips (oven-dried basis) that were roughly uniform in size. After overnight moisture equilibration, nine samples, with a combined weight of over 200 grams (oven-dried basis), were removed for consistency determination (TAPPI Test Method:

T258 om-89). These samples were placed in drying tins and dried in a 105°C oven for at least 24 hours. The resulting consistency measurements gave an average of 0.619 with the standard deviation (S_w) equal to $\pm$ 0.003.

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

Liquor to wood ratio:	4:1
Na_2SO_3: (as Na_2SO_3 on o.d. wood)	10%
Na_2CO_3: (as Na_2CO_3 on o.d. wood)	3%
Temperature:	170°C

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

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

Pulp yield was calculated as follows:

$$\% \text{ Yield} = \frac{\text{weight of pulp X pulp consistency}}{\text{weight of wood X wood consistency}} \times 100$$

$$= \frac{W_p\, C_p}{W_w\, C_w} \times 100$$

The approximate error associated with a given pulp yield value is $\pm$ 0.7. The limits on the range of error were calculated as:

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

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

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

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

Instrumentation

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

All spectra reported here were acquired from samples mounted in a quartz-windowed stationary sample cell. With this sampling arrangement, the area of sample exposed to incident radiation was approximately 2 cm X 4 cm. To compensate for variations in light source energy output and detector response over the wavelength range covered, sample data were corrected by subtracting data acquired from an internal ceramic reference.

The instrument used for fluorescence spectroscopy was a Perkin-Elmer LS-5B luminescence spectrometer controlled by a PC's Limited System 200 personal computer. The excitation monochromator covers the range from 230 to 720 nm and the emission monochromator can range from 250 to 800 nm. The instrument utilizes a stroboscopic (60Hz) xenon light source and a standard photomultiplier detector.

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

FUTURE WORK

Near-infrared Spectroscopy

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

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

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

The different analysis procedures can be evaluated by monitoring the degree of correlation, in the calibration set, between NIRS yield estimations and laboratory yield measurements. The degree of correlation can be assessed via the standard statistical techniques described below.

In evaluating the effect of sample presentation form, three different forms will be used: sheet, fluffed, and unfluffed. The results obtained from these sample forms will provide an indication of the importance of surface homogeneity in the analysis of reflectance. The unfluffed pulp is to be prepared by hand-disintegrating the final washed pulp pad. It contains many, relatively large fiber clumps, or knots. The prevalence of the clumps is significantly decreased by applying the fluffing treatment, and almost completely eliminated in a good quality handsheet. It should be relatively staightforward to quantify surface homogeneity by applying image analysis routines to low magnification optical or electron micrographs of the samples as packed for analysis.

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

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

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

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

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

Raw absorption data is rarely used to develop a calibration equation because the results can be much improved if the raw data is enhanced by mathematical transformation. For this reason, several math options are available in the NIRSystems software including a variety of smoothing

algorithms, first, second, third, and fourth derivatives and a Kubelka-Munk transformation. Although a second derivative transformation is recommended for inhomogeneous samples with broad particle size distribution, the other transformations should be explored. If it turns out that one of the derivative transformations is most useful, the transform algorithm may be further optimized by adjusting specific derivation parameters (i.e. gap size and segment size).

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

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

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

Ultraviolet-Visible Fluorescence Spectroscopy

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

One factor that may further limit our options in the case of the fluorescence work, at least temporarily, is that the operating software lacks derivative transformation capabilities. Since these capabilities appear to be crucial in the analysis of the NIRS data, it may be desirable to develop the appropriate software in order to evaluate any potential benefit that may be realized in applying the transformations to the fluorescence spectra.

Another capability that is missing from the fluorescence software is the automated stepwise linear regression that searches a spectrum and identifies the single wavelength that gives the best correlation between spectral intensity and yield. This should not present a problem, however, because a quick visual inspection of the fluorescence spectra, and the NIR spectra for that matter, reveals, fairly obviously, those wavelengths that offer the best yield correlation potential.

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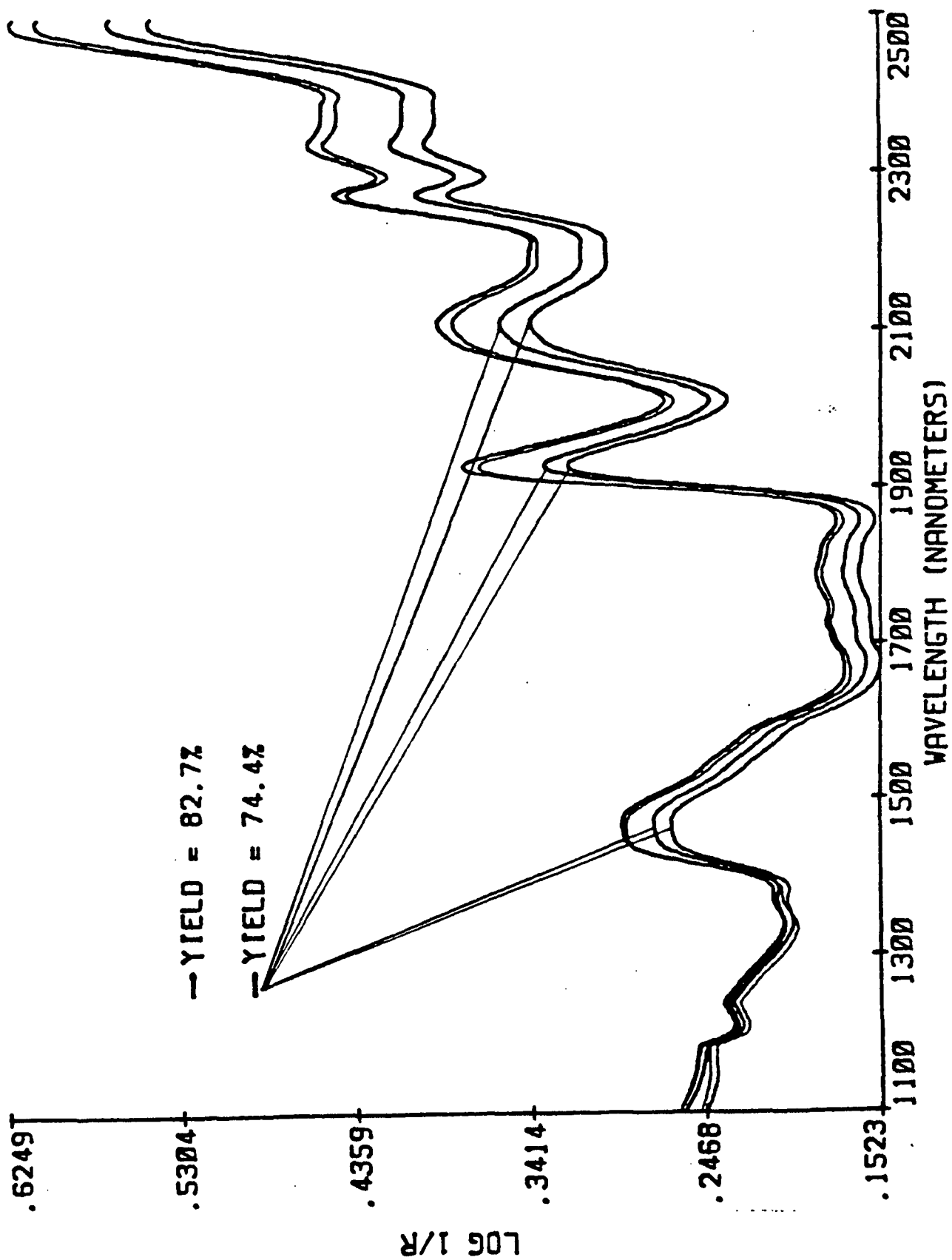
AIR-DRIED PADS

—YIELD = 82.7%
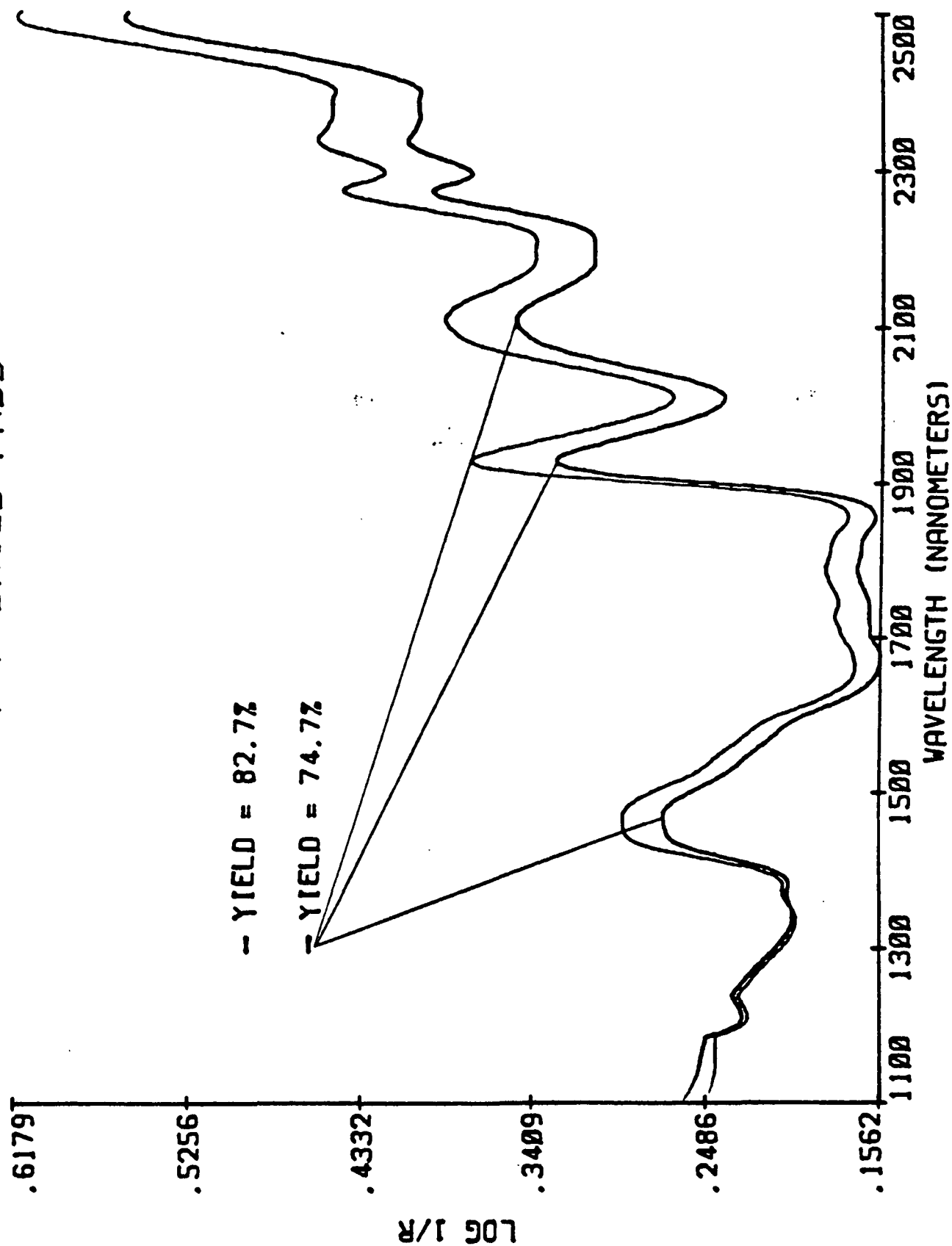—YIELD = 74.4%

LOG 1/R

WAVELENGTH (NANOMETERS)

FIGURE 1

AIR-DRIED PADS

— YIELD = 82.7%
— YIELD = 74.7%

LOG 1/R

WAVELENGTH (NANOMETERS)

FIGURE 2
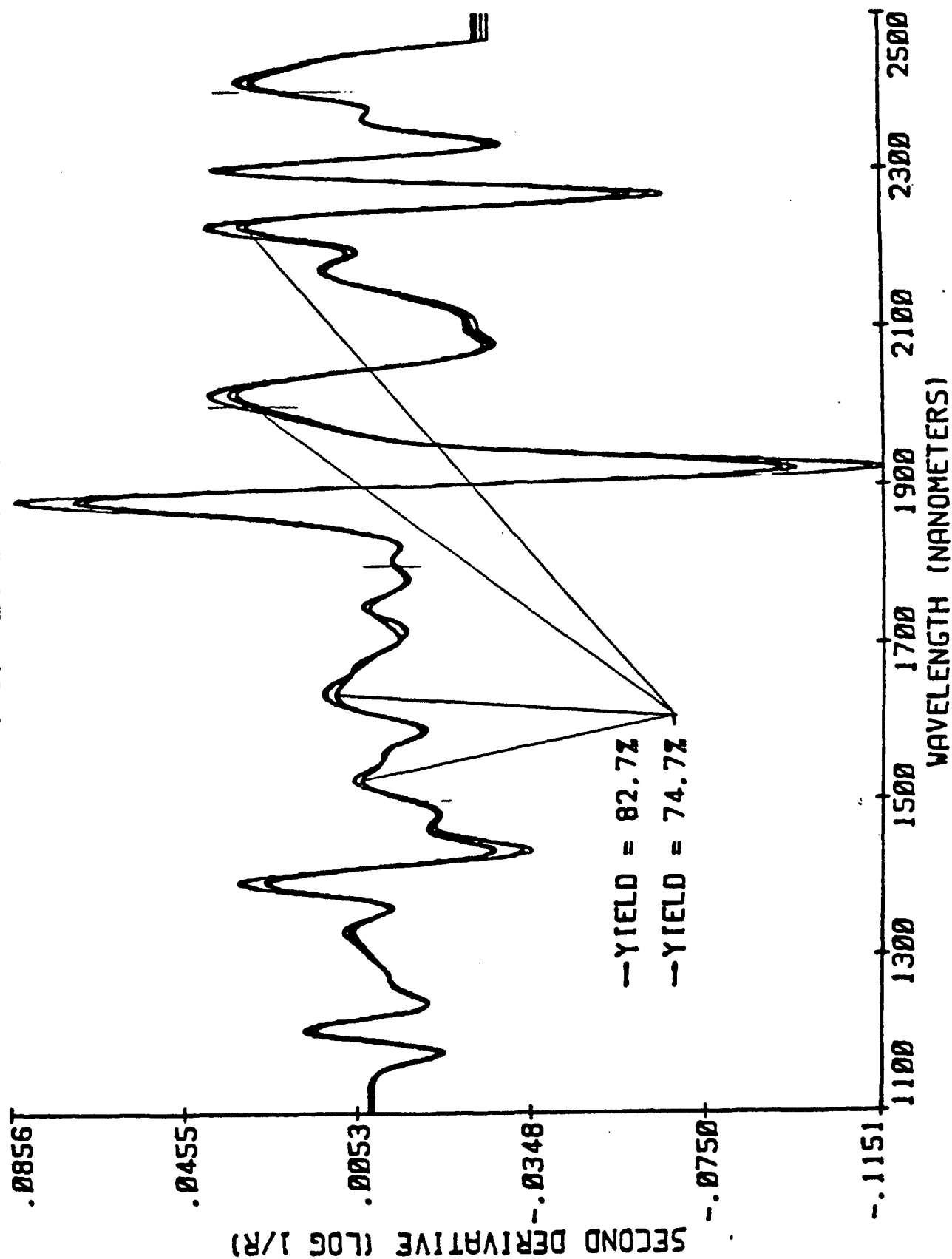
AIR-DRIED PADS

FIGURE 3

—YIELD = 82.7%
—YIELD = 74.7%

SECOND DERIVATIVE (LOG 1/R)

WAVELENGTH (NANOMETERS)

AIR-DRIED PADS

—YIELD = 82.7%
—YIELD = 74.7%

SECOND DERIVATIVE (LOG 1/R)

WAVELENGTH (NANOMETERS)

FIGURE 4

-210-

FIGURE 5

AIR-DRIED PADS

SECOND DERIVATIVE (LOG 1/R)

WAVELENGTH (NANOMETERS)

— YIELD = 82.7%

— YIELD = 74.7%
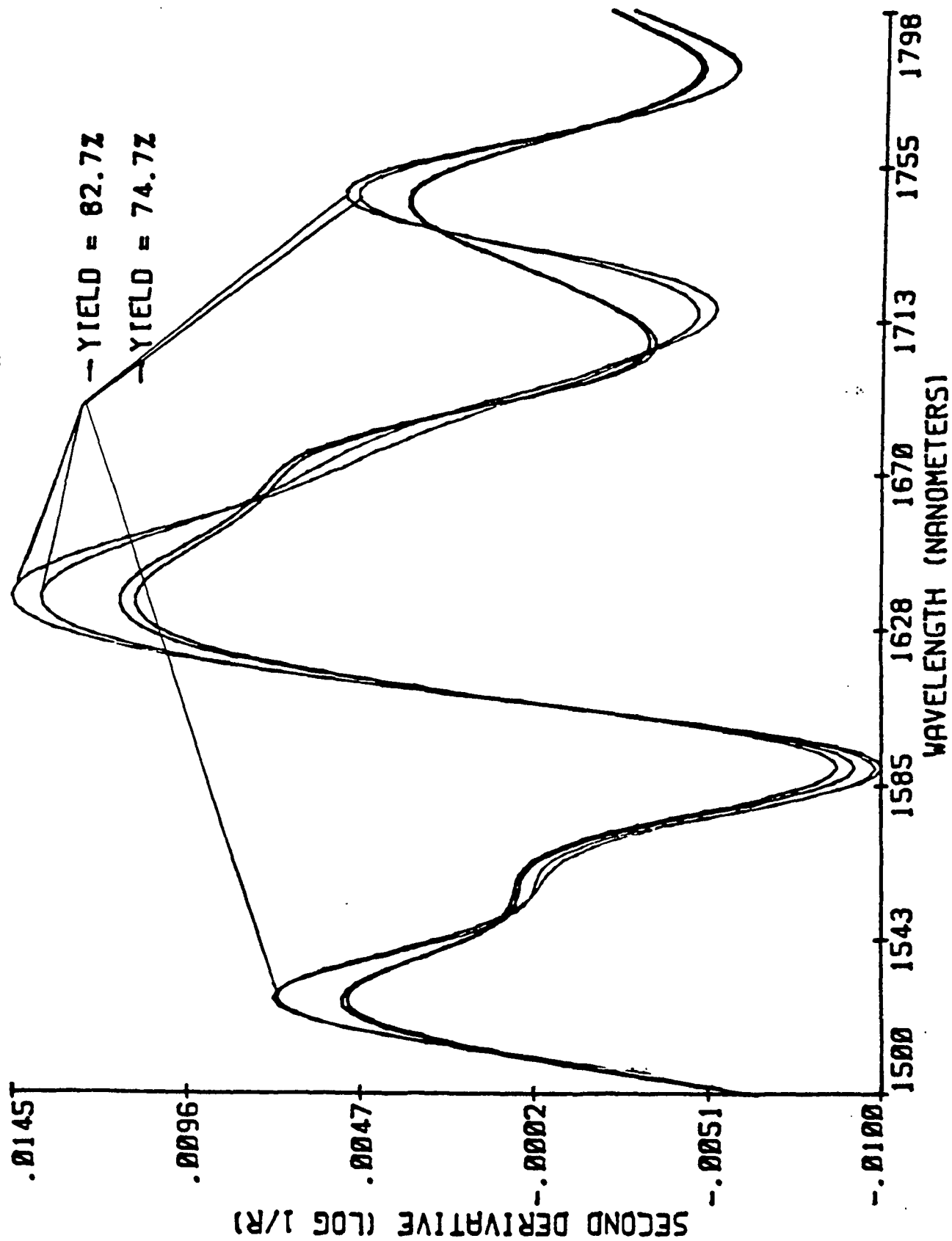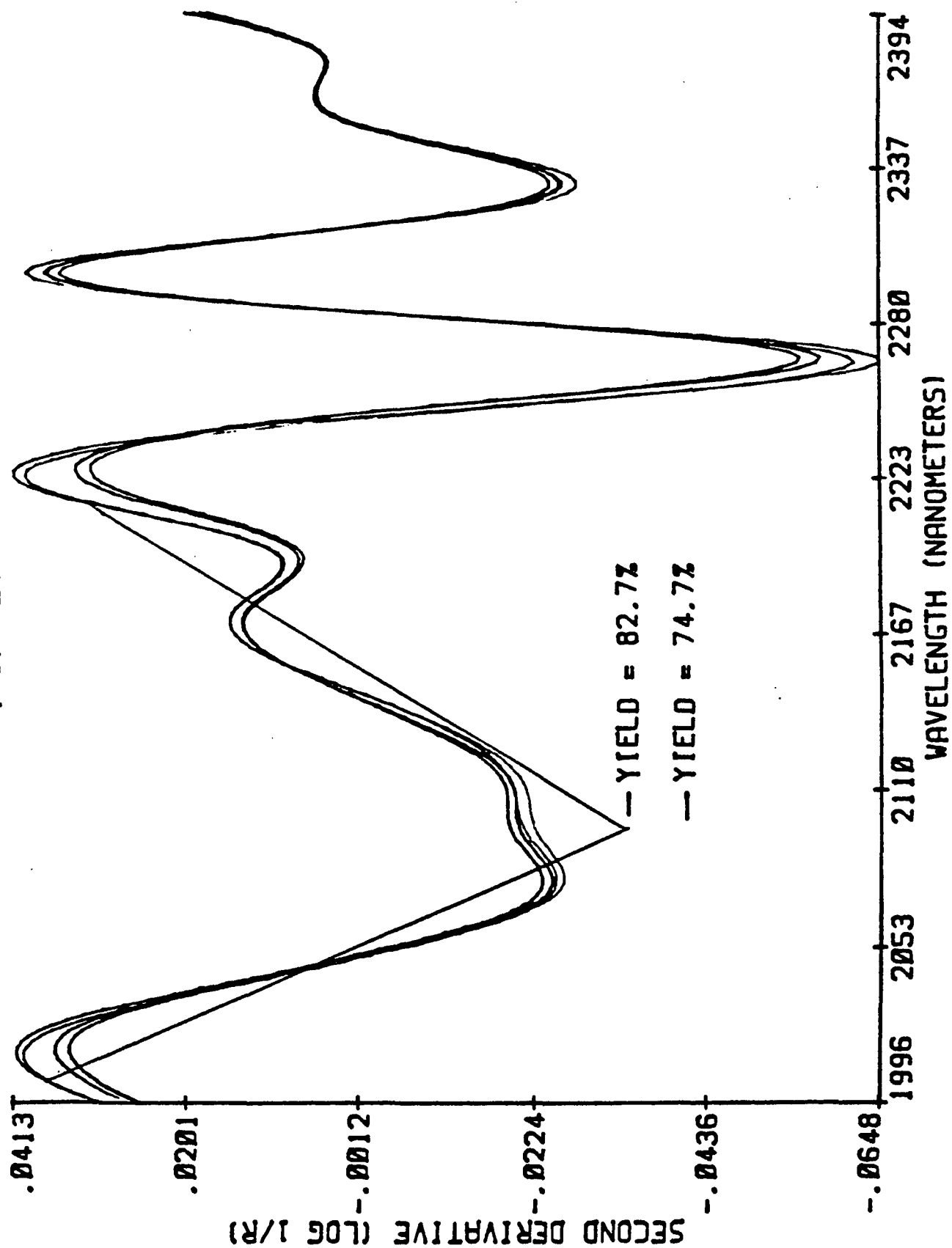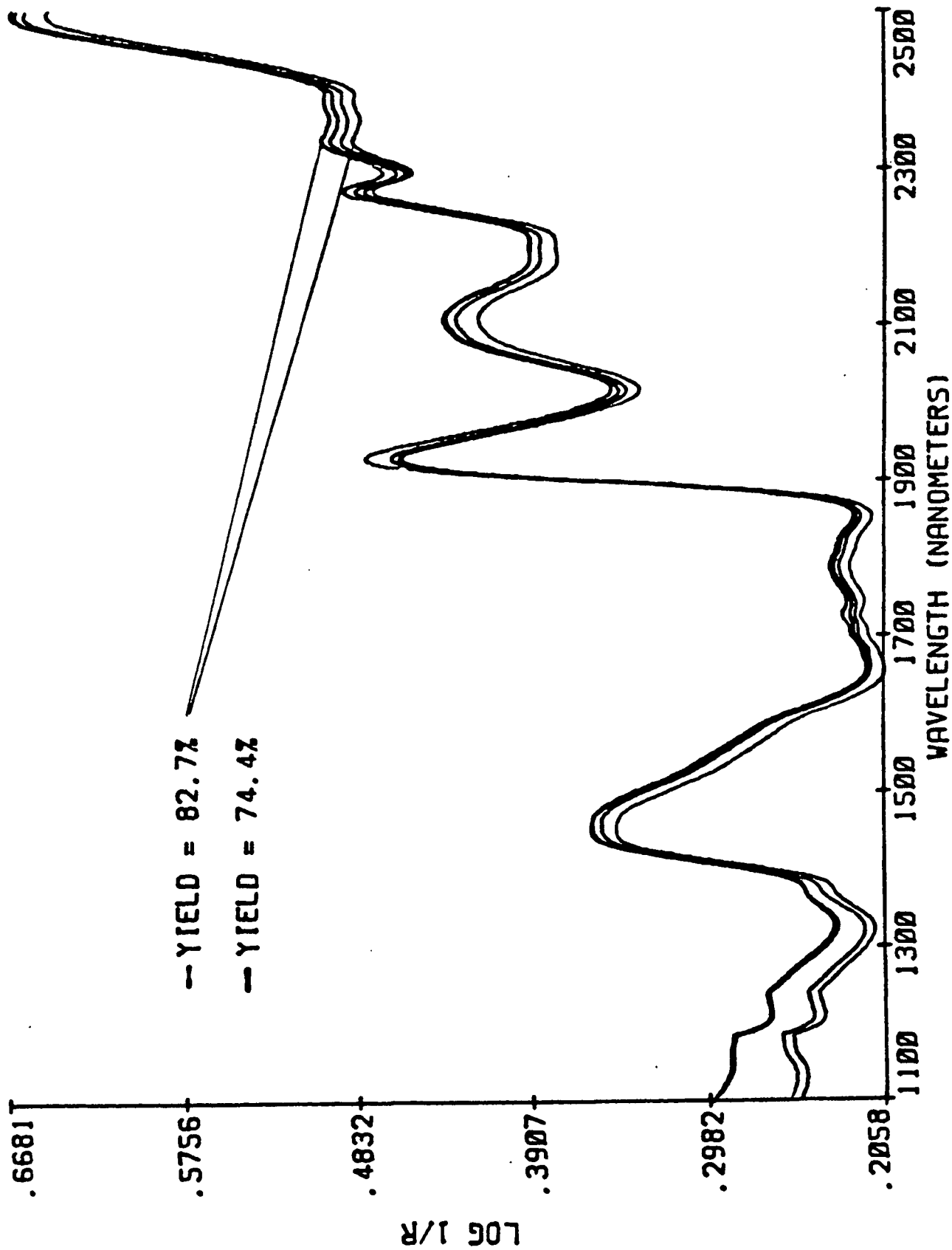
AIR-DRIED FLUFF

FIGURE 6
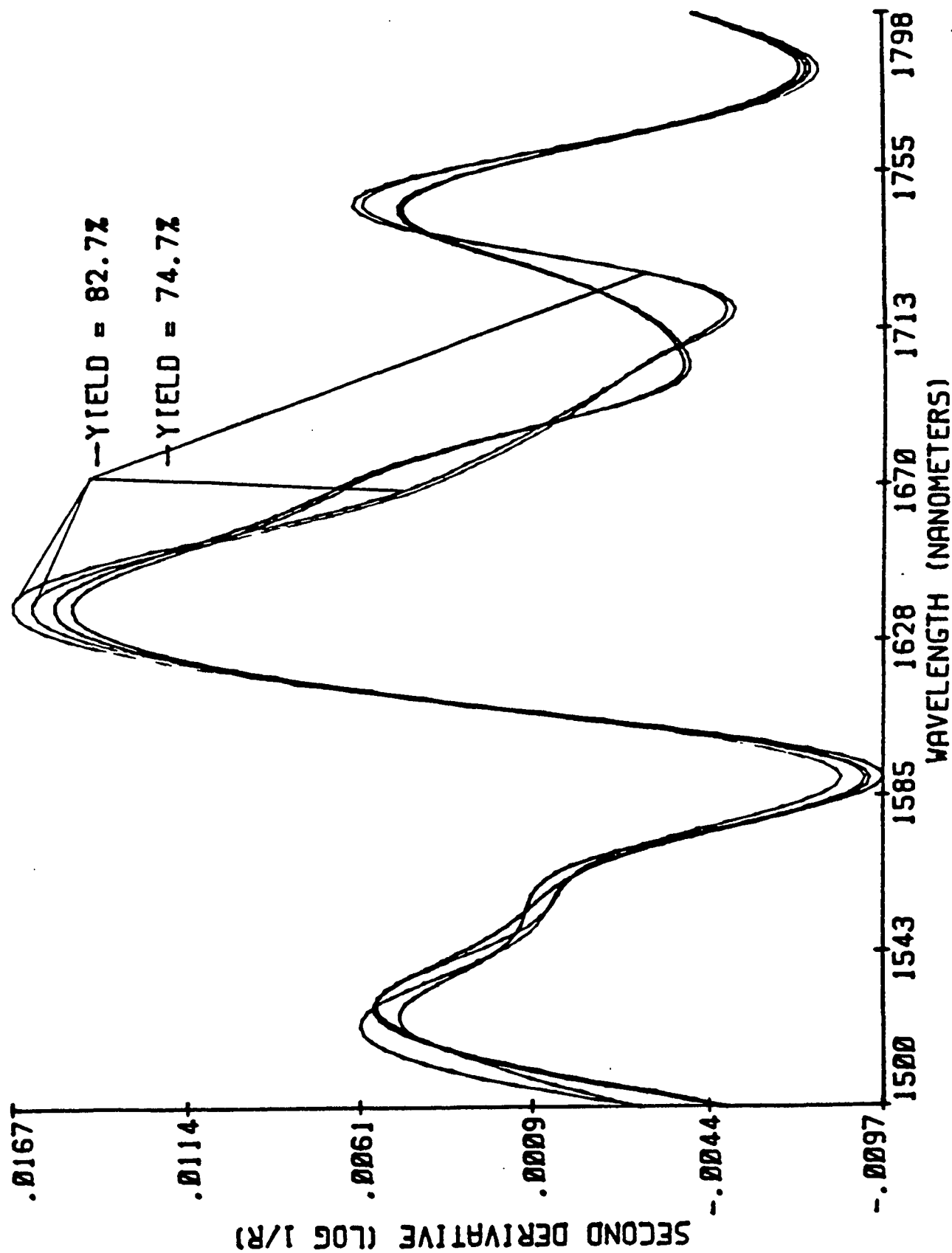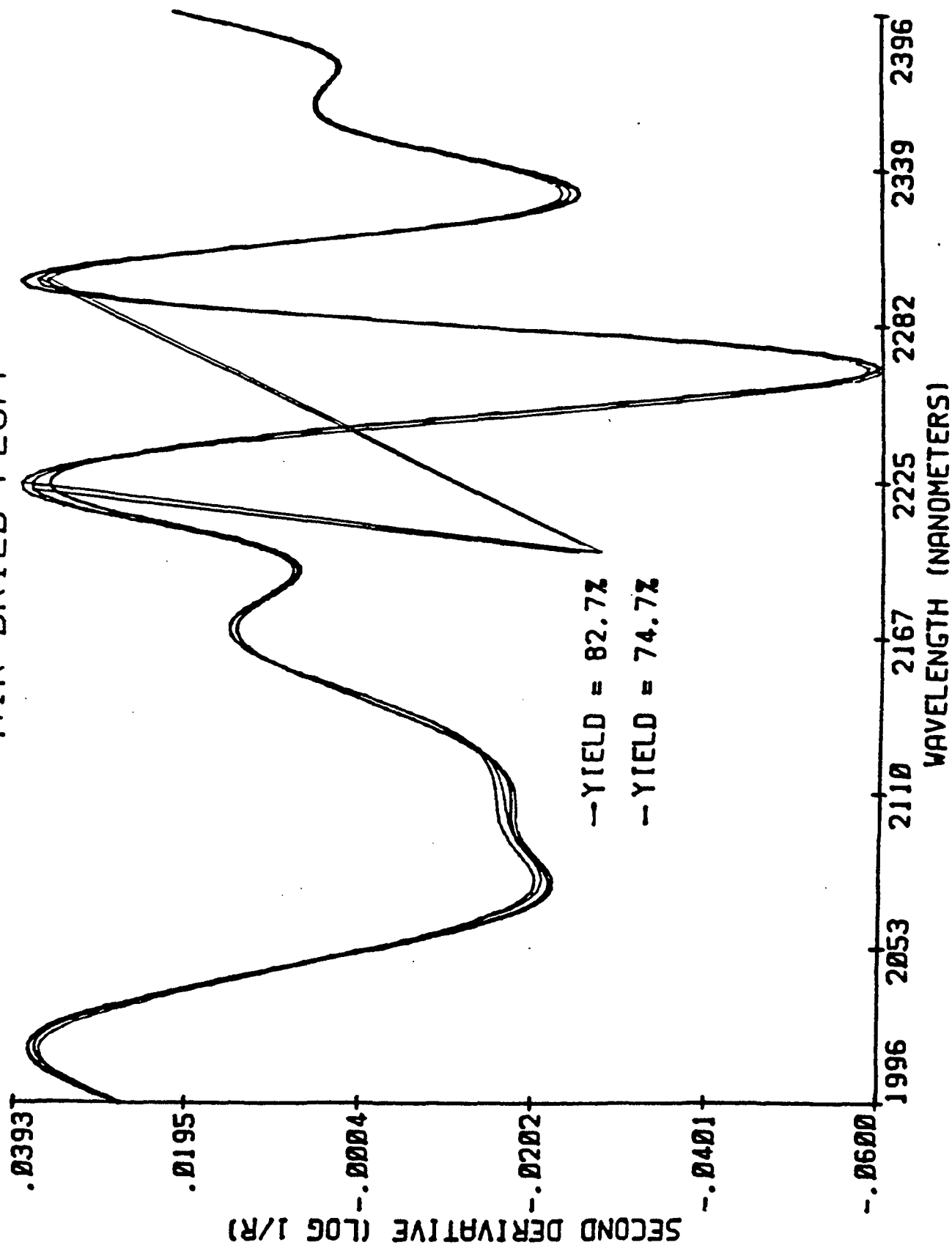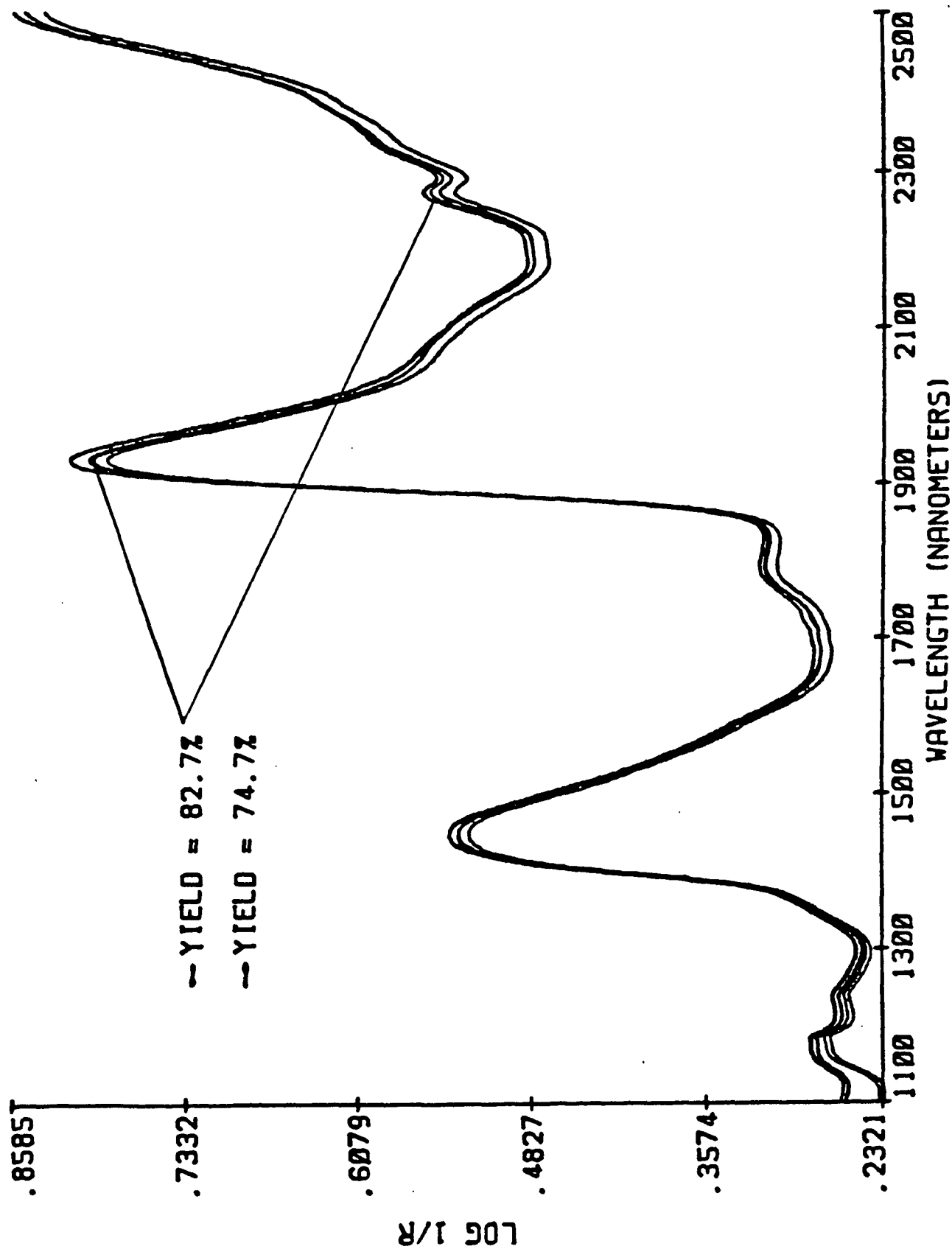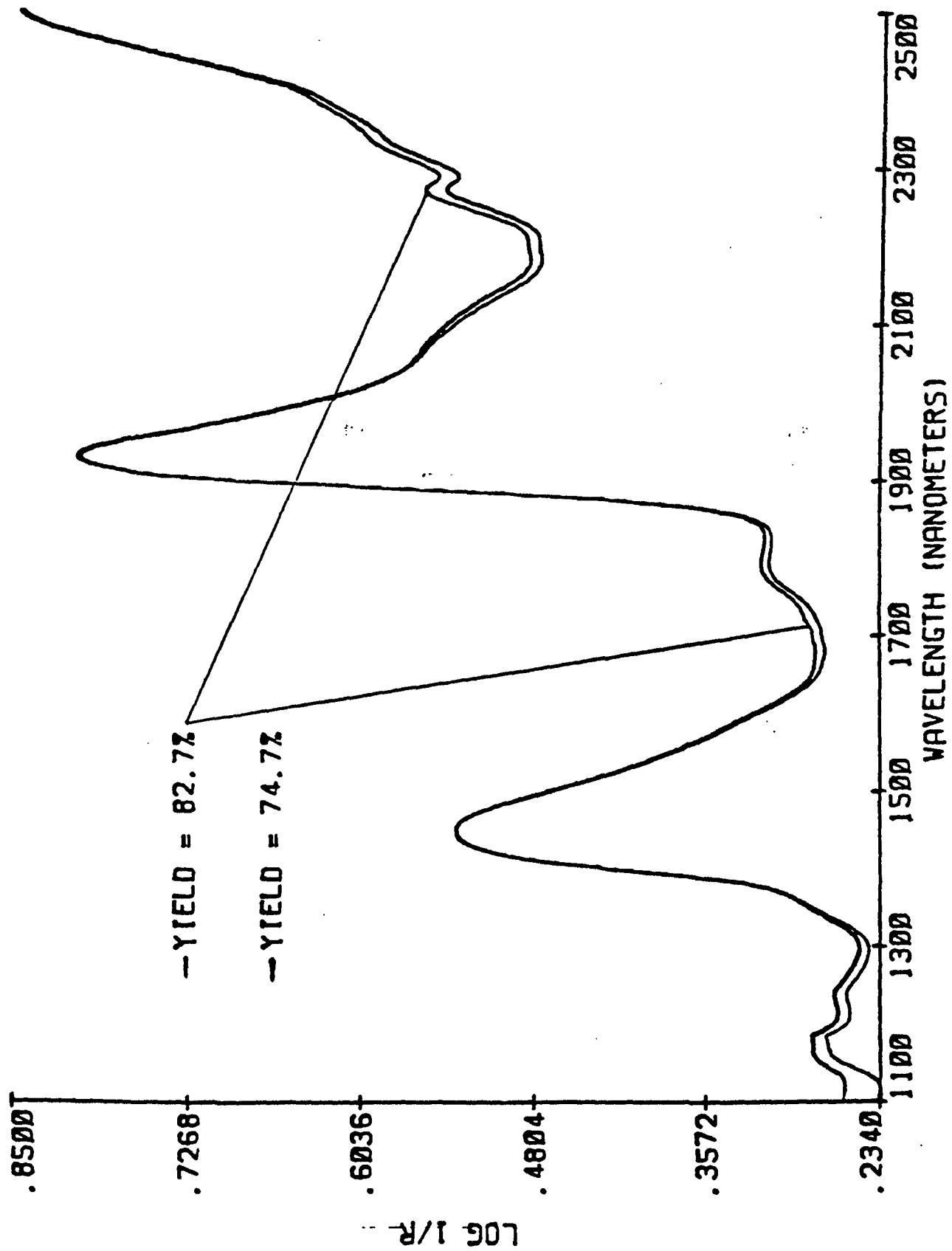
WAVELENGTH (NANOMETERS)

LOG 1/R

—YIELD = 82.7%
—YIELD = 74.4%

FIGURE 7

AIR-DRIED FLUFF

—YIELD = 82.7%

—YIELD = 74.7%

FIGURE 8

SECOND DERIVATIVE (LOG 1/R)

WAVELENGTH (NANOMETERS)

-214-

FIGURE 9

—215—

FIGURE 10

MOIST FLUFF

—YIELD = 82.7%

—YIELD = 74.7%

LOG 1/R ..

.8500

.7268

.6036

.4804

.3572

.2340

1100 1300 1500 1700 1900 2100 2300 2500

WAVELENGTH (NANOMETERS)

FIGURE 11

FIGURE 12

MOIST FLUFF

—YIELD = 82.7%
—YIELD = 74.7%

FIGURE 13

SECOND DERIVATIVE (LOG 1/R)

WAVELENGTH (NANOMETERS)

-219-

Excitation Spectra

Em λ = 490 nm

82.7%

74.7%

Fluorescence Intensity

Excitation Wavelength (nm)
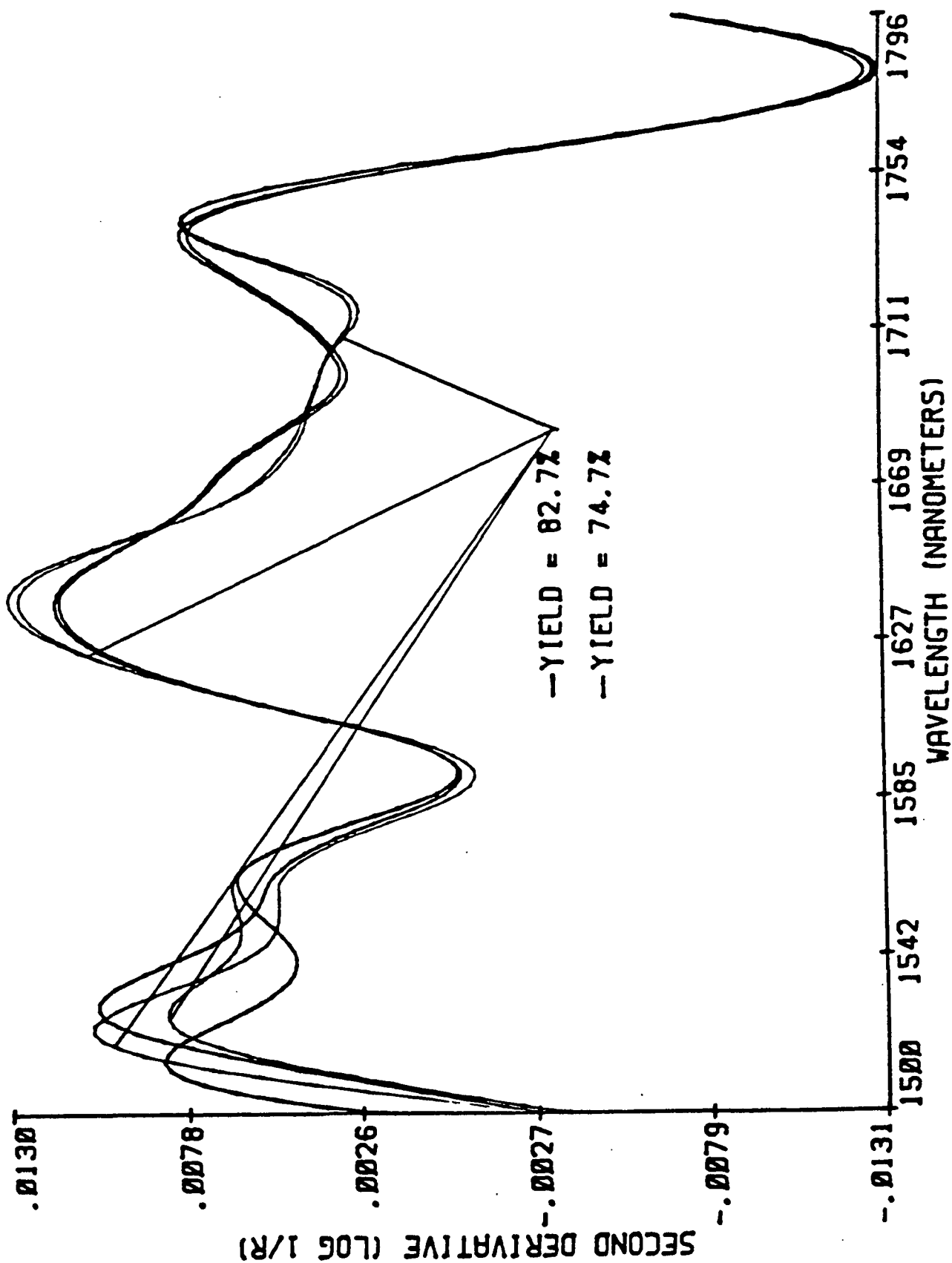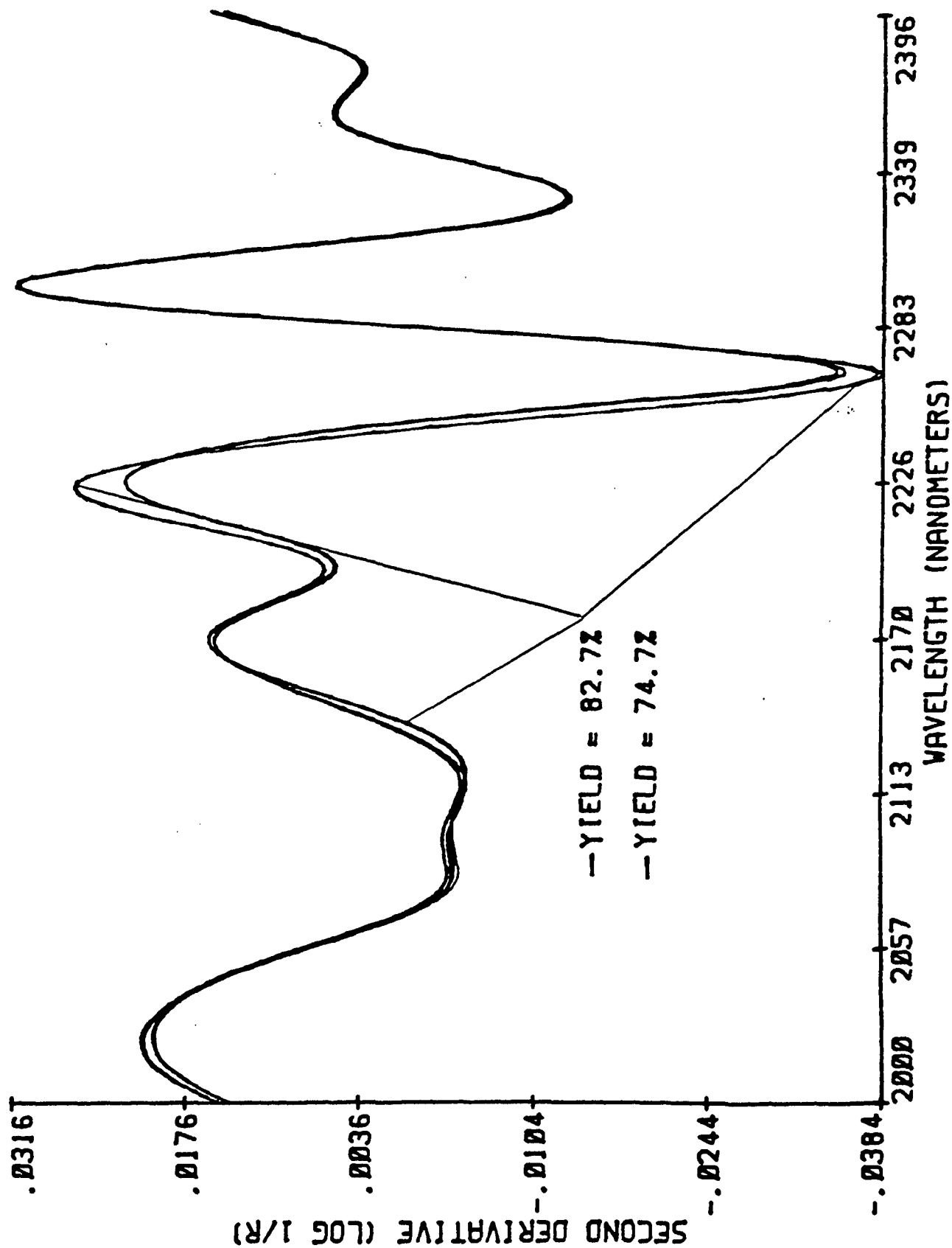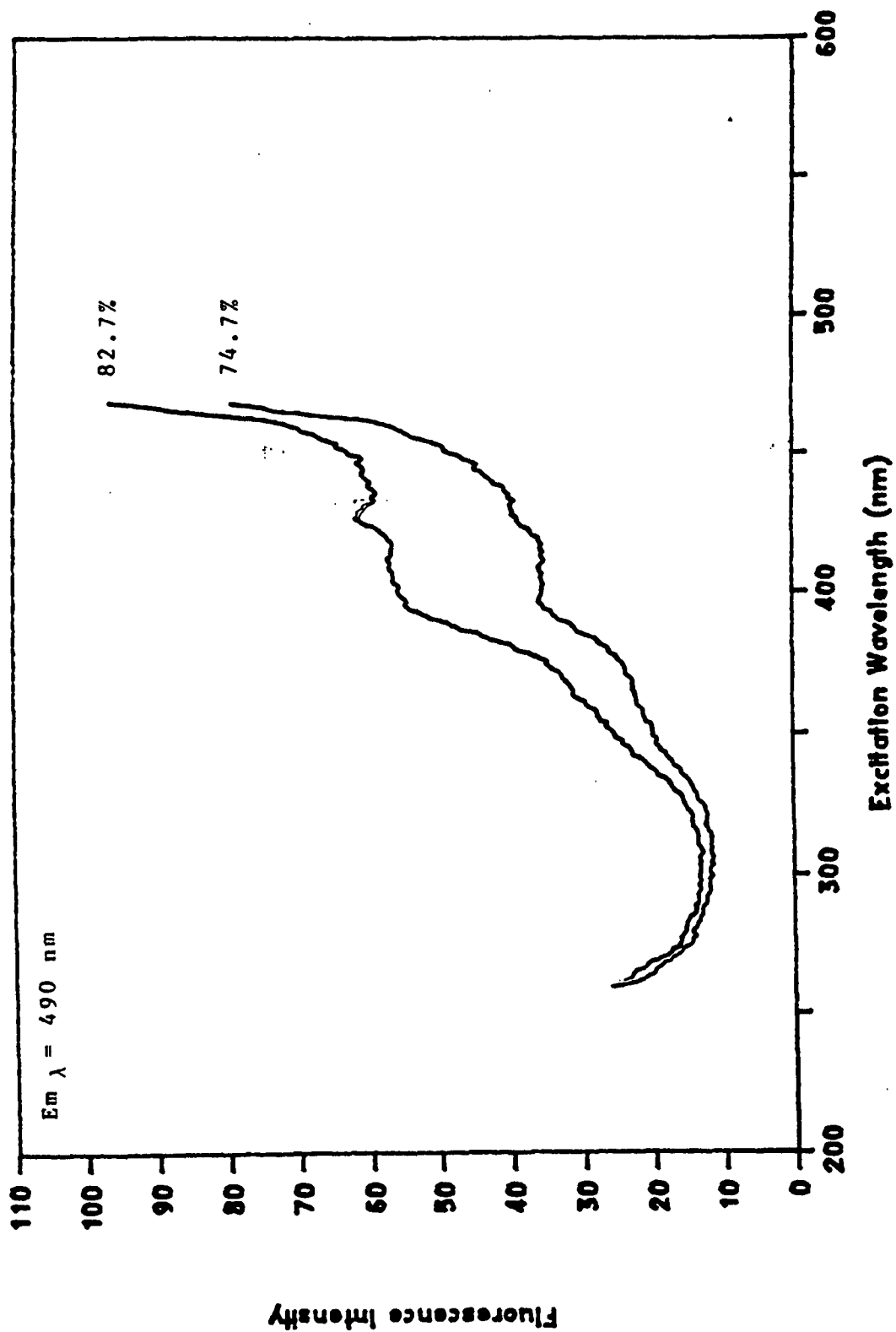
FIGURE 14

Excitation Spectra

Wet vs. Dry

74.7% Yield
Em$_\lambda$ = 490 nm

Fluorescence Intensity

Dry

Wet

Excitation Wavelength (nm)

FIGURE 15