



*Institute of Paper Science  
and Technology*

**SULFUR-FREE SELECTIVE PULPING**

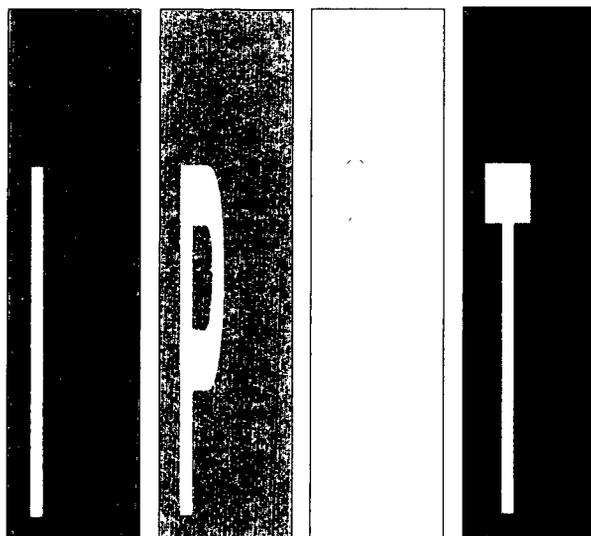
**Project 3661**

**Final Report**

**to the**

**MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY**

**March 1, 1998**



*Atlanta, Georgia*

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

**SULFUR-FREE SELECTIVE PULPING**

Project 3661

Final Report

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

D.R. Dimmel

March 1, 1998

**Forward:**

The research described herein began with the Ph.D. thesis of John Wozniak (IPC, June 1988) and continued, with financial support from the Department of Energy, as IPST Project 3661 from the Fall 1988 to the Fall 1997 (with a 1.5 year interruption in the middle). The DOE-funded project was a joint effort between IPST and the National Energy Renewable Laboratory (NREL). There have been several DOE annual reports and open literature publications in the last eight years. The enclosed report focuses on research conducted in the last two years; however, the earlier research is summarized and referenced. The report is the final annual report submitted to DOE. A reader wishing more detail should contact Donald Dimmel at IPST (donald.dimmel@ipst.edu or 404-894-9705).

**FINAL-FEBRUARY 1998**

**SULFUR-FREE SELECTIVE PULPING:  
SYNTHESIS OF NEW PULPING  
CATALYSTS FOR THE PULP AND  
PAPER INDUSTRY**

**FINAL REPORT**

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## TABLE OF CONTENTS

TABLE OF CONTENTS .....	1
LIST OF FIGURES .....	3
LIST OF TABLES .....	4
1.0 INTRODUCTION/EXECUTIVE SUMMARY .....	5
2.0 PROJECT BACKGROUND .....	7
3.0 RESEARCH DETAILS - OXIDATION OF LIGNIN AND LIGNIN MODELS .....	8
3.1 Introduction .....	8
4.0 OXIDATIONS WITH NITROGEN DIOXIDE .....	9
4.1 Introduction .....	9
4.2 Oxidation of Model Compounds - Catalytic NO <sub>2</sub> .....	11
4.3 Oxidation of Model Compounds - Catalytic NO <sub>2</sub> in the Presence of Metal Catalysts .....	16
4.4 Oxidations of Lignin - Catalytic NO <sub>2</sub> .....	17
4.5 Oxidations of Model Compounds - Stoichiometric NO <sub>2</sub> .....	18
4.5.1 Stoichiometry of NO <sub>2</sub> Oxidations .....	18
4.5.2 Mechanistic Studies of Stoichiometric NO <sub>2</sub> Oxidations .....	18
4.5.3 Consecutive Oxidations of Syringaldehyde and Syringyl Alcohol .....	20
4.6 Oxidations of Lignin - Stoichiometric NO <sub>2</sub> .....	20
4.6.1 Fate of NO <sub>2</sub> in Lignin Oxidations .....	21
4.7 Identification of Suitable Lignin Sources .....	22
4.7.1 Changing Pulping Cooking Times as a Way to Generate Low Molecular Weight Lignins .....	22
4.8 Lignin Pretreatment Methods .....	24
4.8.1 Acidolysis .....	24
4.8.2 Copper Oxide Pretreatments .....	24
4.8.3 Attempted Fractionation of Organosolv Lignins using Pulping Agents .....	25
4.8.4 Attempted Fractionation of Organosolv Lignins using Laccase/ABTS .....	25
4.8.5 Lignin Dimer Model and Lignin Fractionation using Lewis Acid Treatments .....	25
4.8.6 Lignin Fractionating via Solvent Extraction .....	26
4.8.7 Alternatives to NO <sub>2</sub> Oxidation .....	27
5.0 OXIDATIONS WITH HOOH .....	28
5.1 Introduction .....	28
5.2 Background .....	28
5.3 Oxidation of Lignin Models .....	33
5.4 Phase Transfer Oxidations .....	34
5.5 Oxidations with HOOH and Ru Catalysts .....	35
5.6 Oxidations with HOOH and K <sub>6</sub> SiCo(H <sub>2</sub> O)Mo <sub>11</sub> O <sub>39</sub> .....	38
5.7 Oxidations with O <sub>2</sub> .....	39
5.8 Conclusions .....	40
6.0 DETAILED RESEARCH RESULTS - DIELS-ALDER REACTIONS .....	40
6.1 Background .....	40
6.2 Products of the Aqueous Diels-Alder Reaction .....	40
7.0 ALTERNATIVE PREPARATION OF 2,6/7-DIMETHYLANTHRAQUINONE (DMAQ) .....	44
8.0 PULPING AND BLEACHING STUDIES .....	45
8.1 Small Scale Pulping .....	45
8.2 Large Scale Pulping Experiments .....	47
8.3 Bleaching Experiments .....	50
9.0 PULP STRENGTH COMPARISONS .....	56

9.1 Tear -Tensile Comparisons ..... 56  
9.2 Other Strength Comparisons ..... 58  
10.0 ECONOMIC EVALUATION SUMMARY ..... 62  
11.0 APPENDIX ..... 64  
11.1 Work Outline For Final Phase of Project and Milestones ..... 64

## LIST OF FIGURES

Figure 1 - Basic Structure of Guaiacyl and Syringyl Units in Lignin .....	10
Figure 2 - Proposed Mechanism of Quinone Oxidation .....	15
Figure 3 - DMBQ Mole % Yield For The NO <sub>2</sub> Oxidation Of Syringyl Alcohol .....	19
Figure 4 - DMBQ Mole % Yield for the NO <sub>2</sub> Oxidation of Syringaldehyde .....	19
Figure 5 - Possible Mechanism for the Oxidation of Syringaldehyde .....	19
Figure 6 - DMBQ Mole % Yield for the NO <sub>2</sub> Oxidation of Syringaldehyde in the Presence of Catalysts .....	20
Figure 7 - DMBQ Wt% Yield for NO <sub>2</sub> Oxidation of Hardwood Lignins from Kraft and Soda/AQ Pulping .....	23
Figure 8 - DMBQ Wt% Yield for the NO <sub>2</sub> Oxidation of Hardwood Lignins from Organosolv Pulping .....	23
Figure 9 - DMBQ Wt% Yield for the Oxidation of Steam Exploded Yellow Poplar Lignin .....	23
Figure 10 - DMBQ Wt% Yield from the Oxidation of Kraft Hardwood Lignins after Acidolysis .....	24
Figure 11 - NO <sub>2</sub> Oxidation of Fractionated Alcell Lignin .....	27
Figure 12 - DMBQ Wt. % Yield for Oxidation of Solvent Extracted Kraft Hardwood Lignin .....	27
Figure 13 - Interaction of Mo and W Based Oxidation Catalysts with HOOH .....	28
Figure 14 - Mechanism of HOOH Oxidation of Phenophthalein .....	30
Figure 15 - The Ishii-Venturello Complex .....	32
Figure 16 - Proposed Mechanism for Formation of Catalytically Active Oxidizing Agent .....	32
Figure 17 - Alternate Route to Pulping Catalysts from Lignin .....	33
Figure 18 - Definition of Mono- and Bisadducts from Diels-Alder Addition .....	41
Figure 19 - Proposed Reactions of a Monoadduct to Give DMAQ .....	42
Figure 20 - Components in the Aqueous DMBQ/Isoprene Diels-Alder Reaction .....	42
Figure 21 - Preparation of DMAQ from Benzoquinone .....	44
Figure 22 - Activity of non-DMAQ Components in Soda/AQ Pulping .....	46
Figure 23 - Activity of Catalyst Mixture in Soda/AQ Pulping .....	46
Figure 24 - Activity of DMAQ in Kraft/AQ Pulping .....	46
Figure 25 - Activity of DMAQ in PS/AQ Pulping .....	47
Figure 26 - Comparison of Unbleached, Southern Pine Pulps from 1-Kg Soda/Catalyst Pulping .....	51
Figure 27 - Comparison of Unbleached, Southern Pine Pulps from 1-Kg Kraft and Kraft/Catalyst Pulping .....	52
Figure 28 - Comparison of Unbleached, Southern Pine Pulps from 1-Kg Polysulfide/Catalyst Pulping .....	52
Figure 29 - Soda/Catalyst Pulp D2 Brightness Comparison for Constant 0.20 Kappa Factor Bleaching .....	53
Figure 30 - Soda/Catalyst Pulp D2 Viscosity Comparison for Constant 0.20 Kappa Factor Bleaching .....	53
Figure 31 - Kraft Pulp D2 Brightness Comparison .....	54
Figure 32 - Kraft Pulp D2 Viscosity Comparison .....	54
Figure 33 - Comparison of Tear/Tensile Indexes Trendlines for Kraft and Kraft/Catalyst Bleached Pulps .....	57
Figure 34 - Comparison of Tear/Tensile Indexes Trendlines for Soda/Catalysts Bleached Pulps .....	57
Figure 35 - Comparison of Tear/Tensile Indexes for Two Soda/Catalyst Pulps at Four Freenesses .....	58
Figure 36 - Comparison of Average Tear Indexes for Soda/AQ Pulps at Four Freenesses and Soda/DMAQ Pulps at Three Freenesses .....	60
Figure 37 - Comparison of Average Tensile Indexes for Two Soda/Catalyst Pulps at Four Freenesses .....	60
Figure 38 - Comparison of Average Burst Indexes for Two Soda/Catalyst Pulps at Four Freenesses .....	61
Figure 39 - Comparison of Average Zero Span Tensile Indexes for Two Soda/Catalyst Pulps at 4 Freenesses .....	61

## LIST OF TABLES

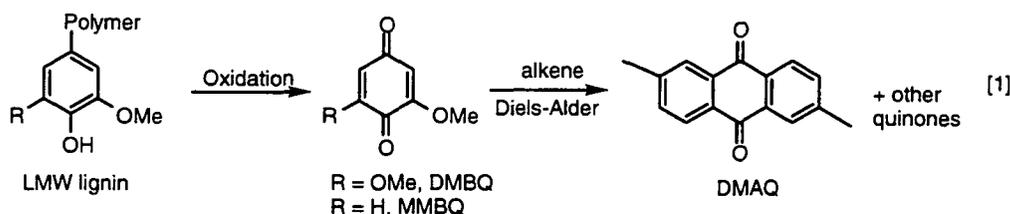
Table 1 - Oxidation of Para-Substituted Phenolics with NO <sub>2</sub> and O <sub>2</sub> .....	11
Table 2 - Summary of Reactions Performed with Catalytic NO <sub>2</sub> .....	13
Table 3 - Results of NO <sub>2</sub> /Cocatalyst Study .....	17
Table 4 - Results of Oxidation of Lignin Samples with NO <sub>2</sub> Under Catalytic Conditions .....	18
Table 5 - Yields of DMBQ for Different Oxidation Conditions Involving Sodium Nitrite .....	21
Table 6 - Elemental Analysis of Hardwood Lignin Samples .....	21
Table 7- Effect of BCl <sub>3</sub> Pretreatment on the Yield of DMBQ from Hardwood Lignins .....	26
Table 8 - Complexes Observed from Reaction of Mo Salts with HOOH as a Function of pH .....	29
Table 9 - Solvent Systems used in Ru/HOOH Oxidations of Syringyl Alcohol .....	36
Table 10- Catalyst Survey for the Oxidation of Syringaldehyde .....	36
Table 11- Ru/HOOH Oxidations .....	37
Table 12- Rhenium Catalyzed Oxidation Of 4-allyl-2,6-dimethoxyphenol .....	38
Table 13- Diels-Alder Reactions of DMBQ and Isoprene in Various Solvents .....	42
Table 14 - Kappa Number Comparison of Polysulfide (1.22%)/Catalyst Pulping of Pine .....	48
Table 15 - Kappa Number Comparison of Soda/Catalyst Pulping of Pine .....	48
Table 16 - Detailed Pulping Results for 1-Kg Pine Cooks .....	49
Table 17 - Detailed Bleaching Conditions and Results .....	55
Table 18 - Comparison of Selected Strength Parameters for Soda/AQ and Kraft/Catalyst Bleached Pulps .....	58

## 1.0 INTRODUCTION/EXECUTIVE SUMMARY

The U. S. pulp and paper industry has embraced the concept of catalysis for the improvement of their pulp making processes. Predominant among the many different technologies investigated is the use of anthraquinone (AQ), a material proven highly effective in catalyzing alkaline (e.g., kraft) pulping. For several years, joint research at the National Renewable Energy Laboratory (NREL) and the Institute of Paper Science and Technology (IPST), has investigated a new but technically challenging concept for the production of much lower cost catalysts designed to equal or surpass the effectiveness of AQ. At the request of the Department of Energy (DOE), this project is now ending. This report will detail the results of the research carried out since the last report, prepared in May 1995.<sup>1</sup>

*The short summary of the project: the results of the research show that the concept works and the investment by DOE has resulted in a near success in the development of two possible approaches to catalysts. A spin off of the research has resulted in a new catalyst synthesis (not from lignin) that looks highly attractive. Patents have been applied for and commercial partners are being sought for this new development. All promised milestones and deliverables have been met on time and on budget. The catalyst-from-lignin concept has the potential to surpass all other economical pathways to preparing pulping catalysts with further focused research in one difficult area of the technology. This focus would also result in additional broader commercial applications of this technology.*

The concept for catalyst production is straightforward (equation 1).



Lignin, an inexpensive byproduct of the pulp and paper industry available in huge quantities, would be chemically converted in two steps to a pulping catalyst or mixture of pulping catalysts. The first step is an oxidation of the lignin to a mixture of two key intermediates, monomethoxybenzoquinone (MMBQ) and dimethoxybenzoquinone (DMBQ), compounds whose structure lay the foundation for the overall catalyst structure. Completion of the catalyst skeleton occurs in the second step through the addition of a simple diene (using the well known Diels-Alder reaction) to this benzoquinone mixture. The resulting catalyst mixture was expected to contain dimethylantraquinone (DMAQ) as the primary active component, as well as other AQ-like products whose behavior, in aggregate, was projected to mimic that of AQ. DMAQ was chosen as the primary component of the catalyst mixture because of its known twofold greater activity than AQ as a pulping catalyst.

The report describes in detail several important discoveries, each of which is crucial to commercial acceptance of the lignin-to-catalyst process:

- The process concept works: this project has revealed that lignin undergoes the desired oxidation and subsequent reaction with a diene to give a pulping catalyst mixture.
- The catalyst mixture has been demonstrated to catalyze pulping at least as effectively as AQ itself. In certain instances, we have observed the activity of the catalyst mixture to be 2 times as high as AQ, resulting in a significant positive impact on the economics of the process.

- Pulp prepared with the catalyst exhibits kappa and viscosity values equivalent to kraft pulp produced using conventional methodology, i.e., our catalyst mixture has no detrimental effects.
- Pulp prepared with the catalyst is easily bleached to high brightness, and shows paper properties equivalent to bleached kraft pulp.
- The process could be economical. Our technoeconomic evaluation indicates that, if certain yield and performance targets are met, this process would be one of the least expensive methods for catalyst production now known.

However, a single technical issue still exists in the first step of the process, oxidation of the lignin. While the oxidation occurs, its yield is, as yet, too low to make the overall process economically viable. In addition, the yield of this step is dependent on the source of lignin used. Success in the first step requires that the polymeric lignin starting material, which is a heterogeneous mixture of dozens of different substructural units, be converted efficiently into a *single* material using a *single* reagent. A large portion of this report details our efforts to develop a method of attaining this goal. Solution of this problem would complete the long list of requirements necessary for positioning this process as a new, commercially viable approach to pulping catalysts.

The authors maintain that a solution to this problem can be found and recommend an additional research effort focused on understanding the chemistry of lignin oxidation at the molecular level. What makes the process tick? What oxidation catalysts or reagents are the best and can their structure be tuned for specific reactivity toward lignin? Why do some substructural lignin units undergo complete decomposition upon oxidation while others are inert? The work described in this report clearly point out that answers to these types questions are needed in order to design the best conditions for the first step of our process. These questions, although fundamental, have a direct and identifiable link to commercial application. This is probably the most important realization of this work: *if we could improve the first step, we believe we would have a commercial process.*

However, these answers would not be obtained by a few additional months of work. The authors' best estimate of such an investigation is about 2 additional years of research, focused on the single aspect of lignin oxidation. Successful completion of this study would result in a complete package to convert inexpensive lignin into high value pulping catalysts. In the long run, the knowledge gained from this additional work would have much broader applications. Lignin has long been identified as potential renewable and "green" feedstock for chemical production, if methods for selective conversion of its heterogeneous structure could be developed. Possible products would include high performance polymers, adhesives, dyes, key chemical intermediates and others. However, with the conclusion of the project, the current forward plan for this work is to present it in its existing form as reports and peer reviewed publications. We will seek input and criticism from the pulp and paper industry as to how we can best improve this process in the future.

Our pulping studies required that we have a pure sample of DMAQ for comparison to the catalyst mixture that comes from lignin. A new, simple, 2-step, high-yield preparation from benzoquinone was developed. The product of the first step proved to be a very effective pulping catalyst, as good as DMAQ itself. Consequently, we now have a one-step, high-yield preparation of a good pulping catalyst that we estimate would cost ~\$1.60/lb to prepare commercially. Because the catalyst is twice as active as AQ, the new catalyst has an equivalent catalyst cost of ~\$0.80/lb. Thus, we have met our target catalyst price of <\$1.00/lb. Steps are being taken to commercialize this material.

The reader will find several sections in this report. This section contains the most concise overview of the results and conclusions of the project. An overview of the rationale behind the project is found in

section 2.0. A detailed technical description of the actual research work is found in sections 3.0 - 9.0. Finally, a summary of the technoeconomic evaluation of the lignin-to-catalyst process is found in section 10.0.

## 2.0 PROJECT BACKGROUND AND RATIONALE

The kraft process is the most widely used method for producing cellulose pulp today. As much as 70% of pulp in the United States is made with this process, which is performed by heating wood chips with a mixture of sodium hydroxide, water, and a sulfur promoter, sodium sulfide. The process has achieved its 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 which result from the efficient regeneration of pulping chemicals in the recovery cycle.

However, the kraft process has a number of shortcomings. First, the yield of cellulose pulp is relatively low. The kraft process also requires an extremely high capital investment for the startup of a new mill, primarily for the installation of the chemical recovery cycle. In addition, the presence of the sulfur promoter leads to the formation of malodorous volatile sulfur compounds that are released to the environment, requiring energy and operating cost expenditures to control these emissions. This project has investigated methods for the preparation of pulping catalysts for improvement of existing alkaline pulping processes and the possible eventual replacement of sulfur in the kraft process, from inexpensive and readily available lignin.

A possible solution to the disadvantages of the kraft process was discovered in 1977. Holton reported that addition of catalytic amounts of AQ significantly promotes alkaline pulping processes. This discovery has become one of the most widely studied effects in paper chemistry in the last 20 years. Pulping is promoted at AQ levels as low as 0.05%-0.1% based on the weight of raw wood feedstock used.

There are a number of benefits associated with the use of AQ as a pulping promoter. Widespread adoption of an AQ based pulping process has been estimated to offer energy savings of up to 0.08 quad/year in the pulping phase of the process alone. More could be realized in downstream operations such as bleaching. Economically, a savings to the paper industry of up to \$236 million/year is possible from a consideration of yield improvements alone. Savings can be realized in the following areas:

- When added to a kraft cook, AQ generally increases the pulping rate at a given temperature, thus improving plant productivity. AQ can also be used to lower the required temperature of pulping, reducing the necessary energy input. Importantly, the amount of carbohydrate degradation decreases in an AQ promoted process, resulting in higher pulp yields. This feature has an important environmental impact since a higher yield results in a minimization of waste and conservation of natural resources. In addition, the pulps obtained have qualities similar to those from noncatalyzed processes, an important economic consideration. The combination of these features translates into lower energy requirements and expense for operating the mill.
- AQ catalyzed pulping can be performed at a lower alkali charge. The lower amount of alkali results in savings in energy and operating costs during the chemical recovery stage of the process. It also decreases the amount of makeup chemicals required and results in less carbohydrate damage and higher pulp viscosity. Initially, AQ catalyzed kraft processes could be operated and realize part of the savings projected. However, AQ can also be used as a sulfur replacement in the kraft process. The avoidance of large quantities of sulfur means that considerably less downstream processing is necessary to meet environmental standards. This will result in both a large capital and energy savings to the industry.

- The pulp derived from a kraft/AQ based process requires less bleaching, because delignification occurs to a greater extent than in the kraft process. The use of kraft/AQ by itself and in conjunction with pulping additives such as polysulfide is leading to the development of new extended delignification processes. Since more lignin can be removed in the pulping digester, less load is put on the bleach plant. The result is lowered bleach plant effluent levels and a net savings in electricity consumption. Moreover, simpler bleaching sequences can be used, suggesting that strategies for chlorine-free bleaching are possible, minimizing the emission of chlorine-containing by-products in the plant effluent. The new process will provide the industry with a waste minimization strategy that could completely avoid discharge of chlorine-derived compounds in the waste stream or eliminate their presence in the final products.

However, widespread use of AQ as a pulping catalyst still has not been widely accepted by the pulp and paper industry; the cost of AQ (about \$1.50 - \$2.00/lb at this writing) has inhibited its use. However, recent changes in the pulp and paper market are again making the wider use of AQ attractive. The use of AQ in kraft mills appears more affordable because recent higher prices for wood pulp. The growing demand for low cost AQ (or its equivalent) is an important opportunity because the nature of the pulp and paper industry is such that relatively small improvements in operational and process costs can have a large impact on a plant's profitability.

The purpose of our research program is to develop a pulping catalyst that exhibits the beneficial properties of AQ, but which can be produced at significantly lower cost. We have been investigating the use of lignin as a starting material for the production of our catalyst. Early in our research program we recognized several structural similarities between AQ and substructural units found in lignin. Our research, which is a joint project between NREL and the IPST, has focused on both the scientific and techno-economic aspects of a lignin to catalyst process. Our approach for the synthesis of pulping catalysts from lignin has been divided into two stages, lignin processing and chemical processing.

The lignin processing stage involves isolation of a low molecular weight (LMW) fraction from a lignin source. Several methods for isolation of this LMW fraction were appraised as part of the program: conventional solvent extraction of lignins, ultrafiltration of concentrated kraft black liquor, and organosolv pulping.

The second stage of the process involves a chemical processing of this LMW fraction and contains two critical chemical steps. In the first step, the LMW lignin is oxidized with an inexpensive oxidizing agent to give a mixture of benzoquinones. In the second step of the chemical processing sequence, the benzoquinones are converted into the catalyst mixture by treatment with a diene, using the well-known Diels-Alder reaction.

### **3.0 RESEARCH DETAILS - OXIDATION OF LIGNIN AND LIGNIN MODELS**

#### **3.1 Introduction**

The first step of the catalyst production process, oxidation of lignin to a mixture of benzoquinones (equation 1), offers a considerable technical challenge. The structure of lignin is incredibly complex; indeed, the complete structure of lignin present in pulping black liquor (a potential source of starting material for this project) is unknown. However, it is well known that lignin contains many different substructural units, each of which could display completely different responses to a given oxidizing agent. The problem becomes more complex when the economic and operational necessities of pulping catalyst synthesis are examined. Although hundreds of oxidizing agents are known in the chemical literature, an economically viable catalyst synthesis requires that the oxidizing agent be inexpensive

and well known to the pulp and paper industry. At the molecular level, a successful process for the oxidation step will exhibit two important features. First, it will oxidize phenolic units in lignin to the quinone oxidation state, and second, it will cleave the alkyl group *para* to the hydroxy group on the aromatic ring.

Several reagents are known that oxidize lignin models to benzoquinones. For example, Fremy's salt,  $(\text{KO}_3\text{S})_2\text{N-O}$ , has been shown to produce high yields of methoxy substituted benzoquinones.<sup>2</sup> However, Fremy's salt is an expensive, stoichiometric reagent which also shows inconsistent reproducibility on large scales.<sup>3</sup> Iron porphyrins have also been used in the oxidation of lignin model compounds and substituted phenols using mCPBA as the oxidant.<sup>4</sup> Despite the development of a catalytic method, the oxidation of phenols such as p-cresol gave poor yields of benzoquinones.

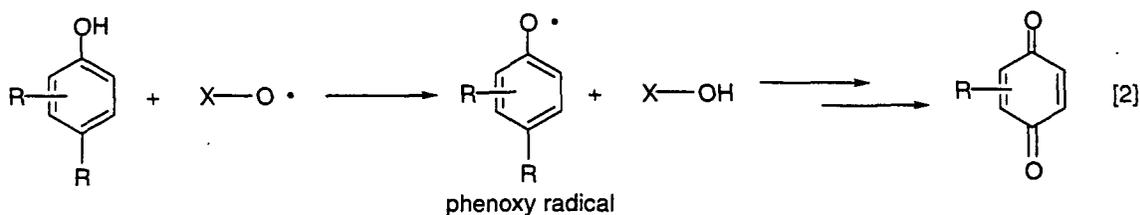
We have chosen to focus on three oxidants,  $\text{O}_2$ , HOOH, and  $\text{NO}_2$ . Each of these oxidants is widely used by the pulp and paper industry, but in a completely different context than needed for catalyst synthesis. The industry uses these materials for removal of residual lignin from cellulose pulp during bleaching sequences. In that context, reaction selectivity (i. e, the ability to make a single product) is not an issue. The only goal is to convert lignin into small, easily removable fragments to facilitate production of a bright bleached pulp. In bleaching,  $\text{O}_2$ , HOOH and  $\text{NO}_2$  are a perfect match for lignin. The nonselective nature of these oxidants means that the great structural diversity becomes irrelevant. Under proper conditions these oxidants facilitate rapid and complete removal of residual lignin in pulp.

In contrast, pulping catalyst synthesis requires that the oxidation be highly selective in order that a high yield of benzoquinones be achieved. The choice of oxidants is still the same, and therefore, methods are needed to control their reactivity during lignin oxidation. To probe the possibility of controlling the reactivity of these three oxidants, we have performed detailed study on new methods for use of  $\text{NO}_2$ . To control the reactivity of  $\text{O}_2$  and HOOH, we have investigated the use of transition metal catalysis.

## 4.0 OXIDATIONS WITH NITROGEN DIOXIDE

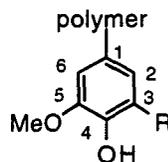
### 4.1 Introduction

The most effective method to date for producing benzoquinones from lignin involves treating a low molecular weight lignin with  $\text{NO}_2$  in methanol solvent. Previous annual reports have discussed this subject in depth and four papers have been published in the last two years.<sup>5</sup> The reader should consult them to learn the intimate details of our previous investigations. Use of  $\text{NO}_2$  has been reported to improve the characteristics and reduce the severity of the conditions normally employed in an oxygen bleaching step by inducing an oxidative decomposition of the lignin.<sup>6</sup> Nitrogen dioxide is structurally and electronically similar to several other oxidants investigated in this work (for example,  $\text{Co}(\text{salen})/\text{O}_2$  complexes<sup>7</sup>). We were interested in learning whether its reactivity could be controlled for the selective conversion of lignin to catalyst precursors. We believed that the key to a selective transformation depended on our ability to use  $\text{NO}_2$  in the formation and control of a phenoxy radical (equation 2,  $\text{X} = \text{ON}$ ). Molecular modeling experiments have been carried out to help discern the nature of this interaction.<sup>8</sup>



In summary, we know the following major facts:

- The lignin unit being oxidized must be phenolic (Figure 1).
- Guaiacyl lignin units, which are ~100% of the units in softwood lignins and ~50-75% of hardwood lignins, are only very poorly converted to MMBQ by NO<sub>2</sub> oxidation (Figure 1). The preferred reaction pathway appears to be substitution of NO<sub>2</sub> on the C-3 (nonmethoxylated) position of the guaiacyl unit. It is possible to block the C-3 position by halogenation and get reasonable yields of DMBQ upon NO<sub>2</sub> oxidation of this derivative; however, this adds a cost that is likely to inhibit production of an attractively priced catalyst.



R = H, guaiacyl unit  
R = OMe, syringyl unit

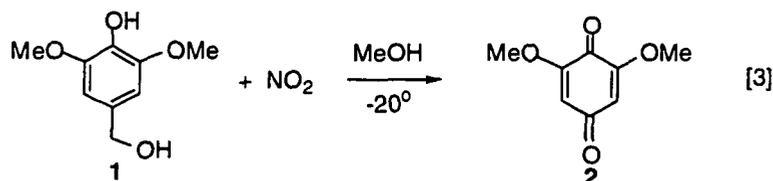
Figure 1 - Basic Structure of Guaiacyl and Syringyl Units in Lignin

- The significance of the first two points is that useful amounts of benzoquinones cannot be made from softwood lignins by NO<sub>2</sub> oxidation and that the yields of useful DMBQ from hardwood lignin is limited by the number of phenolic syringyl units available. If one assumes that a pulped hardwood lignin has ~30% phenolic units that reflects the natural ratio of guaiacyl to syringyl units present before pulping (typically about 3:1), the best yield of DMBQ possible from a common hardwood lignin would be ~8%. This could be a somewhat low estimate, however, since a hardwood lignin probably will have proportionally more syringyl end units after pulping than were present in the native lignin. The proposed investigation into the reactivity of phenols under oxidative conditions described in the executive summary would examine this surprising difference in reactivity between syringyl and guaiacyl units.
- Model studies reveal that the yield of DMBQ from NO<sub>2</sub> oxidation monomeric syringyl lignin units is high (~90%). Thus, an obvious approach to improving DMBQ yields from lignin is to fragment and/or fractionate the lignin into small pieces. Extensive investigations have not led to a low cost, effective way to perform the fragmentation chemistry. Fractionation techniques, on the other hand, have allowed us to roughly double the DMBQ yields in some cases from an isolated lignin.
- The amount of DMAQ formed from DMBQ in the second, aqueous Diels-Alder synthetic step is ~40% of the entire catalyst mixture. Using a DMBQ yield of 7.5% (typical of a small scale oxidation of an unfractionated organosolv lignin) and assuming that DMBQ can be easily isolated from lignin, our research suggests that 100 g of lignin will provide 10 g of equivalent AQ catalyst.

- The DMBQ yields from NO<sub>2</sub> oxidations of unfractionated organosolv lignins vary with scale; typically, a 20 g lignin reaction will give ~4.5% yield, while 1 g reactions give yields of ~7.3%. The risks of performing large scale reactions in our laboratory equipment escalate with the size increase. Better equipment design will be required for scaleup of NO<sub>2</sub> oxidations.

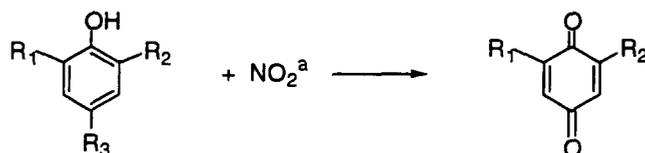
#### 4.2 Oxidation of Model Compounds - Catalytic NO<sub>2</sub>

To better understand the NO<sub>2</sub> process (equation 2, X = ON) prior to attempting it on lignin samples, we studied the reactivity of NO<sub>2</sub> with several lignin models. For example, syringyl alcohol 1 was treated with a stoichiometric amount of NO<sub>2</sub> (generated from 1 equivalent of NaNO<sub>2</sub> and 100 μl of concentrated HNO<sub>3</sub> or HCl) in MeOH under argon at -20°C. DMBQ (2) was isolated in low yield (equation 3).



However, introduction of 1 atmosphere of O<sub>2</sub> to this reaction has a dramatic effect, allowing isolation of 2 in much higher yields. In addition, we find that in the presence of O<sub>2</sub>, only catalytic amounts of NaNO<sub>2</sub> are necessary to give yields of 2 from 1 of 80-85%. Typically 20% NaNO<sub>2</sub> was employed, but 2 is also formed in yields of 70-75% with NaNO<sub>2</sub> levels of 5%. The ability to use catalytic amounts of NO<sub>2</sub> would have a significant impact on the economics of the process. Moreover, these conditions would be easily suited for use in a pulp and paper mill environment. The results of this study are summarized in Table 1.<sup>9</sup>

Table 1 - Oxidation of Para-Substituted Phenolics with NO<sub>2</sub> and O<sub>2</sub>

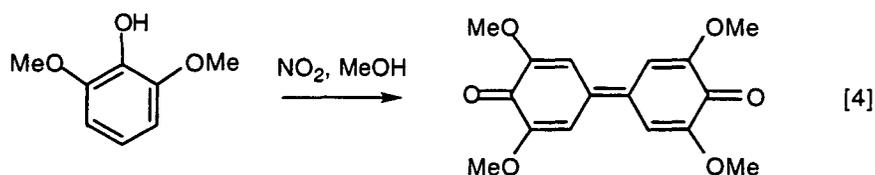


R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	conditions	% yield
OMe	OMe	CH <sub>2</sub> OH	20% NaNO <sub>2</sub> , -20°C, MeOH	88
OMe	OMe	CH <sub>2</sub> OH	5% NaNO <sub>2</sub> , -20°C, MeOH	72
OMe	OMe	CH(CH <sub>3</sub> )OH	20% NaNO <sub>2</sub> , -20°C, MeOH	56
OMe	OMe	CHO	20% NaNO <sub>2</sub> , 0°C, MeOH	50
OMe	OMe	Me	20% NaNO <sub>2</sub> , -10°C, MeOH	12
t-Bu	t-Bu	CH <sub>2</sub> OH	20% NaNO <sub>2</sub> , -20°C, MeOH	0 <sup>b</sup>
t-Bu	t-Bu	CH <sub>2</sub> OH	1 eq NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	37 <sup>c</sup>
Me	Me	CH <sub>2</sub> OH	1 eq NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	9 <sup>d</sup>
Me	Me	OH	20% NaNO <sub>2</sub> , -10°C, MeOH	100
t-Bu	t-Bu	OMe	20% NaNO <sub>2</sub> , -10°C, MeOH	99

<sup>a</sup>NO<sub>2</sub> generated by the reaction of NaNO<sub>2</sub> with 100 μl of concentrated HNO<sub>3</sub> or HCl. <sup>b</sup>The corresponding methyl benzyl ether was isolated in 81% yield. <sup>c</sup>4-Nitro-2,6-di-*t*-butylphenol was isolated in 31% yield. <sup>d</sup>4-Nitro-2,6-dimethylphenol was isolated in 17% yield.

For most reactions, we find that lower temperatures are more effective, probably by causing an increase in the concentration of volatile  $\text{NO}_2$  in solution. MeOH is the best solvent for most reactions: Other solvents employed (MeCN,  $\text{CH}_2\text{Cl}_2$ , ethylene dichloride, i-PrOH, EtOAc) resulted in the formation of significant amounts of side products, predominantly oxidation of the benzylic alcohol (where present) to the corresponding benzaldehyde and nitration of the aromatic ring. For example, treatment of syringyl alcohol with  $\text{NO}_2$  in MeCN gave no quinone, but a 63% yield of the corresponding aldehyde. Substrates with strongly electron donating substituents exhibit a greater ability to form quinone. However, substrates unreactive toward quinone formation under catalytic conditions (e.g.,  $\text{R}_1, \text{R}_2 = \text{t-Bu}$ ,  $\text{R}_3 = \text{CH}_2\text{OH}$ ) can be converted to quinone in the presence of stoichiometric amounts of  $\text{NaNO}_2$  in  $\text{CCl}_4$  solvent. Hydroquinones and hydroquinone monoalkyl ethers are converted to the corresponding benzoquinones in high yield.<sup>10</sup> The results with the benzyl alcohols are particularly interesting since Coombes has reported that similar species undergo reaction with  $\text{NO}_2$  under inert atmosphere to give the corresponding aldehyde and aromatic ring nitration; no quinone is observed.<sup>11</sup>

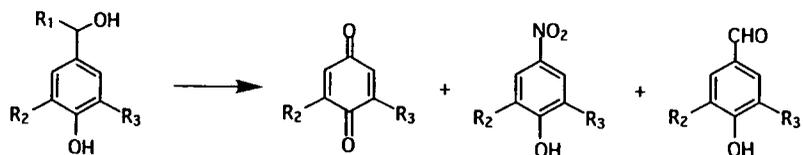
Several compounds fail to undergo conversion to quinone, including vanillyl alcohol, eugenol, and acetosyringone. Syringol undergoes oxidation, but gives a diphenoquinone dimer as a primary product (equation 4).



The addition of oxygen is apparently diverting the normal aromatic nitration pathway. Overall, these results indicate that para-substituents similar to those found in lignin undergo cleavage, a necessary step for the removal of the phenolic units present in lignin. A wide number of other reactions were tried and they are summarized in Table 2.

The mechanism of  $\text{NO}_2$  promoted oxidation is complex because of the number of different oxides of nitrogen that can be formed under these conditions. However, Kochi has shown that the oxidation of hydroquinone dialkyl ethers to quinones occurs via formation of a hydroquinone radical cation, formed from the reaction of the hydroquinone and the  $\text{NO}_2$  disproportionation product  $\text{NO}^+\text{NO}_3^-$ .<sup>12</sup>  $\text{NO}_2$  can be generated *in situ* by the reaction of  $\text{NaNO}_2$  and acid. The reaction initially forms nitrous acid, HONO. HONO undergoes decomposition to give  $\text{HNO}_3$ , water, and nitric oxide, NO.<sup>13</sup> However,  $\text{HNO}_3$  and NO are in equilibrium with dinitrogen trioxide,  $\text{N}_2\text{O}_3$ . Moreover, both NO and  $\text{N}_2\text{O}_3$  are converted rapidly to  $\text{N}_2\text{O}_4$  (the dimer of  $\text{NO}_2$ ) upon reaction with oxygen.

The key oxidant in this process appears to be the nitric oxide cation,  $\text{NO}^+$ , which is formed from the equilibrium disproportionation of  $\text{N}_2\text{O}_4$  to nitrosonium nitrate,  $\text{NO}^+\text{NO}_3^-$ . This equilibrium is normally poor, but is greatly accelerated in polar solvents, or in the presence of good arene donors, such as the lignin models used in this study.  $\text{NO}^+$  causes the arene to undergo a one-electron oxidation to the corresponding radical cation. This species has two fates. In non polar media, it undergoes ion pair collapse with the  $\text{NO}_3^-$  to give oxidation of the arene to the corresponding quinone. However, in polar media, it reacts with excess  $\text{NO}_2$  to cause nitration of the aromatic ring.<sup>14</sup> Oxidation can be promoted in polar media upon the addition of excess  $\text{NO}_3^-$ . In the case of hydroquinone ethers, the intermediate rearranges to give quinone and alkyl nitrite as the final organic products. When hydroquinones undergo



<u>Run number</u>	<u>Substrate</u>	<u>quinone</u>	<u>Nitration</u>	<u>Aldehyde</u>	<u>sm</u>	<u>Conditions</u>	<u>Comments</u>
1771-43	Syr alc	16%	7%	30%	52%	5% NaNO <sub>2</sub> ,rt,CH <sub>2</sub> Cl <sub>2</sub>	Yields by NMR
1771-44	Syr alc	26%	tr	1	0	5% NaNO <sub>2</sub> ,rt,MeOH	Me ether:20 ratio
1771-45	syrald	2%	tr	--	58%	5% NaNO <sub>2</sub> ,rt,MeOH	Note material balance
1771-46	Van alc	0	0	0	0	5% NaNO <sub>2</sub> ,rt,MeOH	59% Me ether
1771-51	Syr alc	8%	tr	tr	0	5% NaNO <sub>2</sub> ,rt,aq MeOH	Messy NMR
1771-53	Syr alc	45%	--	--	--	5% NaNO <sub>2</sub> ,rt,MeOH	No NMR of residue
1771-54	Syr alc	0	0	63%	0	5% NaNO <sub>2</sub> ,rt,MeCN	
1771-56	Syr alc	55%	6%	41%	0	20% NaNO <sub>2</sub> ,rt,MeOH	Some yields by NMR
1771-57	syringol	--	--	--	--		2 prod/2.7:1
1771-62	Syr alc	79%	4%	8%	0	20% NaNO <sub>2</sub> ,-20,MeOH	Some yields by NMR; 94% quinone with residue
1771-63	eugenol	0	0	0	All (TLC)	5% NaNO <sub>2</sub> ,rt, MeOH	
1771-67	Syr alc	72%	1	10	0	5% NaNO <sub>2</sub> ,-20,MeOH	Some DMBQ in residue;complex NMR, Me ether present
1771-68	Van alc	--	--	--	--	20% NaNO <sub>2</sub> ,-20,MeOH	Complex NMR; aldehyde and ether present
1771-69	syrald	24%	0	--	73%	20% NaNO <sub>2</sub> ,-20,MeOH	
1771-71	acetosyr	0	0	0	All (TLC)	20% NaNO <sub>2</sub> ,-20,MeOH	
1771-72	syringol	--	--	--	--	20% NaNO <sub>2</sub> ,-20,MeOH	Similar to 1771-57
1771-73	diMe phenol				All (TLC)	20% NaNO <sub>2</sub> ,-20,MeOH	Surprising result
1771-74	Syr alc	tr	tr	major	0	20% NaNO <sub>2</sub> ,-20,CH <sub>2</sub> Cl <sub>2</sub>	Much cleaner than 1771-43; no prod weight
1771-75	Syr alc	tr	0	major	0	20% NaNO <sub>2</sub> ,-20,MeCN	Very clean; no prod weight
1771-91	Syr alc	54%	0	20% (est)	0	5% NaNO <sub>2</sub> ,-10,MeOH	
1771-92	Syr alc	55%	some	most	0	5% NaNO <sub>2</sub> ,-10,MeOH	High dilution
1771-94	van alc	0	0	0	0	5% NaNO <sub>2</sub> ,0,MeOH	Me ether plus other products
1771-95	van	0	0	0	All (TLC)	5% NaNO <sub>2</sub> ,0,MeOH	
1771-96	acetosyr	0	0	0	All (TLC)	5% NaNO <sub>2</sub> ,0,MeOH	
1771-113	Syr alc	88%	0	0	0	20% NaNO <sub>2</sub> ,-20,MeOH	HNO <sub>3</sub> as acid promoter
1771-114	syrald	39%	0	0	0	20% NaNO <sub>2</sub> ,0,MeOH	Addnl DMBQ in filtrate
1771-115	Di-t-Bu alc	0	12%	0	0	20% NaNO <sub>2</sub> ,-20,MeOH	81% Me ether
1771-116	DiMe ald	0	0	0	All (TLC)	20% NaNO <sub>2</sub> ,-20,MeOH	
1771-119	α-Me syr alc	56%	0	0	0	20% NaNO <sub>2</sub> ,-20,MeOH	No NMR of residue

Run Number	Substrate	quinone <sup>a</sup>	Nitration	Aldehyde	sm	Conditions	Comments
1771-120	DiMe benz alc	4	1	3	0	20% NaNO <sub>2</sub> , -20, MeOH	Me ether:6 ratio; ratios only, no prod weight
2025-1	DiMe ald	0	0	0	All (TLC)	stoich NaNO <sub>2</sub> , 0, MeOH	
2025-2	Syr alc	major	0	tr	0	20% NaNO <sub>2</sub> , -20, MeCN	Big contrast to 1771-54,75; HNO <sub>3</sub> promoter only diff; no prod weight
2025-3	Syr alc	some	some	some	0	20% NaNO <sub>2</sub> , -20, CH <sub>2</sub> Cl <sub>2</sub>	Less clean than 2025-2
2025-4	Syr alc	some	some	some	some	20% NaNO <sub>2</sub> , -20, EtOAc	Less clean than 2025-3
2025-5	Syr alc	72%	--	--	--	20% NaNO <sub>2</sub> , -20, MeOH	100μl HNO <sub>3</sub> , no NMR of residue
2025-6	Syr alc	61%	--	--	--	20% NaNO <sub>2</sub> , -20, MeOH	50μl HNO <sub>3</sub> , no NMR of residue
2025-7	Syr alc	0	--	--	--	-20, MeOH	Control reaction
2025-8	Syr alc	71%	7	2	0	20% NaNO <sub>2</sub> , -20, MeOH	Me ether:2 ratio; no weight on residue
2025-9	DiMe benz alc	1.5	2	tr	0	20% NaNO <sub>2</sub> , -20, MeOH	Me ether:14 ratio; no weight on product
2025-11	DiMe benz alc	2	2	tr	0	20% NaNO <sub>2</sub> , 0, MeOH	Me ether: 15 ratio; no weight on product
2025-12	DiMe benz alc	2.5	2	tr	0	20% NaNO <sub>2</sub> , 0, MeOH	Higher acid; Me ether:13 ratio; no weight on product
2025-13	DiMe benz alc	tr	7	tr	0	20% NaNO <sub>2</sub> , -20, EDC	Me ether:11 ratio; no weight on product
2025-14	DiMe benz alc	10	4	1	16	20% NaNO <sub>2</sub> , 0, MeCN	Complex mixture
2025-15	Di-t-bu alc	0	2	0	0	20% NaNO <sub>2</sub> , -20, MeOH	Me ether: 7 ratio; no weight on product
2025-47	TriMe phenol	--	--	--	--	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Test of Coombes conditions; under argon
2025-48	DiMe benzald	--	--	--	All (TLC)	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Modify one group in Coombes' rxn
2025-49	TriMe phenol	--	--	--	--	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Repeat 2025-47
2025-50	TriMe phenol	--	65%	--	--	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Oxygen atmos; prod assignment not conclusive
2025-51	DiMe benz alc	4%	17%	0	0	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Quinone volatile and lost
2025-53	Di-t-bu alc	19%	40%	0	0	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	
2025-55	Di-t-bu alc	37%	31%	0	0	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Longer time than 2025-53
2025-56	Di-t-bu alc	1	2	0	0	stoich NaNO <sub>2</sub> , rt, MeCN	Several products
2025-57	Di-t-bu alc	1	2	0	0	stoich NaNO <sub>2</sub> , rt, CH <sub>2</sub> Cl <sub>2</sub>	Cleaner than 2025-56
2025-58	syrald	--	--	--	--	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Very messy rxn; subs insol
2025-59	Van alc	--	--	--	--	stoich NaNO <sub>2</sub> , rt, CCl <sub>4</sub>	Very messy rxn; subs insol

this reaction, HONO is one of the reaction products and can be recycled according to the equilibria in Figure 2, giving the possibility of performing the reaction catalytically.

Following the mechanistic model of Kochi, the following mechanism is thought to operate in the catalytic oxidation of lignin model compounds (Figure 2).

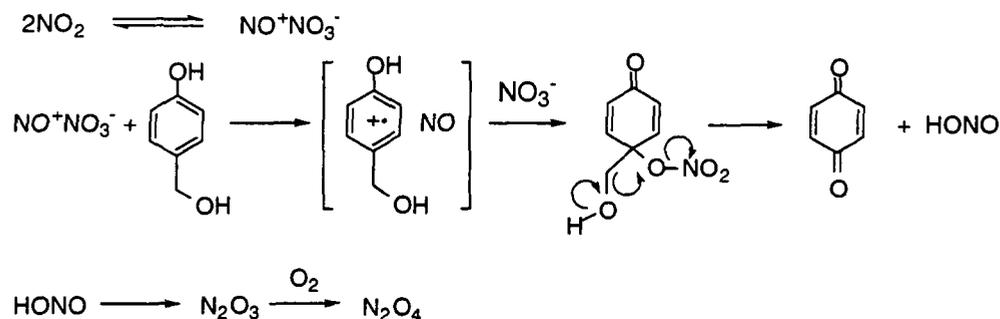
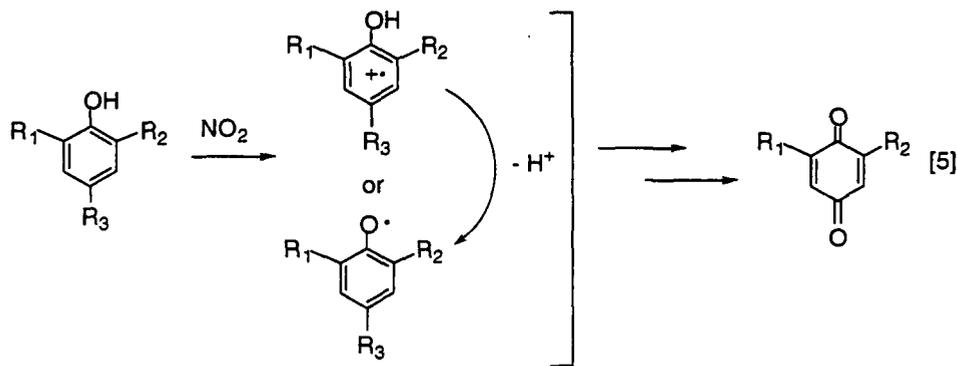


Figure 2 - Proposed Mechanism of Quinone Oxidation

Transformation of the para-substituted phenols would occur by formation of the p-nitrato intermediate and its rearrangement to quinone. This process initially generates nitrous acid (HONO) which is known to rearrange to  $\text{N}_2\text{O}_3$ , and then rapidly react with  $\text{O}_2$  to give  $\text{N}_2\text{O}_4$  and start the catalytic cycle again.

Nitrogen dioxide is also reported to be a useful aromatic nitration reagent<sup>15</sup> and we observed nitration of the model compounds as a side reaction. Interestingly, we observe an increase in ring nitration when the nonpolar  $\text{CCl}_4$  is used as a solvent. This is in contrast to Kochi's results with hydroquinone dialkyl ethers in which increased ring nitration was observed in polar solvents. We note that the amount of ring nitration increases with a decrease in the ability of the phenol to form a phenoxy radical. It is possible that ring nitration of these phenols occurs via phenoxy radical formation, either by direct hydrogen atom abstraction by  $\text{NO}_2$  or by loss of  $\text{H}^+$  from the radical cation and trapping of the resulting radical by  $\text{NO}_2$  (equation 5). The reaction, in this way, mimics the reactivity of phenols observed with Co-Schiff base complexes and  $\text{O}_2$ .<sup>16</sup>



These results suggest that  $\text{NO}_2$  may be a suitable agent for the selective conversion of lignin into useful chemicals.

#### 4.3 Oxidation of Model Compounds - Catalytic NO<sub>2</sub> in the Presence of Metal Catalysts

As shown above, the oxidation of lignin models to DMBQ can be accomplished using catalytic amounts of NO<sub>2</sub> in an oxygen atmosphere. In order to enhance the oxidation capabilities of NO<sub>2</sub>, its use in the presence of a transition metal cocatalyst was investigated. This strategy has previously proven successful as several methods for oxidations using NO<sub>2</sub> with catalytic metal oxides have been reported.<sup>17</sup>

The strategy used was to determine the yield of DMBQ without the cocatalyst and then repeat the oxidation using a known oxidation metal as cocatalyst. In all experiments, 10 mol% of NaNO<sub>2</sub>/acid, 2 mol% of cocatalyst and 1 atmosphere of oxygen at 0°C were used. Table 3 summarizes the results. The initial choices for cocatalysts were RuCl<sub>3</sub> and MeReO<sub>3</sub>, two extremely active oxidation catalysts. We initially used dimethoxyphenol and syringyl alcohol as substrates (entries 1-5). Both showed improved yields using MeReO<sub>3</sub> as a catalyst. However, additional substrates (6-13) failed to show enhanced yields with the rhenium catalyst. Though the initial oxidation in entry 3 was successful, it appears that MeReO<sub>3</sub> is not generally effective. A screening of additional transition metals using syringaldehyde as a substrate (entries 14 - 35) was also undertaken. In the absence of additional catalyst, syringaldehyde is converted to quinone in 50% yield (entry 12). Added catalyst can increase the yield to as high as 67%, however this increase would not justify the additional expense needed for use of the cocatalyst.

These results suggested that an alternative one step conversion of lignin to pulping catalyst should be investigated. This concept is related to prior literature work which involved the oxidation of phenols to benzoquinones, and then *in situ* addition of an isoprene molecule.<sup>18</sup> The use of silver oxide and isoprene resulted in the formation of bicyclic molecules. We attempted to use this literature work for a one step formation of DMAQ. Using syringyl alcohol as a model compound, we isolated DMAQ in 5-10% yields (equation 6). We also applied this technique to LMW lignin and obtained a 4% yield of DMAQ. The drawback of this methodology is the requirement of 2 equivalents of silver oxide. We therefore attempted to use the catalytic amounts of silver oxide in the presence of RuCl<sub>3</sub> and MeReO<sub>3</sub> as cocatalysts. However, no DMAQ was observed in any of these attempts.

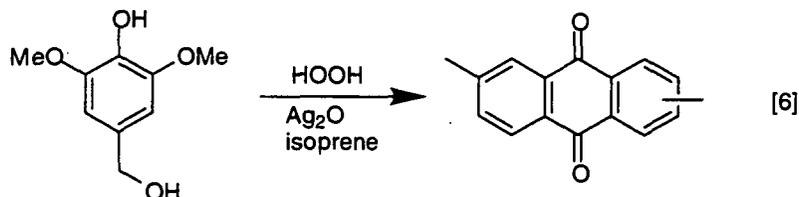
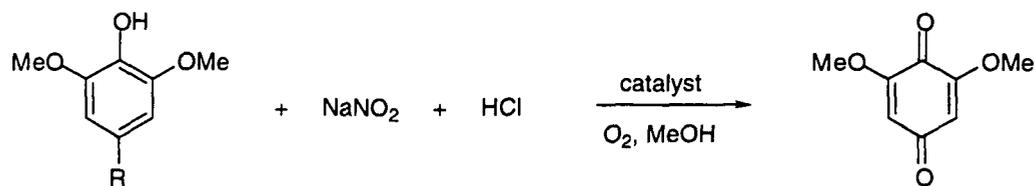


Table 3 - Results of NO<sub>2</sub>/Cocatalyst Study



Entry	R	Catalyst	DMBQ Yield	Entry	R	Catalyst	DMBQ Yield
1	H	None	0%	19	CHO	Fe <sub>2</sub> O <sub>3</sub>	51%
2	H	RuCl <sub>3</sub>	54%	20	CHO	OsO <sub>4</sub> (0.1%)	61%
3	H	MeReO <sub>3</sub>	84%	21	CHO	MnL <sub>3</sub> (1%)	65%
4	CH <sub>2</sub> OH	None	82%	22	CHO	V <sub>2</sub> O <sub>4</sub>	64%
5	CH <sub>2</sub> OH	MeReO <sub>3</sub>	85%	23	CHO	CuO	59%
6	allyl	None	8%	24	CHO	Ag <sub>2</sub> O	63%
7	allyl	RuCl <sub>3</sub>	6%	25	CHO	Cr(acac) <sub>3</sub>	60%
8	allyl	MeReO <sub>3</sub>	9%	26	CHO	Mn(OAc) <sub>3</sub>	59%
9	allyl	RuO <sub>2</sub>	0%	27	CHO	(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	65%
10	CH <sub>3</sub>	None	6%	28	CHO	Pd <sub>2</sub> (C <sub>17</sub> H <sub>14</sub> O) <sub>3</sub>	62%
11	CH <sub>3</sub>	MeReO <sub>3</sub>	6%	29	CHO	(Ph <sub>3</sub> P) <sub>3</sub> RuCl	64%
12	CHO	None	50%	30	CHO	MoO <sub>2</sub> (C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	44%
13	CHO	MeReO <sub>3</sub>	53%	31	CHO	Ru metal (1%)	65%
14	CHO	PdCl <sub>2</sub>	64%	32	CHO	FePO <sub>4</sub> ·2H <sub>2</sub> O	59%
15	CHO	PtO <sub>2</sub>	67%	33	CHO	H <sub>2</sub> PtCl <sub>6</sub>	49%
16	CHO	TiO <sub>2</sub>	64%	34	CHO	Ph <sub>3</sub> P	0%
17	CHO	Co(salen) <sub>2</sub>	58%	35	CHO	NaVO <sub>3</sub>	5%
18	CHO	Pd(OAc) <sub>2</sub>	60%				

#### 4.4 Oxidations of Lignin - Catalytic NO<sub>2</sub>

The reactivity of several types of lignin toward catalytic amounts of NO<sub>2</sub> were examined. The results are summarized in Table 4. Two types of lignin were examined: a commercial organosolv lignin (Alcell) from Repap Corporation and a lignin prepared by the NREL Clean Fractionation process (CF lignin). The Repap lignin proved to be difficult to work with because of the large amount of insoluble material present in the reaction. However, the CF lignin was completely soluble in MeOH, and upon treatment

with NO<sub>2</sub>, gave a precipitate of DMBQ that was isolated by simple filtration. These reactions were unique in that they gave an easily separable DMBQ component in (comparatively) reasonable yield. Previous efforts had always resulted in some DMBQ remaining associated with the dissolved or undissolved lignin.

**Table 4 - Results of Oxidation of Lignin Samples with NO<sub>2</sub> Under Catalytic Conditions**

<u>Lignin Type</u>	<u>Conditions</u>	<u>Yield of DMBQ</u>
Alcell	20% NaNO <sub>2</sub> , -10°C, MeOH	<1%
CF lignin	30% NaNO <sub>2</sub> , 0°C, MeOH	1%
CF lignin	30% NaNO <sub>2</sub> , 0°C, MeOH <sup>a</sup>	3-4%
CF lignin	30% NaNO <sub>2</sub> , 0°C, MeOH, added Co(salpr) catalyst	<1%
CF lignin	30% NaNO <sub>2</sub> , 0°C, MeOH, added Co(salen) catalyst	<1%

<sup>a</sup>Reaction run at a higher concentration of lignin.

#### 4.5 Oxidations of Model Compounds - Stoichiometric NO<sub>2</sub>

##### *4.5.1 Stoichiometry of NO<sub>2</sub> Oxidations*

Certain phenols are less reactive under catalytic conditions. Therefore, the oxidation was also investigated using stoichiometric levels of NO<sub>2</sub>. A series of reactions was conducted to determine the stoichiometry for the NO<sub>2</sub> oxidation of syringyl alcohol and syringaldehyde (Figures 3 and 4). The results show that the reaction of NO<sub>2</sub> with these models is more complex than previously thought; however, the yield of DMBQ seems to be most consistent with 2-5 equivalents of NO<sub>2</sub>. As few as 0.75 equivalents of NO<sub>2</sub> are effective with syringyl alcohol, as expected, given the existence of a catalytic pathway with certain substrates. Yields are much improved by higher levels of NO<sub>2</sub> in the case of syringaldehyde.

##### *4.5.2 Mechanistic Studies of Stoichiometric NO<sub>2</sub> Oxidations*

In addition to the formation of DMBQ, the NO<sub>2</sub> oxidation of syringaldehyde in methanol led to a headspace that contained carbon dioxide, nitrogen, oxygen, water, NO, NO<sub>2</sub>, methanol, methyl formate and methyl nitrite. This qualitative analysis was carried out using GC/MS; quantification was not performed. The presence of CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O was not surprising since no attempts were taken to exclude air. The identification of methyl formate supports our assertion that the actual species undergoing the oxidative cleavage is the hemiacetal of syringaldehyde (Figure 5).

A set of reactions were run in the presence of catalytic amounts of *p*-toluenesulfonic acid and iron (III) sulfate (Figure 6). The former was tested since it would catalyze hemiacetal formation, while the latter might facilitate the formation of phenoxy radicals. Neither reagent was very effective in promoting the oxidation of syringaldehyde (the typical uncatalyzed yield of DMBQ is 80-90%). Both catalysts resulted in the formation of an additional product, 2,6-dimethoxy-4-nitrophenol.

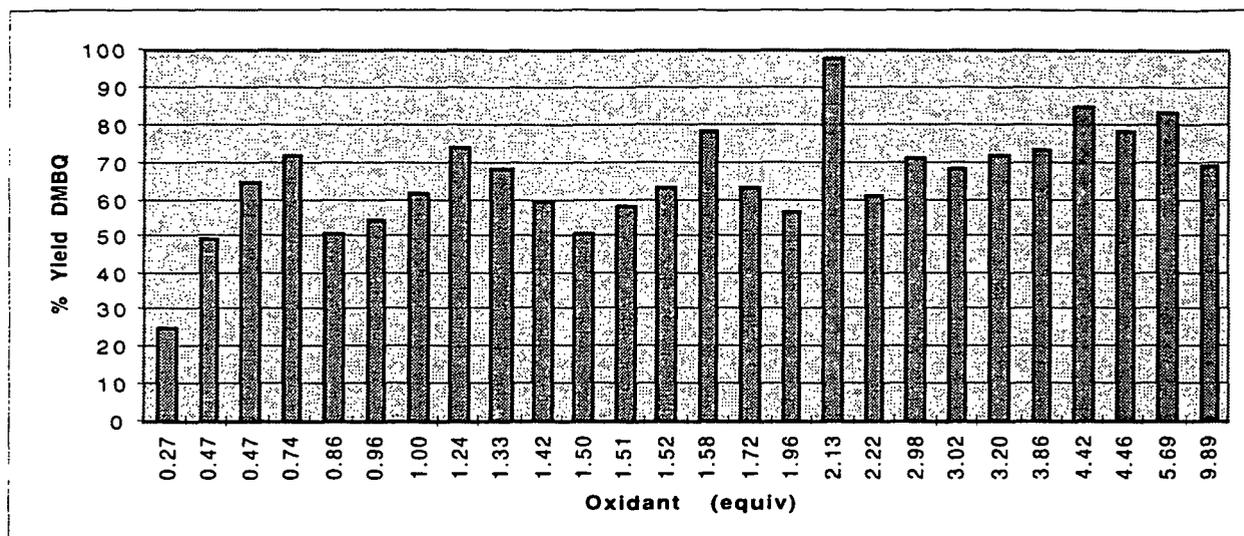


Figure 3 - DMBQ Mole % Yield For The NO<sub>2</sub> Oxidation Of Syringyl Alcohol

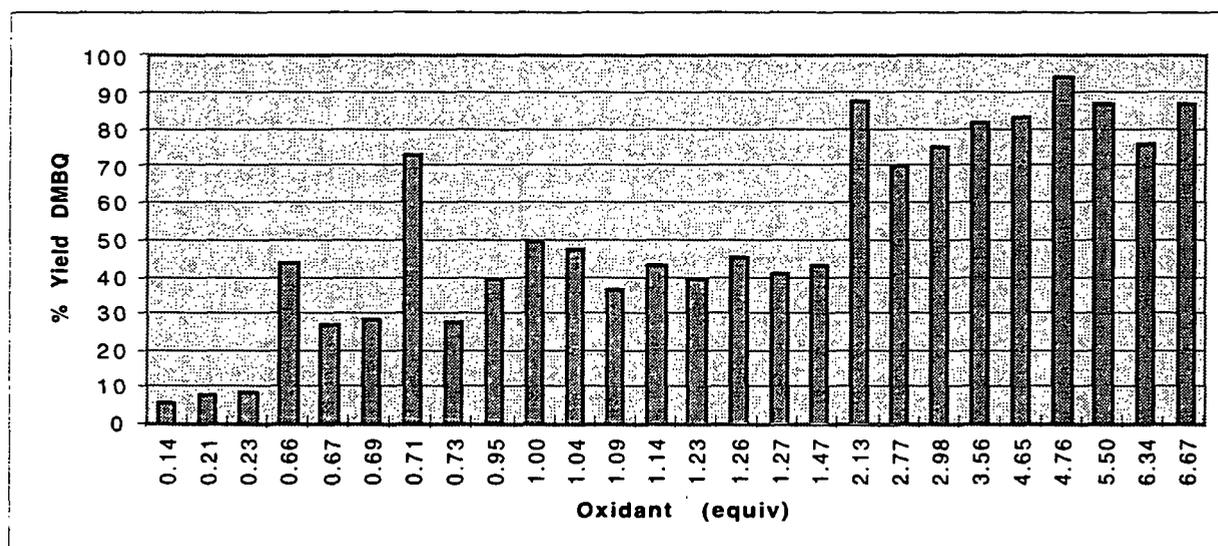


Figure 4 - DMBQ Mole % Yield for the NO<sub>2</sub> Oxidation of Syringaldehyde

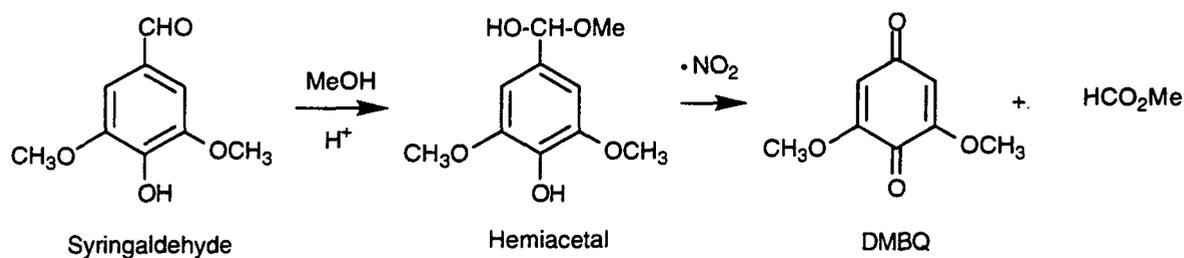


Figure 5 - Possible Mechanism for the Oxidation of Syringaldehyde

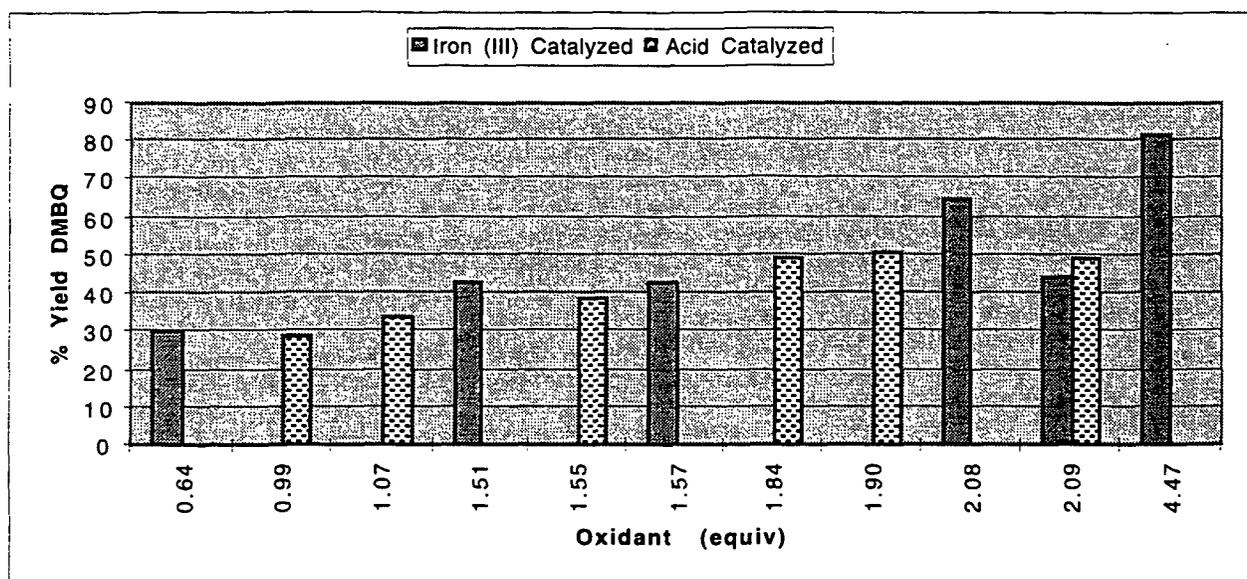


Figure 6 - DMBQ Mole % Yield for the NO<sub>2</sub> Oxidation of Syringaldehyde in the Presence of Catalysts

#### 4.5.3 Consecutive Oxidations of Syringaldehyde and Syringyl Alcohol

The presence of methyl nitrite indicates that NO<sub>2</sub> may react with methanol to give methyl nitrite:  $2\text{NO}_2 + \text{MeOH} \rightarrow \text{MeONO} + \text{HNO}_3$ . This reaction is likely reversible, meaning that methyl nitrite can break down to provide NO<sub>2</sub>, which is presumably the actual oxidant in the system. If so, the spent liquors from an oxidation step may be capable of oxidizing additional model compounds.

To test if this reaction is reversible, we performed an experiment in which the filtered solution from one oxidation (that employed 6 equiv. of NO<sub>2</sub> to give a 76% yield of DMBQ) was used to conduct another oxidation of a new batch of substrate; the headspace was flushed between oxidations. The DMBQ yield was 56% on the first solution reuse and 36% on a second reuse. Addition of K<sub>2</sub>CO<sub>3</sub> to the first solution dropped the DMBQ yield to 11%; K<sub>2</sub>CO<sub>3</sub> neutralizes the HNO<sub>3</sub> needed to regenerate NO<sub>2</sub> from methyl nitrite. These results show that under stoichiometric conditions, the NO<sub>2</sub> oxidation liquors contain the active oxidant, NO<sub>2</sub>, in the form of methyl nitrite, and that substantial amounts of oxidant still remain in solution after one oxidation. The mechanistic link between these results and those observed under catalytic conditions is unclear.

#### 4.6 Oxidations of Lignin - Stoichiometric NO<sub>2</sub>

A large number of reactions between Alcell lignin, NaNO<sub>2</sub> and HNO<sub>3</sub> in methanol have been conducted in order to optimize the yield of DMBQ. Since DMBQ was difficult to separate from the dissolved and undissolved lignin (not all of the lignin dissolves in methanol), we relied on GC analysis of whole samples to determine DMBQ yields. The methanol reactant solution was spiked with a GC standard in methylene chloride and injected directly into the GC. The DMBQ yields generally varied between 3-8% depending on the conditions employed (Table 5). Some of the variation was unexplained, for example, the decreased yield when the lignin/NaNO<sub>2</sub> ratio was high (entry two). The optimum reaction time and lignin/NaNO<sub>2</sub> molar ratio appear to be 1 hour and 1/0.5, respectively. In contrast to the results seen with model compounds and catalytic NO<sub>2</sub>, the DMBQ yield in these runs was adversely

affected by dropping the temperature to 0°C. There seems to be little yield difference when the reaction was done in an open vs. closed vessel. [Presumably, gaseous NO<sub>2</sub> would escape in an open vessel.] Reaction size (50 vs. 1 mmol of lignin) and longer reaction times also had little effect.

Table 5 - Yields of DMBQ for Different Oxidation Conditions Involving Sodium Nitrite

mmol Lignin	mmol NaNO <sub>2</sub>	mL MeOH	mL HNO <sub>3</sub>	Time (hrs)	Rxn conditions	DMBQ % Yield
1	5.2	10	0.5	3	RT, open vial	7.7
1	10	10	0.5	3	RT, open vial	3.6
1	0	10	0.5	3	RT, open vial	0.0
50	25	500	0.5	3	RT, open vial	7.3, 7.4
0.1	0.5	10	0.5	3	RT, open vial	8.6
1	0.5	10	0.5	3	RT, open vial	8.4, 10.7
1	0.5	10	0.5	3	iced, open vial	7.4, 0.8, 0.0
1	0.1	10	0.5	3	RT, closed vial	6.4, 5.6, 5.9
1	0.25	10	0.5	0.5	RT, closed vial	3.7, 4.0
1	0.25	10	0.5	1	RT, closed vial	4.7, 4.9
1	0.25	10	0.5	3	RT, closed vial	4.1, 5.2
1	1	10	0.5	3	RT, closed vial	3.1, 3.9

A series of experiments was conducted separating (after reaction) the insoluble lignin from the NaNO<sub>2</sub>/HNO<sub>3</sub>/methanol solution and adding another batch of lignin (but no more oxidant) to the solution five times. The scale of the reaction was 10 g (50 mmol) lignin each time and an initial charge of 50 mmoles of NaNO<sub>2</sub>, 3 mL of HNO<sub>3</sub>, and 500 mL of methanol. The new yield of DMBQ in the solution was ~3-4% each time; in other words, the yield of DMBQ in the solution kept increasing, even though fresh NaNO<sub>2</sub> and HNO<sub>3</sub> were not added. Extraction of the insoluble lignins and GC analysis of the extract showed no DMBQ. By the end of the second lignin treatment, we had exceeded the solubility (0.29 mg/mL) of DMBQ in methanol. Apparently, the acid and lignin in the solution are influencing the solubility of DMBQ. There is a portion (~20%) of the Alcell lignin that is not methanol soluble: roughly 80% of a 10 g sample of lignin dissolved in 5, 10, or 20 mL of methanol. The insoluble material does not give DMBQ when treated with NaNO<sub>2</sub>/HNO<sub>3</sub>/methanol solution.

#### 4.6.1 Fate of NO<sub>2</sub> in Lignin Oxidations

The above results were somewhat surprising in that separate experiments with NO<sub>2</sub> indicate that substantial amounts of NO<sub>2</sub> are consumed in unproductive lignin reactions. Elemental analyses (Table 6) indicated that Alcell lignin had a molecular formula of C<sub>10</sub>H<sub>13.1</sub>N<sub>0.06</sub>O<sub>4.7</sub>, while the lignin after NO<sub>2</sub> treatment had the formula of C<sub>10</sub>H<sub>12.9</sub>N<sub>0.46</sub>O<sub>6.8</sub>. The data indicate that approximately 50% of the aromatic rings on the residual lignin had been nitrated. Based on this result, we would expect that the reuse of spent liquors to carry out further oxidations will be less effective.

Table 6 - Elemental Analysis of Hardwood Lignin Samples

Lignin Before NO <sub>2</sub> Treatment				Lignin After NO <sub>2</sub> Treatment			
Element	Trial 1	Trial 2	Mean	Element	Trial 1	Trial 2	Mean
C	57.25%	57.16%	57.21%	C	48.43%	48.36%	48.40%
H	6.23%	6.25%	6.24%	H	5.13%	5.19%	5.16%
N	0.41%	0.38%	0.395%	N	2.62%	2.61%	2.615%
O <sup>a</sup>			36.15%	O <sup>a</sup>			43.83%

<sup>a</sup> Assumes that the remainder of the mass corresponds to oxygen.

#### 4.7 Identification of Suitable Lignin Sources

The results of both the model compound studies and the lignin oxidation work indicated that smaller lignin fragments were more effectively converted to quinones than were larger pieces. Therefore, several lignin fragmentation and pretreatment methods were investigated to develop a more suitable lignin starting material.

##### 4.7.1 Changing Pulping Cooking Times as a Way to Generate Low Molecular Weight Lignins

Efforts were directed at finding a lignin source that gave higher yields of DMBQ upon NO<sub>2</sub> or NaNO<sub>2</sub> oxidation. In general, the lignin should have a low molecular weight and contain mostly phenolic syringyl units. A lignin that we suspected would give high DMBQ yields when oxidized was a Kenaf soda lignin. Kenaf is known to have a high ratio of syringyl to guaiacyl units. However, Kenaf core and bast lignins gave DMBQ in only 1.3% and 3.5% yield, respectively, when evaluated under standard NO<sub>2</sub> oxidation conditions. A different sample (periodate hardwood lignin) gave only trace amounts of DMBQ under similar conditions.

Lignins from black liquors taken at different times over the course of kraft, soda/AQ and organosolv hardwood pulping have also been examined. The goal was to find a liquor that contained a large amount of uncondensed LMW lignin. Maximum DMBQ yield from NO<sub>2</sub> oxidation of the different kraft and soda/AQ lignins was observed in liquors sampled from about 15 minutes into the cook (Figure 7). For the organosolv liquors, the DMBQ yield from NO<sub>2</sub> oxidation of lignins isolated after different cook times was at a maximum at the harshest conditions (Figure 8).

We also evaluated three steam exploded lignins obtained from the laboratory of Prof. W.G. Glasser. Yellow poplar steam exploded lignins were obtained at three different severities (log Ro = 3.99, 4.23, and 4.50). The lignin sample prepared under the most vigorous conditions (log Ro = 4.50) gave the highest DMBQ yield (9.3%) after a standard NO<sub>2</sub> oxidation (Figure 9). This is the highest yield that we have obtained from a lignin sample which had not been subjected to a solvent extraction step. While cellulose obtained from steam explosion processes is not suitable for the preparation of paper, it can serve as a valuable feedstock for the chemical industry.

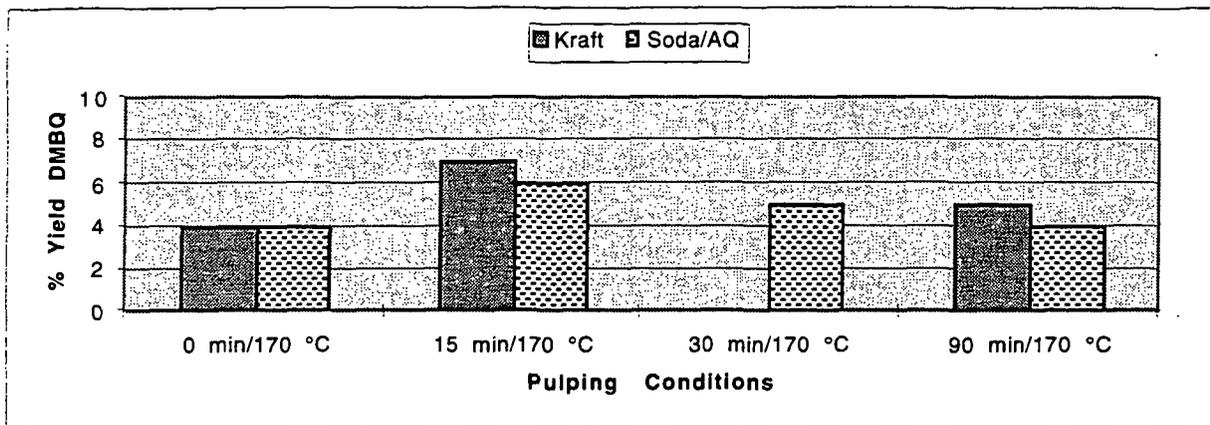


Figure 7 - DMBQ Wt% Yield for NO<sub>2</sub> Oxidation of Hardwood Lignins from Kraft and Soda/AQ Pulping

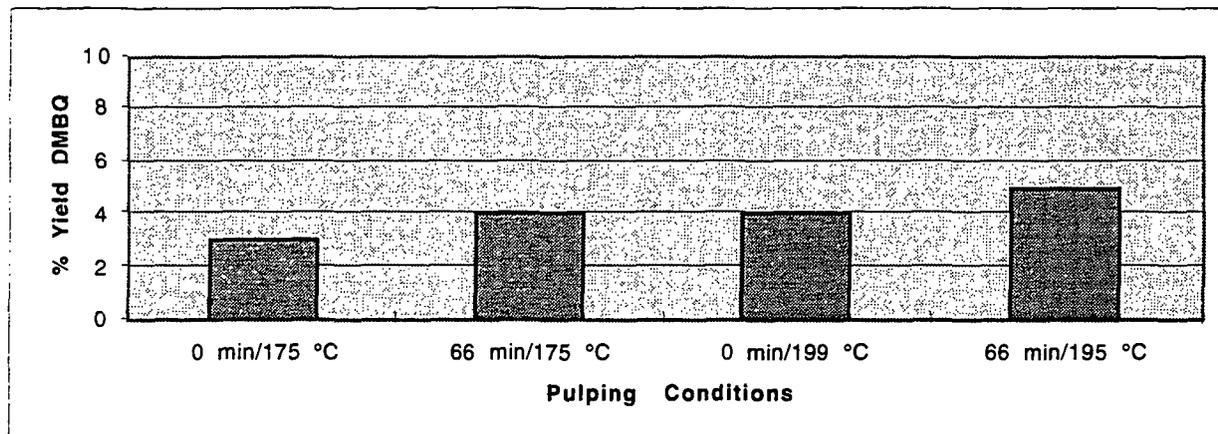


Figure 8 - DMBQ Wt% Yield for the NO<sub>2</sub> Oxidation of Hardwood Lignins from Organosolv Pulping

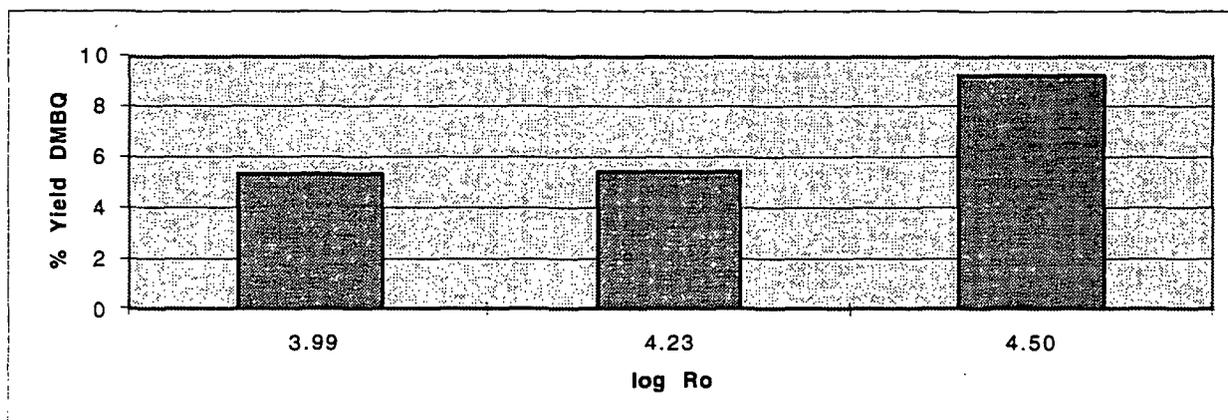


Figure 9 - DMBQ Wt% Yield for the Oxidation of Steam Exploded Yellow Poplar Lignin

## 4.8 Lignin Pretreatment Methods to Generate Low Molecular Weight Lignin

### 4.8.1 Acidolysis

Lignins were treated with 0.2M HCl in aqueous dioxane (90%), a procedure known to cause depolymerization, and then oxidized with  $\text{NO}_2$ . The effect of acidolysis time on the yield of DMBQ obtained from the oxidation step was monitored (Figure 10). The yield of DMBQ varied considerably and, except for a 34% increase at 3 hr, was generally less than the control. It appears that the cost vs. value of implementing an acid pretreatment step would be unfavorable.

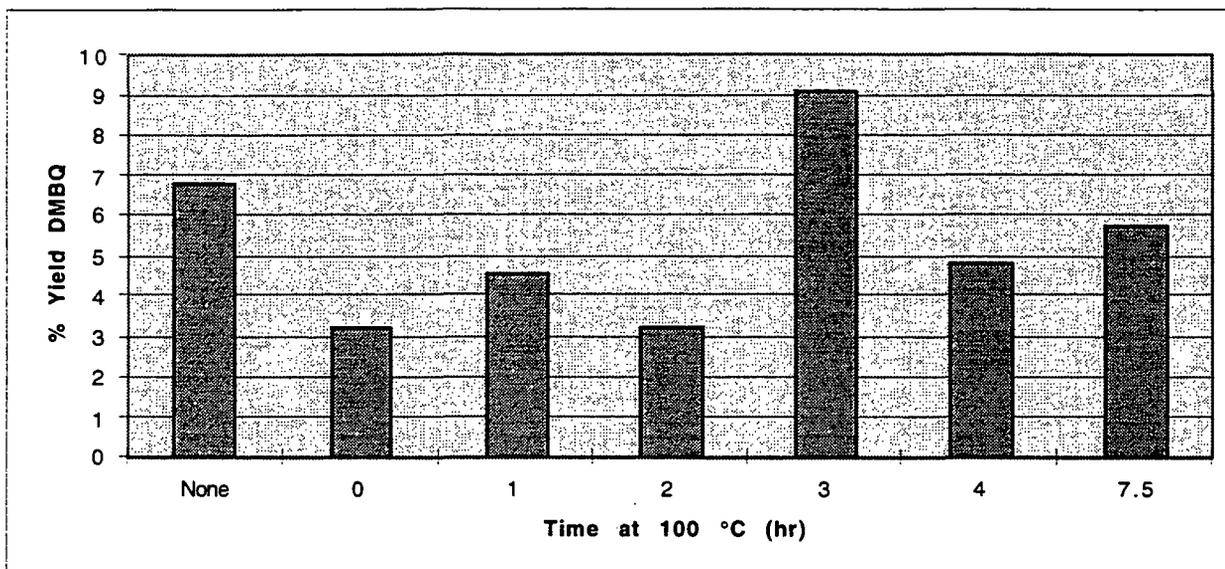


Figure 10 - DMBQ Wt% Yield from the Oxidation of Kraft Hardwood Lignins after Acidolysis

### 4.8.2 Copper Oxide Pretreatments

We studied the use of a copper oxide ( $\text{CuO}$ ) lignin pretreatment. Previous work has shown that treatment ( $170^\circ\text{C}$ , 1-5 hr) of lignin with an excess (7.5 equiv.) of  $\text{CuO}$  in aqueous  $\text{NaOH}$  resulted in significant depolymerization of lignin. The principal monomeric products formed by this pretreatment step were identified as vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone and syringic acid. The yield of DMBQ obtained from  $\text{NO}_2$  oxidation of the  $\text{CuO}$ -treated lignin was as high as 16.4%. This amounts to a two- to threefold increase in the yield of DMBQ, as compared to the unfractionated lignin. However, the use of stoichiometric amounts of  $\text{CuO}$  or  $\text{Cu}(\text{OH})_2$  on an industrial scale is probably not practical.

Investigations into the possible use of catalytic quantities of copper for lignin depolymerization were undertaken since it is well known that  $\text{Cu}(\text{I})$  is readily oxidized to  $\text{Cu}(\text{II})$  in the presence of oxygen. We observed poorer DMBQ yields from the  $\text{NO}_2$  oxidation of  $\text{CuO}/\text{O}_2$  treated lignin than an untreated lignin (5.1%); however, the yield was better when 0.50 equivalents of  $\text{CuO}$  were used than for 7.5 equivalents (4.1% vs 2.9%). Most likely, the oxygen caused the aldehydic  $\text{CuO}$  products to be further oxidized to  $\text{NO}_2$  inactive acidic products. Consequently, this method does not appear promising.

#### 4.8.3 Attempted Fractionation of Organosolv Lignins using Pulping Agents

Since organosolv lignins are obtained in the absence of traditional pulping agents (NaOH and NaSH), they may contain functionality which can be further degraded by subsequent treatment with these agents. An organosolv hardwood lignin was treated with aqueous solutions of NaOH, NaSH,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , ethanolamine and ethylenediamine at  $170^\circ\text{C}$  for 30 min. The lignins were then isolated by acidification to pH 1 or 7 using HCl and subjected to  $\text{NO}_2$  oxidation. In every case, the yield of DMBQ decreased. The effluents from these reactions were found to contain only trace amounts of soluble organic compounds.

#### 4.8.4 Attempted Fractionation of Organosolv Lignins using Laccase/ABTS

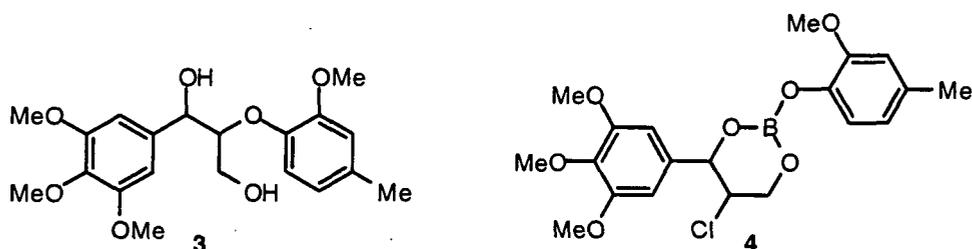
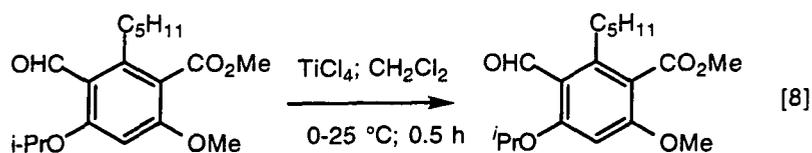
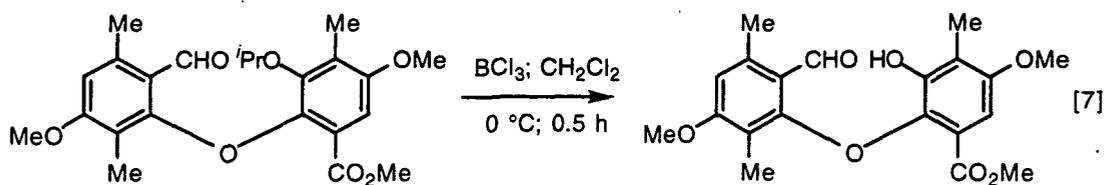
Recent literature references document the ability of laccase/ABTS to delignify kraft pulps without out substantial degradation of cellulose. We examined the use of laccase/ABTS as a lignin pretreatment to fractionate hardwood lignins into smaller units suitable for  $\text{NO}_2$  oxidation. Since little is known with regard to the reaction of dissolved lignin with laccase/ABTS, we set up a statistically designed experiment to examine several factors: type of lignin (kraft versus organosolv using the same chip source); amount of laccase and ABTS (2-3% versus 10-11% based on lignin) and time (1 hr and 24 hr). The effectiveness of each trial was determined by subsequent  $\text{NO}_2$  oxidation on the isolated lignins. The yield of DMBQ from each of the enzyme treated lignin samples was compared to that of the parent lignin. Unfortunately, in all cases the yield of DMBQ was significantly lower than that of the untreated lignins. These results suggest that the principal mode of delignification by the laccase/ABTS catalyst involves demethylation.

#### 4.8.5 Lignin Dimer Model and Lignin Fractionation using Lewis Acid Treatments

Substantial increases in the yield of DMBQ should be possible if the  $\beta$ -O-4 ether linkages in lignin can be cleaved without demethylation. Sala and Sargent have described a simple, highly selective method for the cleavage of isopropyl aryl ethers (equations 7 and 8). Treatment of the substrate with an excess of either boron trichloride or titanium tetrachloride followed by treatment with aqueous 1.0 M HCl, gave the corresponding phenol in high yield. Boron trichloride was found to react more rapidly and gave less complex reaction mixtures than titanium tetrachloride.

Since the major linkage in lignin is the  $\beta$ -O-4 ether (actually a functionalized isopropyl ether), application of either  $\text{BCl}_3$  or  $\text{TiCl}_4$  might dramatically increase the number phenolic end groups present and increase the yield of DMBQ. Prior to investigating the effectiveness of these reagents for aryl ether cleavage in lignin, we synthesized a nonphenolic syringyl- $\beta$ -O-4 guaiacyl lignin dimer 3 to determine if the hydroxyl groups on  $\text{C}_\alpha$  and  $\text{C}_\gamma$  would adversely effect the course of the reaction.

Treatment of 3 with  $\text{BCl}_3$  under a variety of conditions resulted in yields of 2-methoxy-4-methylphenol (an ether cleavage product) between 36-50%. Analysis of the crude reaction mixtures by  $^1\text{H-NMR}$  indicated that only trace amounts of the  $\beta$ -O-4 ether linkage remained. The low recovery of phenol product, together with the absence of starting material, suggests that the hydrolysis of expected intermediate phenol-borate ester 4 may be incomplete, and/or other nondetectable products are formed. Since the presence of the hydroxyl groups did not seem to adversely effect the reaction, we also carried out the reaction in methanol; however, the yields were lower.



Samples of organosolv and kraft hardwood lignins, as well as steam exploded yellow poplar lignin, were treated with  $\text{BCl}_3$  in methanol (30 min), then  $\text{NO}_2$  was added to the solution. Pretreatment of the lignin with  $\text{BCl}_3$  failed to increase the yield of DMBQ in the subsequent  $\text{NO}_2$  oxidation step (Table 7).

**Table 7- Effect of  $\text{BCl}_3$  Pretreatment on the Yield of DMBQ from Hardwood Lignins**

Lignin Type	Yield of DMBQ	
	with $\text{BCl}_3$ (%)	without $\text{BCl}_3$ (%)
Alcell <sup>a</sup>	6.4	7.7
Kraft <sup>b</sup>	6.8	6.8
Organosolv <sup>a</sup>	5.2	6.8
Steam Exploded <sup>d</sup>	6.9	9.3

<sup>a</sup> Commercial sample from REPAP. <sup>b</sup> Prepared using standard kraft conditions on mixed hardwood chips at 170°C for 15 min. <sup>c</sup> Prepared using a 90:10 mixture of EtOH and  $\text{H}_2\text{O}$  on mixed hardwood chips at 195°C for 60 min. <sup>d</sup> Steam explosion pulping of yellow poplar with a log  $R_0$  of 4.50.

#### 4.8.6 Lignin Fractionating via Solvent Extraction

We have previously shown that the yield of DMBQ can be substantially increased by selectively extracting the LMW components from a hardwood lignin sample with methyl isobutyl ketone before performing the  $\text{NO}_2$  step. Alcell hardwood lignin was subjected to a variety of solvent extractions and acid pretreatments (Figure 11). The ether extraction led to the most dramatic increases in the yield of DMBQ; however, the cost vs. benefit of implementing an ether extraction step would likely be unfavorable since this adds a processing step and, thus, a cost. Since the  $\text{NO}_2$  oxidation step is carried out in methanol, it was hoped that a method could be developed for the selective extraction of LMW components using methanol. A comparison has been made between a methanol and methyl isobutyl ketone extraction prior to  $\text{NO}_2$  treatment of a kraft hardwood lignin (Figure 12). Methanol extraction resulted in a 22% increase in the yield of DMBQ (6.8%  $\rightarrow$  8.3%), however, the yield went down with the MIBK extraction.

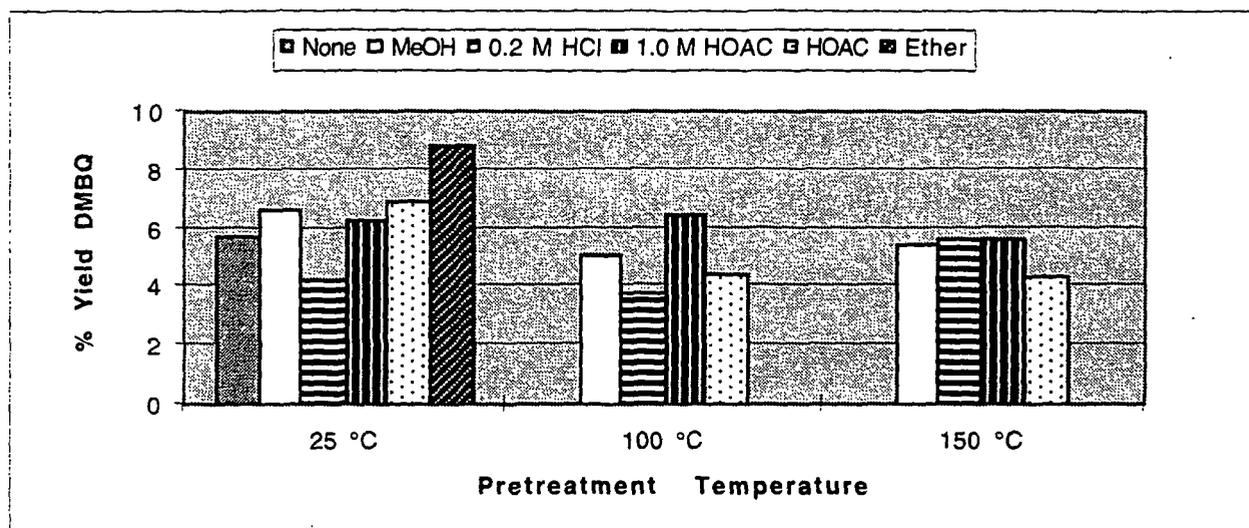


Figure 11 - NO<sub>2</sub> Oxidation of Fractionated Alcell Lignin

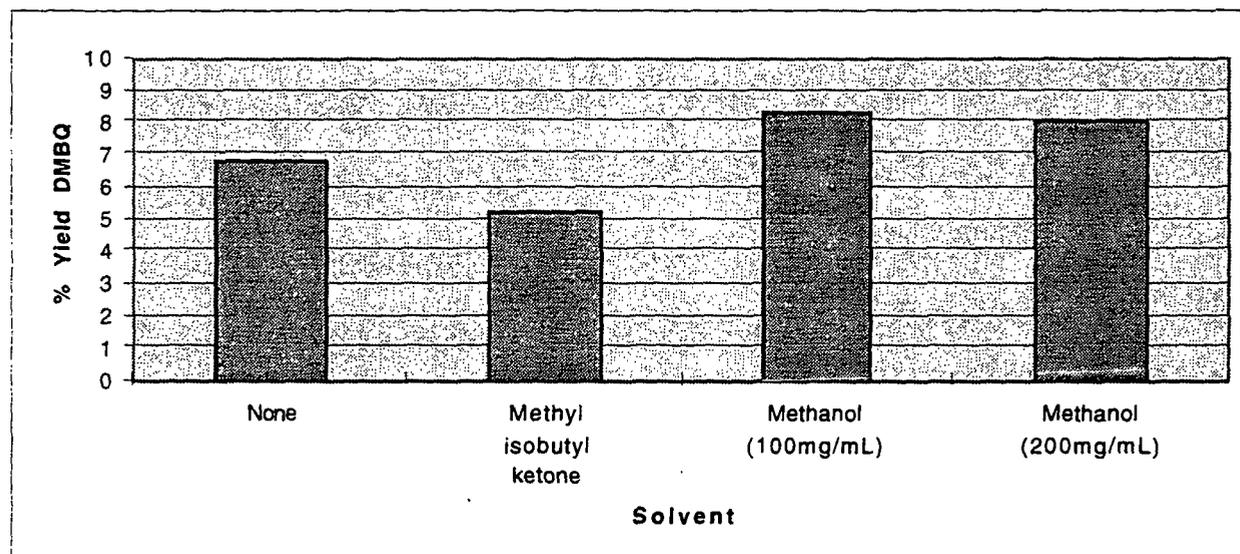


Figure 12 - DMBQ Wt. % Yield for Oxidation of Solvent Extracted Kraft Hardwood Lignin

#### 4.8.7 Alternatives to NO<sub>2</sub> Oxidation

Several attempts were directed at finding an alternative to NO<sub>2</sub>. The use of oxygen in methanol was examined. Here, we hoped to take advantage of the low solubility of DMBQ in methanol. Many different model compounds and different reaction conditions were explored; however, none or only very small amounts of DMBQ were observed. Singlet oxygen, generated from aqueous sodium hypochlorite/HOOH, provided incomplete (but clean) conversions of model compounds to DMBQ, but was very ineffective (<1% yield) with a hardwood lignin. The combination of ClO<sub>2</sub> and alkaline HOOH gave a 68% yield of DMBQ from syringaldehyde; when the reagents were used separately, the DMBQ yields

were 0 and 14%, respectively. The combination gave <1% yields of DMBQ from a hardwood lignin. Catalytic quantities of polyoxometalates with HOOH also proved ineffective as a way to increase DMBQ yields. Several different mole ratios were tried with each of the oxidants described above; however, significant yield improvements were not observed. Nitrogen dioxide remains the best oxidant examined.

## 5.0 OXIDATIONS WITH HOOH

### 5.1 Introduction

Hydrogen peroxide is an oxidant well known to the pulp and paper industry. The literature reports a class of catalysts, based mainly on Mo and W, that mediates the high reactivity of HOOH toward lignin and lignin-like compounds. The structures of these catalysts can be highly varied, starting from simple salts such sodium molybdate,  $\text{Na}_2\text{MoO}_4$ , up to the much more complex heteropolyacids (HPAs), which consist of several metal atoms in a network of oxygen atoms. A typical example of an HPA is phosphomolybdic acid,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . These complexes exhibit high oxidation states at the metal, so that the oxidative decomposition is not a problem. They also exhibit catalytic activity at very low levels, 1% or less. Moreover, many synthetic methods are known for adding different metals or ligands to the complex, allowing "tuning" of the reactivity of a given complex simply by choice of ligand.<sup>19</sup> These features combined to make these catalysts attractive alternatives to others investigated, for example, the Co-Schiff base/ $\text{O}_2$  catalysts described in previous reports.<sup>8</sup> The literature reveals many different uses of these materials as catalysts for different types of oxidations, all of which proceed by the formation of metal peroxo complexes.<sup>20</sup> Important to the project was the realization that several different catalytic species could be tested on lignin and lignin models because of the ready interchangeability of these species with one another using fairly simple changes in reaction conditions.

### 5.2 Background

Despite the different levels of structural complexity observed for these Mo and W based catalysts, the literature reveals that their interaction with HOOH results in a convergence upon a few common structural types, regardless of the nature of the starting catalyst. Each of these common structures can exhibit catalytic activity. A summary of the observed reactivity between different metal complexes and HOOH is shown in Figure 13.

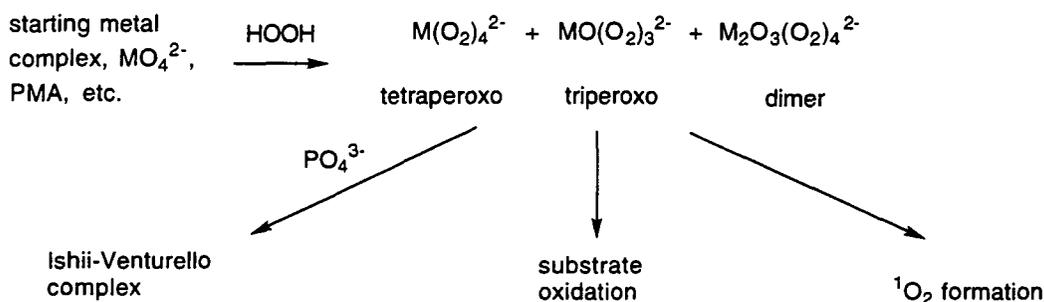


Figure 13 - Interaction of Mo and W Based Oxidation Catalysts with HOOH

In general, a Mo or W based complex undergoes reaction with HOOH to form three different structures, a reactive and fairly unstable tetraperoxo complex, a triperoxo metal oxide, and a dimeric peroxo complex. The proportion of each of these materials depends on the pH of the reaction medium. Depending on the substrate and the reaction conditions employed, each of these materials has been

demonstrated to exhibit catalytic activity for oxidation of different substrates. In the absence of substrate, singlet oxygen formation is observed with Mo based catalysts. Finally, treatment of many of these materials with HOOH and  $\text{PO}_4^{3-}$  results in the assembly of these species into a four-metal complex called the Ishii-Venturello complex, a material proven useful in the oxidation of several different substrates. Not all HPAs undergo this transformation. For example,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and  $\text{H}_5\text{BW}_{12}\text{O}_{40}$  are found to maintain their structural integrity upon treatment with HOOH.<sup>21</sup> However, their catalytic activity (using epoxidation of olefins as the model) is almost zero. It appears that the formation of the species shown in Figure 13 is a necessary prerequisite for catalytic activity.

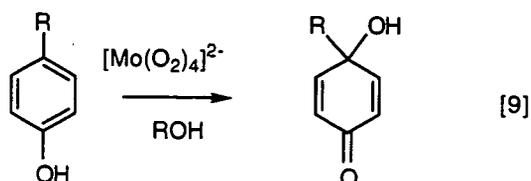
The composition of this mixture in solution depends on the pH of the solution. The different types of complexes formed in aqueous solution from molybdate and tungstate salts in the presence of HOOH have been investigated by several groups.<sup>22</sup> Using both Raman and  $^{95}\text{Mo}$  nmr, Griffith made the following assignments (Table 8).

Table 8 - Complexes Observed from Reaction of Mo Salts with HOOH as a Function of pH

pH range	complex
>9	Deep red solutions of highly unstable species
9 - 5	from pH 8.8 - 8.2, $[\text{Mo}(\text{O}_2)_4]^{2-}$ with excess HOOH from pH 7.2 - 5.0, $[\text{Mo}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ , (although it persists to about pH 2.5), and possibly the triperoxo species $[\text{Mo}(\text{O}_2)_3]^{2-}$ and $[\text{MoO}(\text{O}_2)_3(\text{H}_2\text{O})]^{2-}$
5 - 2.5	$[\text{Mo}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$
<2.5	$[\text{MoO}(\text{OH})(\text{O}_2)_2]$ and $[\text{MoO}_3(\text{O}_2)]^{2-}$ along with other monoperoxo species
<1.3	Species become unstable and lose oxygen

The initial structure of the catalyst does not affect this transformation. More complex peroxo species are broken down into these simpler complexes upon dissolution in water and treatment with HOOH, while simpler species are assembled to the higher HPAs of Figure 13. For example,  $[\text{NH}_4]_8[\text{Mo}_{10}\text{O}_{22}(\text{O}_2)_{12}]$  hydrate gives identical spectra in the solid state and solution, showing that its structure is maintained. However, addition of HOOH results in the formation of the simpler species described in Figure 13. Phosphomolybdic acid also undergoes this reaction with HOOH.<sup>23</sup> However, simple species, such as  $\text{Na}_2\text{MoO}_4$  also are converted to these intermediate complexes. Tungsten based species behave similarly with only minor variations.

The simplest metal/peroxo complex,  $\text{Mo}(\text{O}_2)_4^{2-}$ , can be prepared upon the direct interaction of alkali metal molybdates or tungstates with HOOH under neutral conditions.<sup>24</sup> This somewhat unstable tetraperoxomolybdate complex has been used stoichiometrically for the oxidation of phenolics to quinols (equation 9).



The actual oxidant in this neutral process has been suggested to be chemically generated singlet oxygen, as described in Figure 13. Several groups have successfully probed similar reactions for evidence of its involvement.<sup>25</sup> The rate of singlet oxygen production from these complexes appears to reach a maximum at about pH 10.5.<sup>26</sup> The source of singlet oxygen has been determined to be the triperoxymolybdate,  $\text{MoO}(\text{O}_2)_3^{2-}$ .<sup>27</sup> Other results had suggested that a diperoxy complex,  $\text{MoO}(\text{O}_2)_2^{2-}$  was the source, but this complex is predicted to be ten times as stable as the triperoxy species, based on measured rate constants.

The involvement of singlet oxygen appears to be concentration dependent. Studies on the oxidation of phenolphthalein by  $\text{HOOH}$  in the presence of metal catalysts have been carried out to investigate the mechanism of bleaching by  $\text{HOOH}$ , and the possible involvement of singlet oxygen.<sup>28</sup> At low ( $1 - 50 \mu\text{mol}/\text{dm}^{-3}$ ) metal concentrations, the oxidation rate was significantly increased over the control. However, no effect on this increased rate was seen in the presence of metal sequestering agents, free radical traps, or singlet oxygen traps. In the absence of metals, the oxidation mechanism for phenolphthalein is thought to be as shown in Figure 14.<sup>29</sup>

Presumably, the metal catalyzed process would proceed in a similar manner with a metal peroxo complex replacing the  $\text{HOOH}$ . Two general mechanisms for the key epoxidation step have been postulated. A process suggested by Mimoun involves initial formation of a metal-olefin  $\pi$ -complex, followed by addition to form a 5-membered oxametallacycle.<sup>30</sup> Subsequent theoretical work<sup>31</sup> shows such a five membered system to be too high in energy, and an alternate process suggested by Sharpless involving an epoxidation via a three member transition state is considered more reasonable following initial formation of the  $\pi$ -complex.<sup>32</sup> The active species in the metal catalyzed process, at low metal concentrations, appears to be the tetraperoxo molybdate,  $\text{Mo}(\text{O}_2)_4^{2-}$ . Interestingly, when the metal concentration is increased to  $\text{mmol}/\text{dm}^{-3}$  levels, singlet oxygen traps slow the reaction. The authors conclude that the reaction is "directly" catalyzed at low metal concentrations. However, as the metal concentration increases, a new "indirect" process, involving singlet oxygen, begins to take over.

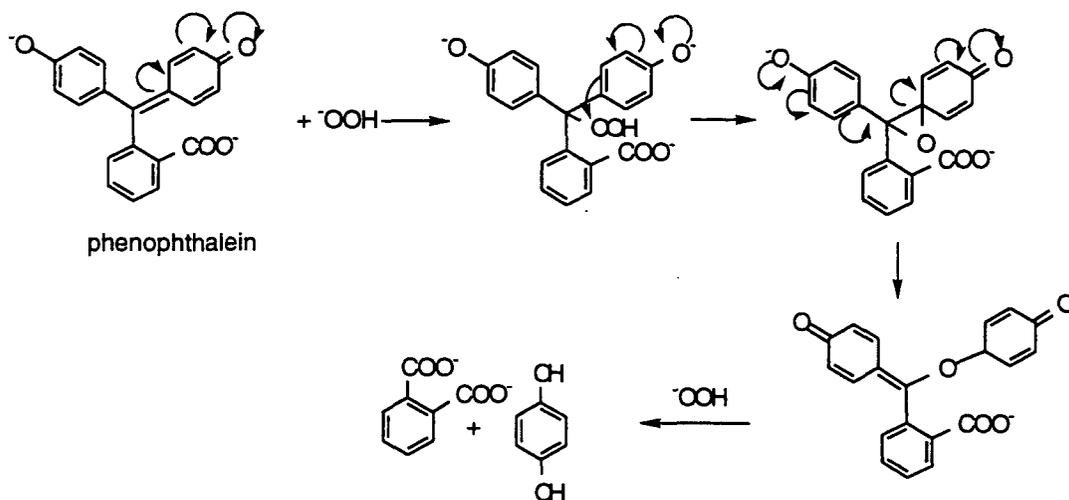
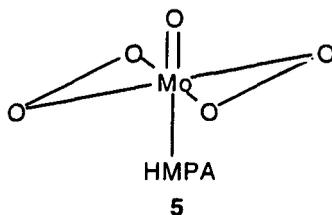
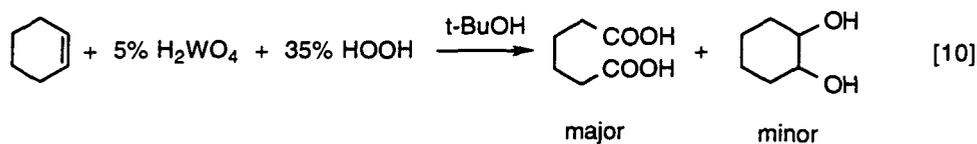


Figure 14 - Mechanism of  $\text{HOOH}$  Oxidation of Phenolphthalein

Under acidic conditions, yet another peroxomolybdate can be prepared. This complex was first described in 1964,<sup>33</sup> but its structure (and that of related complexes) was not known until later.<sup>34</sup> The complex can be isolated and characterized as its HMPA adduct 5; other ligands can also serve the same purpose.



This complex, sometimes referred to as the Milas reagent,<sup>21</sup> has proven useful for the oxidation of a variety of different substrates. Methodology for supporting this catalyst on an Amberlyst backbone has been described.<sup>35</sup> This mixture, and variations on it, has been used for oxidation of a variety of materials. Cyclic olefins have been cleaved to dicarboxylic acids in an attempt to make adipic acid from cyclohexene (equation 10).<sup>36</sup>



Tungstic acid appeared key to this oxidation. The yield of products was much lower using either molybdic acid or sodium tungstate. Since diol was observed in most examples, the oxidation was suggested to proceed through the diol and then to the dicarboxylic acid.

This complex was initially formed in alcoholic solvents, however, its rate of reaction in polar media is low. The oxidation rates are increased by changing to less polar solvents, but HOOH solubility becomes a problem. To overcome these issues, the reactions have been performed under phase transfer conditions. The effectiveness of the transfer under these conditions has been examined.<sup>37</sup> Two methods of performing this phase transfer process have been employed. The first, and more traditional, uses a cationic quaternary ammonium salt as the phase transfer agent. The second uses the ligand attached to complex 5 to effect the transfer. The difference between these approaches is that cationic ligands extract anionic oxidants such as  $[\text{MO}_5(\text{OH})(\text{H}_2\text{O})_m]^-$ , while neutral ligands extract neutral species, such as complex 5. This difference suggests that different oxidation mechanisms exist depending on the species extracted.<sup>38</sup> The effectiveness of the extraction of the catalyst by neutral ligands indicates that there are several factors that influence the effectiveness of the oxidation, including acidity of the aqueous phase and lipophilicity of the neutral ligand.<sup>37</sup>

The neutral ligand method has been used successfully for the oxidation of nucleophilic substrates such as sulfides and the epoxidation of olefins.<sup>39</sup> Alkynes also undergo oxidation to keto aldehydes with this technique.<sup>38</sup>

Alcohols undergo much more ready oxidations in less acidic media. A phase transfer approach was used at higher pH than reactions using the neutral ligand transfer method by substituting a cationic quaternary ammonium salt (Aliquat 336) as the phase transfer agent.<sup>40</sup> At these pH values, the oxidizing agent is anionic, which is normally poor for nucleophilic substrates such as alcohols. Since the reactions proceed well, a different mechanistic path has been suggested. The paper also compares the results of the alcohol oxidation approach to methodology that was successful for olefin epoxidation.<sup>41</sup>

The other complexes described in Figure 13 also show utility as oxidants for a variety of different substrates. At literature pH values used in certain oxidations, the dimer would be the major species for both molybdate and tungstate catalyzed processes. However, dimer formation is concentration

dependent. At low metal concentrations, it does not form.<sup>42</sup> Identification of the dimer as the key species in several oxidations has been obtained by the use of isolated dimeric complexes as starting materials in oxidations of alcohols<sup>40</sup> and amines,<sup>43</sup> and for the epoxidation<sup>44</sup> and cleavage of olefins.<sup>45</sup> The structure of the dimer has been verified by x-ray analysis.<sup>46</sup> Note that while the previous researchers may not explicitly describe the intermediacy of the dimeric complex in each of these papers, the conditions they report are completely consistent with those needed for dimer formation.

These Mo and W catalysts also undergo self assembly in the presence of  $\text{PO}_4^{3-}$  to form a catalyst known as the Ishii-Venturello complex (6, Figure 15). The structure of 6 has been probed by x-ray.<sup>47</sup> This complex can be prepared in a number of ways, and was the source of some confusion because of the similar results in olefin epoxidation realized by different groups using different approaches. However, 6 appears to be the catalytically active species in these systems.

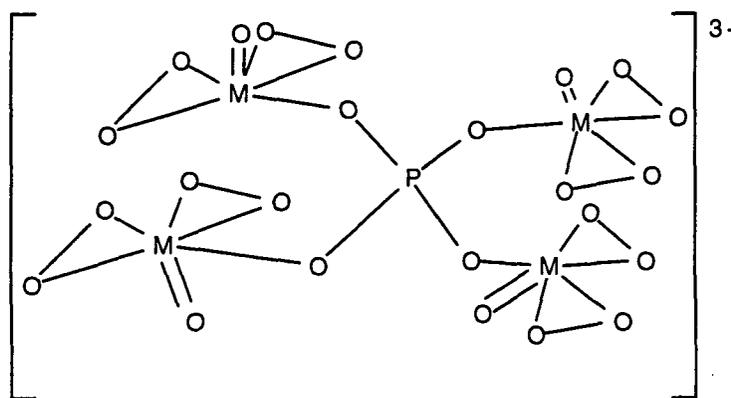


Figure 15 - The Ishii-Venturello Complex (6)

Compound 6 has been identified as the catalytically active species in oxidations of several substrates, including amines and alcohols,<sup>48</sup> olefin epoxidation<sup>49</sup> and cleavage.<sup>50</sup>

A more detailed kinetic and mechanistic evaluation of these materials has appeared and proposes a simple mechanistic scheme (Figure 16).<sup>51</sup>

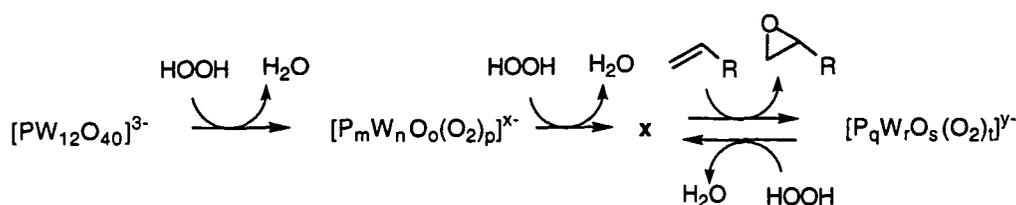


Figure 16 - Proposed Mechanism for Formation of Catalytically Active Oxidizing Agent

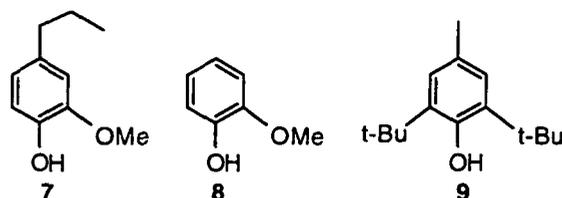
The starting heteropolyanion is broken down in successive steps to give the catalytically active complex 6. Compound 6 transfers an oxygen to the olefin, giving the epoxide and is itself converted into a mixture of "subsequent peroxo substances". These materials are reoxidized with HOOH to complex 6 to complete the catalytic cycle.

Several examples of these complexes have been reported for different applications. Cyclohexene has been converted to the corresponding diol upon treatment with a polyoxometallate and HOOH in the presence of a phase transfer catalyst. Both simple heteropolyanions and "filled lacuna" heteropolyanions were used. A closely related work indicates that the diols can also be further converted to carboxylic acids.<sup>48</sup> Slightly different conditions were reported effective for the cleavage of cyclopentene to the corresponding dialdehyde.<sup>51</sup> Although mechanisms are not suggested, one can assume that complex 6 is a key player given the similarity of the reported reaction conditions in each.

### 5.3 Oxidation of Lignin Models - HOOH with Mo and W Catalysts

Based on our investigation of the literature, the approach chosen for the first step in the lignin-to-catalyst sequence has been to use readily available, inexpensive, and environmentally benign oxidants, such as HOOH and oxygen. However, these materials are generally too reactive to use directly, and considerable work has been reported describing methods for mediating the reactivity of HOOH and oxygen, and thus, greatly improving the selectivity of the oxidations through the use of catalysts. We have investigated several different catalysts for these oxidations and have studied their effectiveness by testing them on materials that model lignin. Based on the considerable diversity of complexes available with fairly simple modification of reaction conditions, we investigated Mo and W based catalysts for the oxidation.

Several of the complexes available from the reaction of HPAs and simpler molybdates and tungstates have been investigated as selective activators for HOOH to oxidize lignin and lignin models. Several lignin models were chosen for investigation. Given earlier information indicating that the alkyl side chain of the lignin possessed few oxygenated groups, 4-propylguaiacol (7), guaiacol (8), and di-*t*-butyl-*p*-methylphenol (9) were investigated as model substrates. Treatment of these compounds with the simple tetraperoxo Mo complex  $\text{Mo}(\text{O}_2)_4^{2-}$  was investigated as a way to convert the phenolics into the corresponding quinols as described above in equation 9.



Production of quinols instead of quinones suggested a conceptually new way of looking at the production of pulping catalysts from lignin (Figure 17).

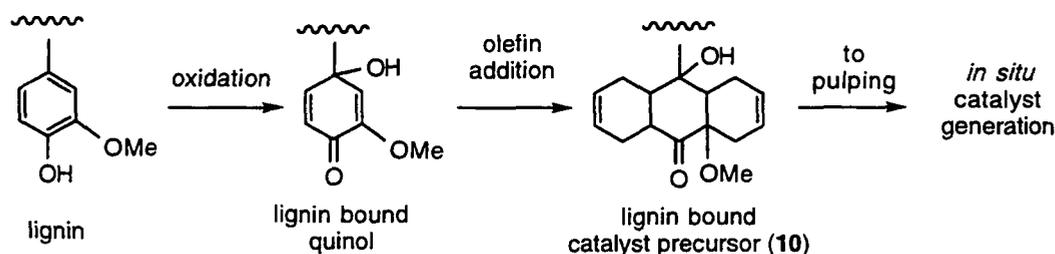
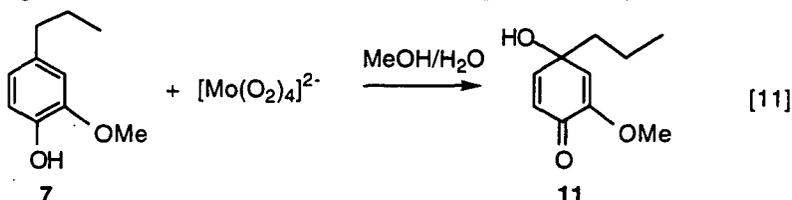


Figure 17 - Alternate Route to Pulping Catalysts from Lignin

In general, oxidation methods that cleave the group *para* to the aromatic OH have been pursued in order to convert lignin to benzoquinones (equation 1). However, that approach has been followed in

order to prepare a substrate that undergoes a ready addition of olefin in the second step. Since quinols possess the same functionality as quinones, they should undergo a similar olefin addition and lead to lignin bound catalyst precursor 10. This material might easily be converted to an active pulping catalyst *in situ* during the actual pulping run. This approach has the additional advantage of being able to use milder oxidizing agents, and could increase the relative amount of lignin converted to active pulping catalyst. Requiring that the *para* group be cleaved during oxidation requires the presence of certain functional groups on the lignin side chain. In contrast, quinol formation appears to be insensitive to the type of side chain present in lignin. Use of AQ-type catalyst precursors has been reported by others to be effective.<sup>52</sup>

Initial treatment of 7 with stoichiometric amounts of this material in aqueous methanol using literature conditions gives conversion to the corresponding quinol (11, equation 11).



The material balance of the reaction is low, and may indicate the presence of nonproductive side reactions.

Investigation into developing a catalytic version of this process was also carried out. Surprisingly, very little quinol is observed upon decreasing the amount of Na<sub>2</sub>MoO<sub>4</sub> to 25 mol%. Starting phenol is the major product. At least a stoichiometric amount of quinol (i. e., 25%, reflecting the amount of catalyst employed) would be expected from this reaction, yet considerably less than that amount is observed. Suspecting that HOOH was undergoing decomposition rather than acting as an oxidant, we performed the reaction adding the HOOH over a long period of time via syringe pump. Starting material was consumed and the amount of quinol present increased. However, other side products were also observed.

#### 5.4 Phase Transfer Oxidations

Other approaches have been studied under conditions optimized for production of other catalytic species shown in Figure 13. Much of the reported work used phase transfer conditions to facilitate the transfer of the oxidant to the organic reactant and minimize over-oxidation. Reaction of 7 with HOOH in the presence of WPCP under phase transfer conditions in CHCl<sub>3</sub> at room temperature was unsuccessful.<sup>48</sup> Compound 7 proved largely inert to these conditions and starting material was recovered in high yield. When the reaction was performed at higher temperature, starting material was consumed but the reaction was not selective; several products were observed. The failure of this reaction was apparently not a function of the presence of the *para*-propyl group. Reaction of guaiacol (8) under the same conditions gave only recovery of starting material. Surprisingly, reaction of 2,6-di-*t*-butyl-4-methylphenol (9), a widely used, easily oxidizable phenol, under the same conditions also resulted in the recovery of starting material. The reason for the failure of these reactions is not clear, however, the catalyst/HOOH mixture is reported to be suitable for olefin epoxidation. Application of the mixture for oxidation of phenolics has not been reported.

The first set of reactions investigated the use of Na<sub>2</sub>WO<sub>4</sub> in the presence of quat salts with HOOH as a catalyst. The reactions were based on literature precedent.<sup>38,51</sup> These phase transfer reactions using a large number of quat salts as phase transfer catalysts allow reaction to take place in an organic phase

while regenerating the catalyst in the aqueous phase, normally with HOOH as the oxidant. At room temperature, only small amounts of reaction were seen, while at 55°C, nonselective decomposition occurred. A change in quat salt according to the literature<sup>38</sup> gave no improvement. Only very small amounts of any kind of reaction were observed. In fact, even 8 failed to undergo any reaction under these conditions, which was very surprising.

Compound 7 was studied with catalytic tungstate in the absence of quat salt and was decomposed nonselectively with HOOH in aqueous MeOH. Stoichiometric tungstate, surprisingly, gave almost all starting material as the only isolable product, but in poor material balance.

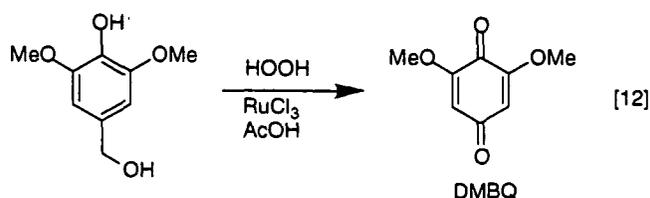
Under the proper conditions, some oxidation was observed. For example, compound 9 was converted into the corresponding quinone upon treatment with peracetic acid. This particular reaction was first carried out in the presence of phosphomolybdic acid according to conditions reported in the literature.<sup>53</sup> However, appropriate control reactions demonstrated that a mixture of HOOH in HOAc (which forms peracetic acid) was sufficient to induce oxidation. The catalyst was not involved. Moreover, peracetic acid is probably too expensive to use in a lignin-to-catalyst process.

### 5.5 Oxidations with HOOH and Ru Catalysts

Recently, numerous publications on the ruthenium catalyzed epoxidation of olefins,<sup>54</sup> and oxidation of alcohols<sup>55</sup> and phenols<sup>56</sup> have appeared. These methodologies use catalytic amounts of ruthenium complexes, produce high yields of single products and need only peroxides or pyridine N-oxides as the oxidant. In view of these results, we chose to apply the ruthenium systems towards the conversion of lignin models to benzoquinones.

A recent literature report described the utility of Ru based catalysts for the oxidation of phenolic compounds: A series of reactions was carried out on lignin models using RuCl<sub>3</sub> as a catalyst, and peroxide reagents (HOOH and t-BuOOH) as the oxidants. The summary of this study is simple. The conditions were almost always too harsh for the lignin models, and gave product mixtures often characterized by low material balances. Interestingly, models that were typically inert to other sets of conditions (eugenol, acetosyringone) were consumed by these conditions, but nonselectively.

We initially used the method of Matsumoto for the oxidation of syringyl alcohol. This involved the addition of HOOH to a mixture of syringyl alcohol and RuCl<sub>3</sub> in acetic acid (equation 12). Conversion of the starting syringyl alcohol was quantitative, however only trace amounts of DMBQ were isolated. We attributed this to decomposition in the acidic medium.<sup>57</sup> Importantly, there also appears to be a competition in the reaction between oxidation of the lignin model and metal promoted decomposition of the HOOH. Certain Ru complexes can cause decomposition of HOOH. The key to overcoming this decomposition appears to be adjusting the conditions to favor substrate oxidation. To this end, we have investigated controlled addition of the HOOH to the reaction, changing solvents, and increasing the reaction temperature. Of these modifications, a change of solvent appears to have the greatest effect. These results are shown in Table 9 using syringyl alcohol as a model. Since DMBQ is insoluble in methanol, we felt that use of methanol as the solvent would drive the reaction to completion by causing precipitation of the DMBQ as it is formed. This would prevent decomposition and also facilitate workup of the reaction, as filtration is all that would be required. We found that conversion of syringyl alcohol to DMBQ occurs in moderate yields in a 2:1 mixture of methanol/acetic acid, however optimal results were produced by simply using methanol as the solvent (65%).



**Table 9 - Solvent Systems used in Ru/HOOH Oxidations of Syringyl Alcohol**

Solvent System	% Isolated Yield
Ethyl acetate/MeCN	2
Ethyl acetate/ethanol	0
Ethyl acetate/methanol	0
Ethyl acetate/CH <sub>2</sub> Cl <sub>2</sub>	8
Acetic Acid	5
Acetic Acid/methanol	51
Methanol	65

We have also investigated the effect of lower concentrations of HOOH by changing from 70% peroxide to 30% peroxide. Interestingly, the reaction appears to need the more concentrated concentration. In preliminary experiments, use of 30% peroxide gave no indication of quinone formation with a variety of lignin models. This result could indicate that the concentration of water present in the oxidation could be important. Finally, raising the reaction temperature has produced a lowering of product yield. For example, using 4-allyl-2,6-dimethoxyphenol as a substrate and raising the temperature from 25°C to 45°C, a decrease in isolated yield was observed (40 to 10%). A survey of various ruthenium catalysts was performed using syringaldehyde as the control and 70% HOOH as the oxidant in methanol. RuCl<sub>3</sub> appears to be the optimal catalyst (Table 10).

**Table 10- Catalyst Survey for the Oxidation of Syringaldehyde**

Entry	Catalyst	Yield DMBQ
1	RuCl <sub>3</sub>	65%
2	RuBr <sub>3</sub>	48%
3	RuI <sub>3</sub>	49%
4	Ru(NO)Cl <sub>3</sub> H <sub>2</sub> O	15%
5	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	21%
6	Cl <sub>2</sub> [Ru(NH <sub>3</sub> ) <sub>5</sub> Cl]	12%
7	Cl <sub>2</sub> Ru(COD)	27%
8	Ru(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	10%
9	H <sub>3</sub> Ru(SO <sub>3</sub> ) <sub>2</sub> OH	46%

A series of phenols have been screened using ruthenium chloride and 70% peroxide. The results are listed in Table 11. Methanol was used as the solvent with 5 mol% of the catalyst. A 5 mol% catalyst amount appears to be required as lowering the amount of catalyst results in a lower yield of product. Additionally, a slow addition of peroxide to phenol and catalyst in methanol must be performed at 0°C followed by warming of the reaction to room temperature. In entries 1 and 3 the addition of concentrated HCl greatly improves the reaction.

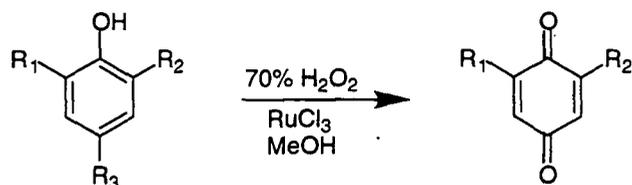


Table 11- Ru/HOOH Oxidations of Different Lignin Models

Entry	Substrate	Yield	Additive
1	R <sub>1</sub> ,R <sub>2</sub> = OMe; R <sub>3</sub> = CH <sub>2</sub> OH	65	
2	R <sub>1</sub> ,R <sub>2</sub> = OMe; R <sub>3</sub> = CHO	45	HCl
3	R <sub>1</sub> ,R <sub>2</sub> = OMe; R <sub>3</sub> = Me	12	-
4	R <sub>1</sub> ,R <sub>2</sub> = OMe; R <sub>3</sub> = allyl	40	HCl
5	R <sub>1</sub> ,R <sub>2</sub> = OMe; R <sub>3</sub> = COMe	12	HCl
6	R <sub>1</sub> ,R <sub>2</sub> = tBu; R <sub>3</sub> = OMe	41	-
7	R <sub>1</sub> ,R <sub>2</sub> = tBu; R <sub>3</sub> = CH <sub>2</sub> OH	52	-
8	R <sub>1</sub> ,R <sub>2</sub> = Me; R <sub>3</sub> = CHO	88	-
9	R <sub>1</sub> ,R <sub>2</sub> = Me; R <sub>3</sub> = H	42 (as a dimer)	-
10	R <sub>1</sub> =H, R <sub>2</sub> = Me; R <sub>3</sub> =OH	87	
11	R <sub>1</sub> =H,R <sub>2</sub> =OMe; R <sub>3</sub> =CH <sub>2</sub> OH	0	-
12	R <sub>1</sub> =H,R <sub>2</sub> = OMe; R <sub>3</sub> = CHO	0	-

A final attempt at this type of oxidation was performed using 1 mol% MeReO<sub>3</sub> as the catalyst and 4-allyl-2,6-dimethoxyphenol as substrate. As seen in Table 12, unacceptable yields were obtained. This observation, combined with the high cost of MeReO<sub>3</sub>, prompted us to abandon this approach.

A few examples additional examples of controlled reactions were also conducted. Syringyl alcohol underwent benzylic oxidation with t-BuOOH and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in 63% yield under similar conditions. Syringaldehyde gave a very low yield of DMBQ and vanillyl alcohol was converted primarily to vanillin. 2,6-Dimethoxyphenol was converted to the diphenoquinone.

Table 12- Rhenium Catalyzed Oxidation Of 4-allyl-2,6-dimethoxyphenol

temperature	solvent	peroxide	conv (isol. yield)	Product
25° C	AcOH	HOOH	80 (48)	DMBQ
40° C	AcOH	HOOH	100 (20)	DMBQ
25° C	EtOAc	90% tBuOOH	100 (15)	DMBQ <sup>a</sup>
25° C	AcOH	90% tBuOOH	100 (10)	DMBQ
25° C	EtOAc	t B u O O H i n decane	90 (50)	B u O O c y c l o h e x a - dienone
25° C to 150	EtOAc	tBuOOH	0	DMAQ
25° C to 100	EtOAc	tBuOOH	0	DMAQ

<sup>a</sup> Flash chromatography destroyed the initial product (BuOOcyclohexadienone) to give DMBQ, yield of initial BuOOcyclohexadienone is unknown.

### 5.6 Oxidations with HOOH and $K_6SiCo(H_2O)Mo_{11}O_{39}$

The complex  $K_6SiCo(H_2O)Mo_{11}O_{39}$  was investigated as a possible catalyst. This material is a member of a class of HPAs called mixed lacunar complexes. It is well known that the HPAs could be considered models of metal catalyst clusters. It is further known that catalysis occurs at defects in clusters. The HPAs are labile enough to allow selective substitution of a single Mo atom in the matrix with different transition metals, resulting in a "defect" (the "lacuna"). It has been suggested that this particular "defect" allows the surrounding atoms more opportunity to form peroxo sites, and thus, concentrate oxidizing power at a single location.<sup>45</sup>

However, this material was singularly unsuccessful in promoting any oxidations. Several substrates were studied: 7, 8, (to see if the absence of para-substituent helped the reaction) and vanillin. Despite a considerable variation in conditions (time, temperature, phase transfer conditions and phase transfer catalysts, solvent), these reactions usually returned starting material when the oxidation was carried out with HOOH in  $CHCl_3$  under phase transfer conditions. Changing the solvent to toluene completely shifted the reactivity of the process. Under these conditions, substrate 7 was completely, but nonselectively consumed.

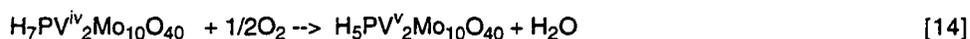
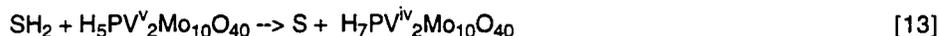
These specific results may be expected. Given the apparent requirement that successful oxidations proceed through simpler catalytic forms (Figure 13), this complex may not break down upon treatment with HOOH. Structurally similar complexes do not decompose in the presence of HOOH to smaller pieces.<sup>49</sup>

More generally, however, the results observed with these catalysts are surprising in their lack of specificity or their lack of reactivity. Two possible explanations exist. First, substrates possessing only an alkyl chain at the para position may have need to reach a critical point after which the reaction is kinetically very fast. At this point, the products end up being more reactive than the starting material, leading to nonselective consumption. In addition, open reactive sites are present on the aromatic ring of the substrate, and ring opening side reactions could be occurring. Pr guaicol seems to be an all or nothing substrate, except in the quinol formation, described later. The poor material balance observed in many of the reactions indicates that oxygenated systems, as would be expected in lignin,

have many oxidation paths available to them, in contrast to systems reported in the literature. Alternatively, we may be observing the effect of  $^1\text{O}_2$  on the lignin models. The literature reports that singlet oxygen formation is a viable reaction path for HPAs and HOOH. If this material is the active oxidant, it would be as uncontrolled as HOOH or  $\text{O}_2$ . That is, we are simply converting one nonselective oxidant (HOOH) into another ( $^1\text{O}_2$ ). None of the many metal peroxo species that are expected to be formed in these processes are active. This conclusion might be unique to phenols. The conditions of their reaction might favor formation of the molybdate dimer, but this is unclear. The only species that seems to exhibit reactivity is  $\text{Mo}(\text{O}_2)_4^{2-}$ , and that species is known to form  $^1\text{O}_2$ . Workers that have used that complex have suggested a  $^1\text{O}_2$  based mechanism.<sup>25</sup>

### 5.7 Oxidations with $\text{O}_2$

We have continued to investigate the use of oxygen as an oxidant in the presence of metal catalysts. Phenols have been reported to undergo selective oxidation to materials closely related to quinones using oxygen and molybdovanadate complexes as catalysts.<sup>58</sup> Quinones can also be prepared from phenols using these reagents.<sup>59</sup> These complexes have also been used to activate oxygen in the oxidation of  $\text{MeOH}$ <sup>60</sup> and higher alcohols,<sup>61</sup> amines,<sup>62</sup> and alkyl aromatics.<sup>63</sup> In contrast to the Mo and W complexes described above, these catalysts are not broken down to simpler species under the reaction conditions. Rather, redox chemistry occurs at the vanadium center according to equations 13 and 14:<sup>58</sup>



However, interaction of the vanadate species with the substrates is postulated to proceed through a radical cation mechanism similar to that observed for  $\text{NO}_2$  oxidations.<sup>58</sup> Several molybdovanadate complexes were prepared according to literature methods<sup>64</sup> and tested as oxygen activation catalysts.

Overall, these conditions were not successful in forming quinone from any of several lignin models investigated, using either  $\text{O}_2$  or HOOH as the oxidant. Most work was performed using  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  hydrate as the catalyst. Interestingly, most lignin models treated with oxygen and this catalyst showed little reactivity. Even substrates reported to undergo ready oxidation with this catalyst displayed low reactivity in our hands. 2,6-Dimethylphenol was consumed very slowly, in contrast to the literature report,<sup>58</sup> despite modification in temperature, oxygen pressure, and solvent. Attempts were made to promote the reaction through the addition of Cu(II) salts, but the conversion of starting material to product remained low.

Some consumption of starting material was observed when the reaction solvent was changed to 95/5 AcOH/ $\text{H}_2\text{O}$ , while using an oxygen pressure of <50 psi. 2,6-Dimethylphenol under these conditions was converted to 2,6-dimethylquinone in about 50% yield (by NMR), confirming the literature report.<sup>58</sup> However 7 was consumed nonselectively to give no identifiable products other than a small hint of vanillin. Vanillyl alcohol was treated under these conditions, but instead of oxidation, the benzyl alcohol was esterified to give the corresponding benzyl acetate. Syringyl alcohol was oxidized to syringaldehyde under these conditions. Application of these conditions to other substrates resulted in similar nonselective reactions.

The reaction was also carried out in MeCN as the primary solvent, with a small amount of added HOAc. Vanillyl alcohol was completely consumed and converted to a mixture of the benzyl acetate and vanillin. However, these products were less than 10% of the mixture. The bulk was an insoluble material. This result was repeated with syringyl alcohol.

## 5.8 Conclusions

Despite the large number of HOOH and O<sub>2</sub> activating catalysts screened, little progress was made in finding a system that would selectively oxidize phenols (and hence, lignin) to quinones. The reactions in this series oscillated between complete and nonselective consumption of starting material to a complete lack of reactivity of the starting material. There may be some utility of these complexes in bleaching processes, similar to those systems described by Weinstock, because of their ability to destroy the lignin models. These results are surprising, but emphasize the need for a concerted investigation of the controlling factors behind phenolic oxidation at the molecular level.

## **6.0 DETAILED RESEARCH RESULTS - DIELS-ALDER REACTIONS**

The Diels-Alder reaction of a benzoquinone with an inexpensive diene, the second step in the chemical processing stage, has been described in detail in the 1994 annual report. The following section provides a brief background and then a description of the work performed to since the 1994 annual report.

### 6.1 Background

In a normal Diels-Alder reaction, a diene adds to a dienophile to form a new six membered ring. Isoprene has been the primary diene studied because of its low cost and the resulting production of 2,6/7-DMAQ, a highly reactive pulping catalyst. Both fully aromatic DMAQ and a mixture of nonaromatic AQ precursors are obtained when isoprene is reacted with DMBQ. In addition, both mono- and bisadduct nonaromatic structures are obtained (Figure 18).

The goal of the diene addition step is the addition of two molecules of the diene to the benzoquinone. The formation of aromatic naphthoquinones or DMAQ in the aqueous Diels-Alder reaction is a consequence of losing methanol and hydrogen units. The loss of the hydrogen is considered to be a result of a set of disproportionation reactions, in which hydrogen is being transferred from one adduct to another, the one becoming richer in double bond units and the other becoming poorer. This leads to a very complex reaction mixture. Good yields of bisadducts likely require the initial production of an aromatic naphthaquinone monoadduct, 2-methoxy-6-methylnaphthaquinone. The latter will be much more reactive than a non aromatic monoadduct towards a second isoprene addition. Good yields of DMAQ also hinge on promotion of rapid disproportionation reactions instead of enolization to an inactive naphthahydroquinone (Figure 19). The diene addition gives primarily two isomeric bisadducts and, thus, two isomeric DMAQs.

Previous studies have shown that a Diels-Alder reaction using 1 g of DMBQ and excess isoprene gave 2 g of a mixture of 2,6- and 2,7-DMAQ and isoprene byproducts. A crude chromatography removed several isoprene byproducts. The resulting 1.3 g of product contained 40% DMAQ and 20% three ring related components; the yield of DMAQ from DMBQ was 37 mole %.

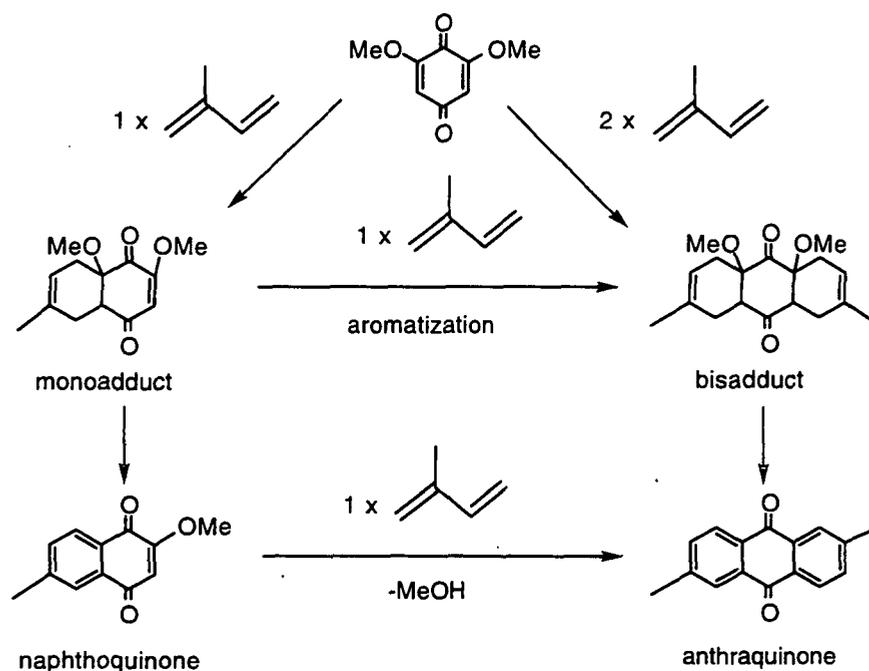
### 6.2 Products of the Aqueous Diels-Alder Reaction

Analysis by GC-MS of the crude reaction mixture formed in the aqueous Diels-Alder reaction of DMBQ allowed for the tentative structural assignments for several components of the mixture (Figure 20). Several attempts to isolate specific fractions, i.e., non aromatic bisadducts failed since several components of the mixture are not stable to chromatography. The NMR spectra of crude reaction products agree with proposed product composition. It appears that those components that convert to DMAQ upon chromatography will do the same during pulping and, thus, contribute to the mixture's pulping activity. The other components will likely be inactive.

### 6.3 Optimization of Diels-Alder Reactions

As a possible way to increase the yield of DMAQ in the aqueous Diels-Alder reaction, we examined the affects of the addition of oxidants to the DMBQ/isoprene mixture; the goal was to convert more of the monoadducts to aromatic naphthoquinones, which are key components in generating bisadducts. In general, the addition of polyoxometalates and other oxidants led to lower total combined yields of DMAQ and nonaromatic DMAQs. There were a few exceptions, such as  $V_2O_5$ ; however, the small yield improvements probably would not offset the cost of the reagent. Several aqueous Diels-Alder reactions were also conducted in the presence of metal salts, such as iron, but the yields of DMAQ did not improve.

The value of water as a solvent in Diels-Alder reactions has been attributed to a rate enhancement due to entropy effects, "micellar catalysis." There is a reduction in the difference between the volume associated with the product and that of the hydrophobic reactants. Since changes in solvent can often have dramatic effects on the course of Diels-Alder reactions, we decided to examine solvent effects on the isoprene-DMBQ reaction. The results, as shown in Table 13, verified that water was the best of the solvents examined for providing reasonable yields of DMAQ and bisadducts from DMBQ.



Note: for clarity, only one of the Me positional isomers is shown.

Figure 18 - Definition of Mono- and Bisadducts from Diels-Alder Addition

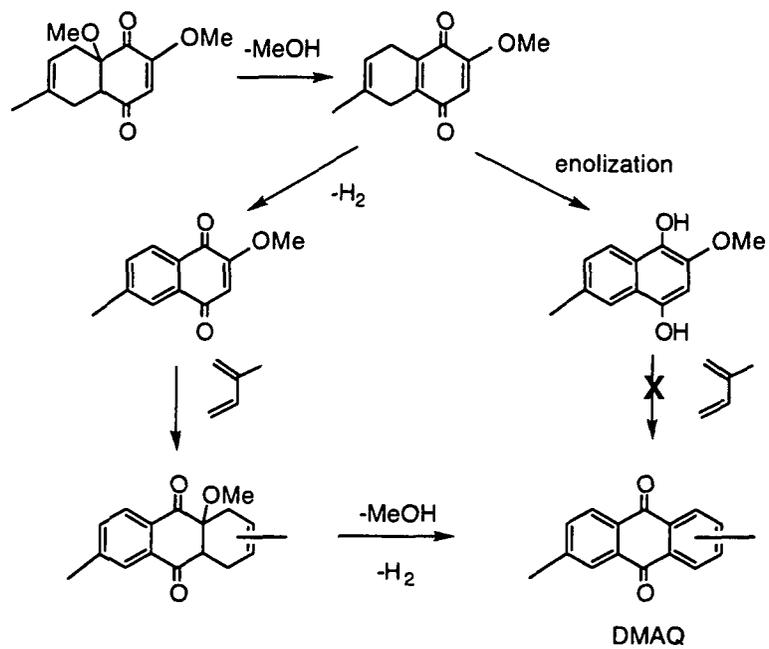


Figure 19 - Proposed Reactions of a Monoadduct to Give DMAQ

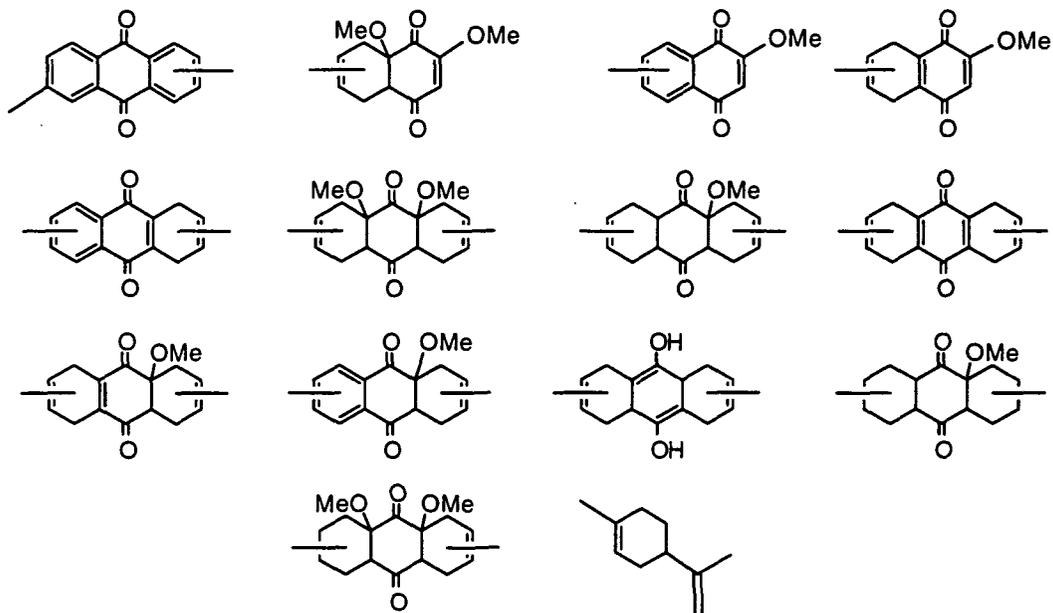


Figure 20 - Components in the Aqueous DMBQ/Isoprene Diels-Alder Reaction

Table 13- Diels-Alder Reactions of DMBQ and Isoprene in Various Solvents<sup>a</sup>

Solvent	Isoprene:DMBQ		Percent			
	(molar ratio)	DMBQ	MMNQ	Monoadducts	Bisadducts	DMAQ
Neat	3:1	31	2	none	none	0.5
Hexane	3:1	16	8	none	none	none
Ethyl ether	3:1	20	9	none	none	none
Ethyl acetate	3:1	15	11	none	none	none
Acetone	3:1	24	9	none	none	none
Isopropanol	3:1	4	17	10	0.9	0.4
Butanol	3:1	none	9	11	2	none
Acetic Acid	3:1	5	8	6	12	none
Methanol	3:1	17	28	none	none	14
Methanol	6:1	3	28	8	3	18
Methanol	10:1	1	29	16	7	8
Water	3:1	none	4	none	11	22
Water	6:1	none	2	9	20	17
Water	10:1	none	none	none	18	21

<sup>a</sup> Reactions were carried out in steel bombs (4.0 mL capacity) at 160 °C for 16-17 h.

As the polarity of the reaction mixture decreased, the quantity of bisadducts and DMAQ in the product mixture also decreased; some DMBQ was recovered in the nonaqueous cases. Also, in many cases, the major product was 2-methoxy-6-methylnaphthaquinone (MMNQ). This component may, in part, be formed during the GC analysis through loss of methanol and oxidation of a monoadduct. The modest yields of these products from reactions carried out in methanol and water suggest that increasing the molar ratio of isoprene to DMBQ should result in an increase in the amount of DMAQ formed; however, this was not observed.

Note that the DMAQ yield in water for the study summarized in Table 13 was not as good as previously observed. When the aqueous Diels-Alder method was first developed, we generally got DMAQ yields of >50%. However, in scale up experiments, only ~30% direct DMAQ yields were observed. The yield rose to ~40% after silica gel chromatography, which caused some aromatization of some reaction components. Recent Diels-Alder studies indicate that there are subtleties associated with the aqueous Diels-Alder reaction that we do not understand. For example, the yields differ as a function of the investigator. The results reported above used fresh DMBQ and nanopure water. Recent reactions, by yet another investigator, have provided even poorer yields (~10%) of DMAQ and bisadducts in general.

In experiments that have used both 300 mL Parr and 4 mL minibomb reactors, we have examined several factors: DMBQ age, DMBQ/water and /isoprene ratios and water type (nanopure vs. tap). In all cases, the yield of DMAQ continued to be low. The primary products were identified by GC-MS to be nonaromatic adducts. We have checked the purity of the isoprene and DMBQ, looked for potential leaks in the reactors, and determined that no problems exist here. We are puzzled by the low yields.

We proceeded with larger scale Diels-Alder reactions between DMBQ and isoprene in water. Our goal was to prepare a large batch of pulping catalyst mixture to be used for pulping studies. The large scale reactions employed a 10:1 ratio of isoprene to DMBQ in 235 mL of water in a 300 mL Parr reactor; the mixture was heated at 168°C for 18 hr. The crude reaction mixture was filtered through silica gel to remove large amounts isoprene related hydrocarbon materials; in the process, some non aromatic bisadducts were converted to DMAQ. The yield of DMAQ relative to charged DMBQ was, for two reactions of this type, 12 and 20%. The two reaction mixtures were combined to give a mixture containing 12.5 wt. % DMAQ.

We tested the practicality of performing the Diels-Alder reaction on the crude lignin-DMBQ mixture. The reason for such an experiment is that there will be many (perhaps most) cases in which the lignin that is being oxidized by NO<sub>2</sub> in methanol is not completely soluble in methanol; an Alcell lignin is an example. The DMBQ precipitates as the NO<sub>2</sub> reaction proceeds and becomes intimately associated with undissolved lignin. Separation of the DMBQ will likely be difficult and costly. [With soluble lignin models and certain lignins (i.e., one coming from NREL's Clean Fractionation process), solubility factors aid in the isolation of DMBQ away from the other reactants.] Treatment of a crude lignin-DMBQ mixture with isoprene (5.5 or 27.5 equivalent) resulted in very low yield (0.4 - 4.3%) of DMAQ. The situation is further complicated by the probable need to isolate the DMAQ from lignin after the Diels-Alder step. Attempts to separate the DMAQ by steam distillation have been unsuccessful. These latest Diels-Alder results suggest that this step in the synthesis, which we previously assumed would not present a major hurdle, could in fact be quite limiting if these problems are not solved. The issues of reproducibility would be addressed in additional work.

#### 7.0 ALTERNATIVE PREPARATION OF 2,6/7-DIMETHYLANTHRAQUINONE (DMAQ)

Our pulping studies require that we have a pure sample of DMAQ to compare with the catalyst mixture obtained from aqueous Diels-Alder reaction. Very early in this research project, we examined the Diels-Alder reactions of several substrates as means to understand differences between DMBQ and other dienophiles. One of the reactions examined was that of benzoquinone (BQ) with isoprene. We observed a 98% yield of two types of adducts: a monoadduct in 30% yield and bisadducts (mixture of isomers) in 68% yield. We have reexamined the reaction with different solvents, reactant ratios, temperatures, and time and have found conditions that provide bisadducts in high yields. The best conditions, while economizing starting materials, were a 2:1 ratio of isoprene to BQ in absolute ethanol and mixed well for 2 hours at 165°C. Gas chromatography indicated a 93% yield of a nonaromatic bisadducts related to 2,6/7-DMAQ. The isolated (not optimized) yield from large scale runs have varied from 65-80%. The structure of the bisadducts is shown in Figure 21, with the key species being octahydroDMAQ (12). Treatment of the bisadducts with oxygen and KOH in an organic solvent gave DMAQ in 93% isolated yield.

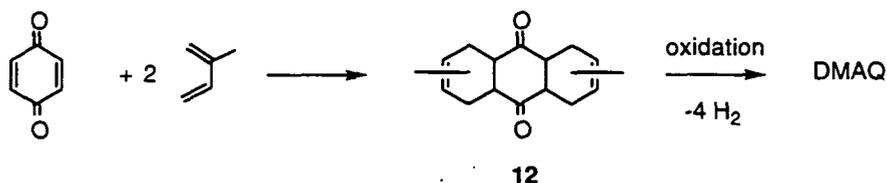


Figure 21 - Preparation of DMAQ from Benzoquinone

As will be seen in the data of the next section, 12 is a very good pulping catalyst. The key to the commercialization of 12 is an inexpensive synthesis of BQ. Eastman Chemical makes BQ from photographic grade hydroquinone; benzoquinone has a small market and sells for \$7-10/lb. The price

spread reflects packaging and shipping costs associated with BQ, an irritant. Obviously, this method for preparing ultrapure BQ would not be appropriate in our case. In fact, a more likely synthesis of the bisadduct might employ a crude stream of (never isolated) BQ reacting with isoprene. It has been reported that the most common industrial process for manufacture of BQ is by a "high yield" oxidation of either aniline or phenol. A literature search has revealed several newer ways to prepare BQ; these include various types of electrochemical oxidations of benzene, a very cheap raw material.

A crude cost calculation for BQ has been made based on  $MnO_2$  oxidation of phenol, *assuming* that the patent's claimed high yield conversion meant a 90% conversion to BQ and that solvent losses are insignificant. [SunTech has a patent for a 90% BQ yield by an enriched air oxidation of phenol in the presence of  $CuCl_2$  in aqueous acetonitrile.]

The raw material costs of the bisadduct =  $\$0.18/\text{lb}$  (isoprene) +  $\$0.76/\text{lb}$  (BQ) =  $\$0.94/\text{lb}$ . Assuming that raw material costs make up 60% of the total production costs, dividing  $\$0.94/\text{lb}$  by 0.6 and adding  $\$0.04/\text{lb}$  for solvent losses gives  $\$1.60/\text{lb}$  production cost. Note that a large part of the DMAQ raw material cost is related to the benzoquinone cost which is, in turn, related to the oxidant cost. There would appear to be large opportunities to economize the synthesis by the selecting a good pathway to make benzoquinone.

Presently, there are ~40 US mills using AQ on a consistent basis. If one assumes an average mill produces 1500 tons of pulp/day from 3,333 tons of wood (45% yield) and that the mill uses a conservative AQ level of 0.06% on wood, a mill will use 4,000 lb of AQ per day or 1.4M lb/yr. Presently, the U.S. market for AQ is  $\sim 40 \times 1.4M = 56M$  lb/yr. However, if the catalyst price was substantially lower than the present AQ cost and the whole industry (60M tons/yr) turned to catalyst pulping, the market would be 160M lb/yr. Since the bisadduct would be used at half the level of AQ and sell for  $\sim \$1.50/\text{lb}$ ., projected sales of bisadduct would  $\$45M/\text{yr}$ . for the present market and  $\$128M/\text{yr}$ . whole US market.

## 8.0 PULPING AND BLEACHING STUDIES

### 8.1 Small Scale Pulping

Small scale pulping studies refer to runs involving 50 g of chips. The advantage of small scale experiments is that several comparisons can be performed over a short period of time. The disadvantage is that chip variability require that duplicates and triplicates be performed to get confident numbers. In addition, yield determinations are not very precise.

Previous investigations into the effectiveness of the aqueous Diels-Alder reaction mixture suggested that the non-DMAQ components exhibited some catalytic activity. In order to verify this finding, we subjected the Diels-Alder reaction mixture to column chromatography in order to isolate the nonaromatic components from the mixture and determine their activity separately. However, during the chromatography, several of the nonaromatic components were converted to DMAQ. The components that aromatized by the silica gel will also likely be aromatized during pulping; separating and determining their activity will be difficult and possibly fruitless. Soda pulping studies with an isolated non-DMAQ portion of the mixture showed that it was a relatively ineffective delignification catalysts (Figure 22). Since the lignin content decreased with increased amounts of applied material, the non-DMAQ components do possess some activity.

In addition, we have compared the catalytic activity of AQ, DMAQ, and the catalyst mixture containing ~40% DMAQ in soda/AQ, kraft/AQ and polysulfide/AQ (Figures 23, 24 and 25). The results indicate that DMAQ is twice as effective as AQ in catalyzing delignification for soda and kraft pulping and that the non DMAQ components add little to the observed activity.

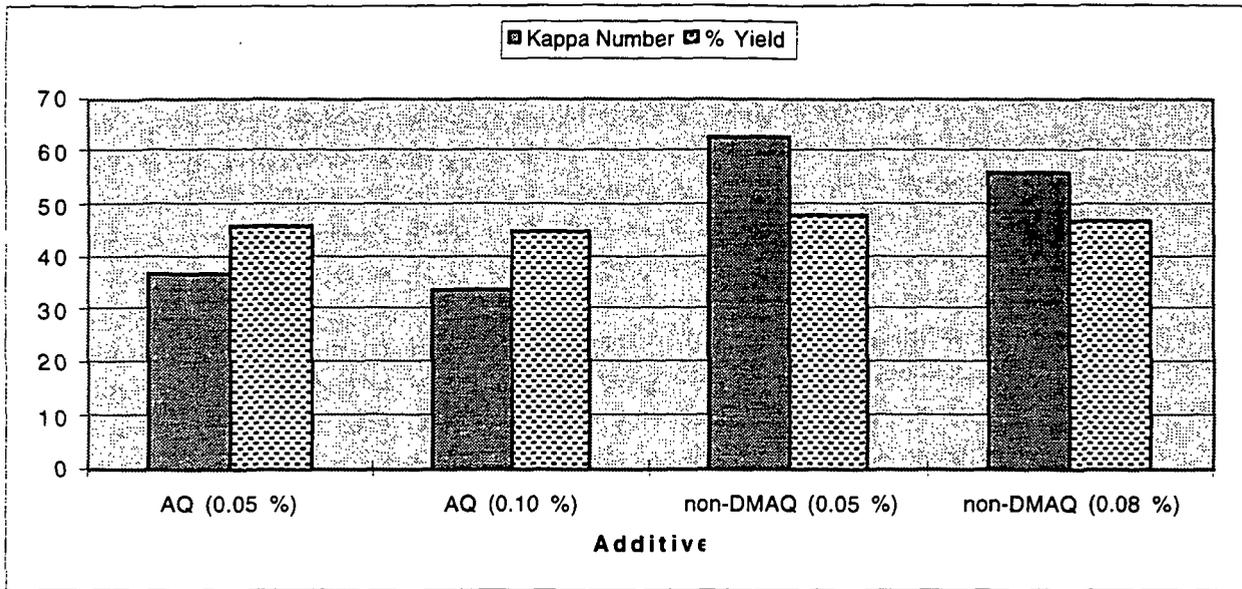


Figure 22 - Activity of non-DMAQ Components in Soda/AQ Pulping

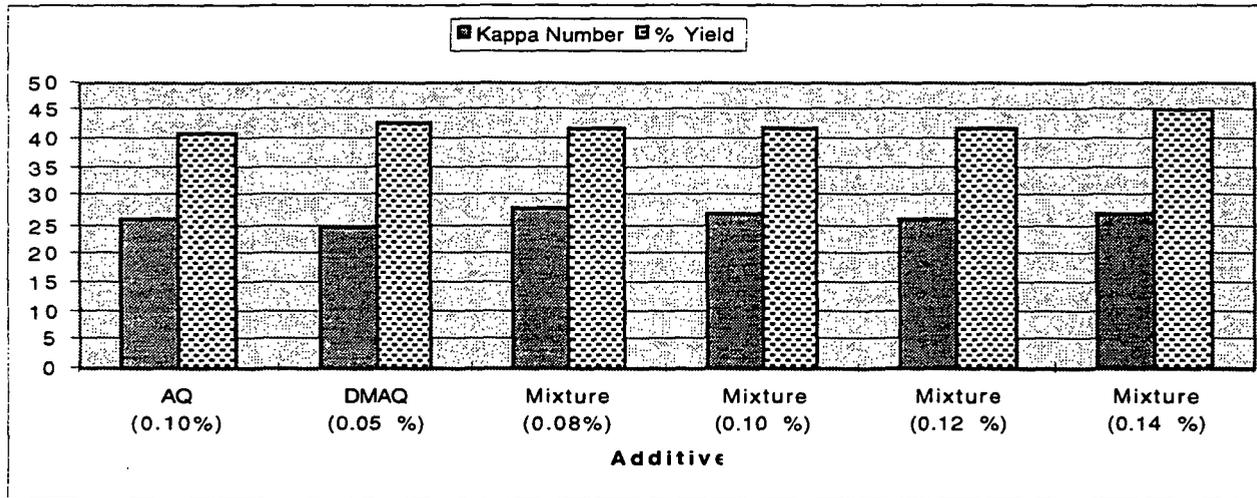


Figure 23 - Activity of Catalyst Mixture in Soda/AQ Pulping

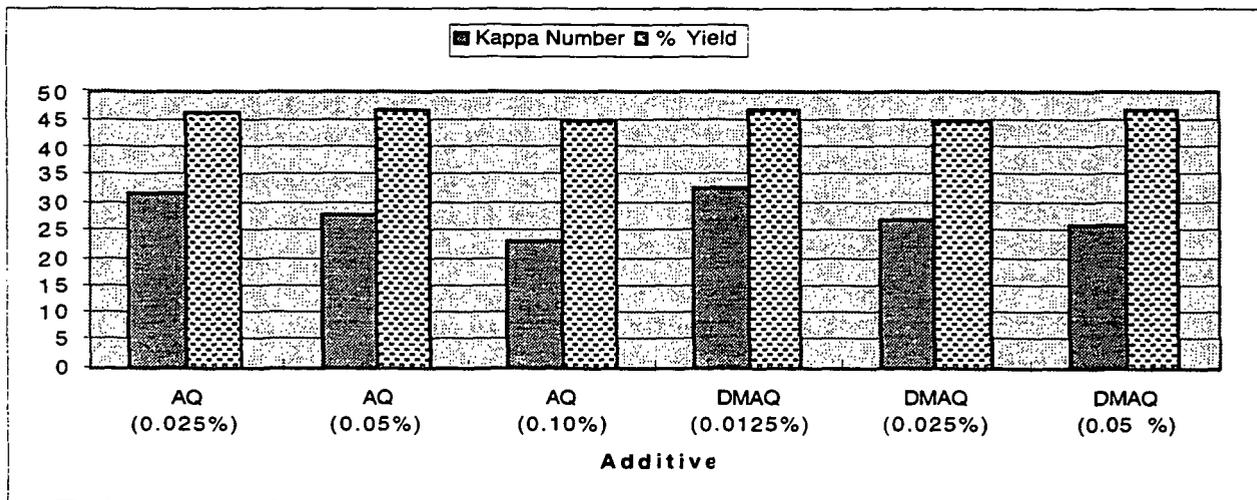


Figure 24 - Activity of DMAQ in Kraft/AQ Pulping

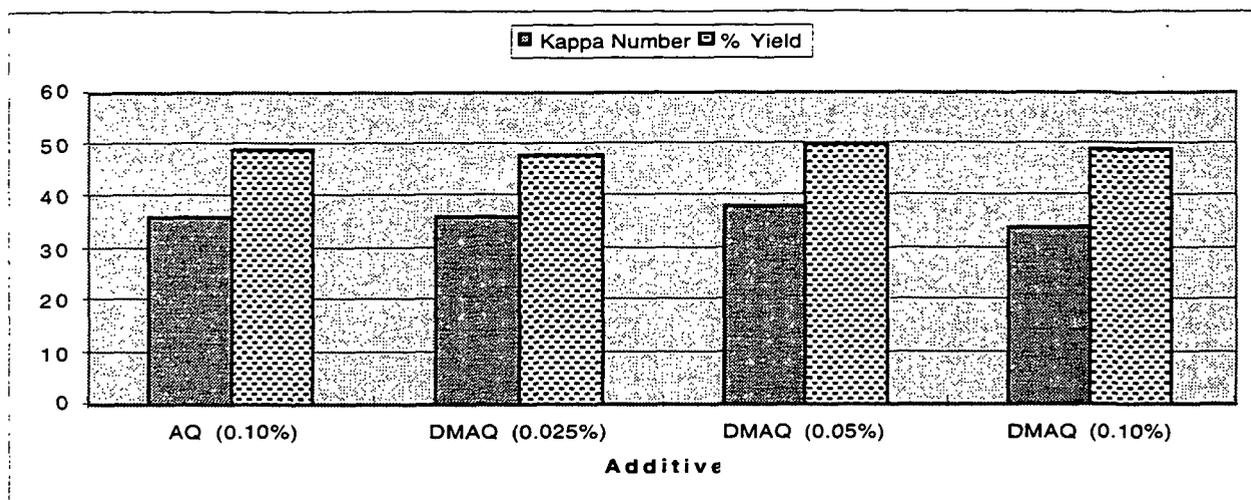


Figure 25 - Activity of DMAQ in PS/AQ Pulping

Since the data in Figure 25 had some scatter, we conducted another set of polysulfide cooks (Table 14). Four identical pulping experiments were conducted for each condition. The data conclusively show that DMAQ is 2-3 times more effective. Since a two times effective factor exists in soda and kraft pulping systems (earlier project results), it is likely that the factor is two in this case.

Our interest in polysulfide/AQ stems from the recent reports of the effectiveness of employing the two reagents together in extended delignification pulping systems. Extended pulping systems remove greater amounts of lignin (while improving selectivity) by leveling out the alkali, reducing the cooking temperature, and optimizing the use of the pulping chemicals. Several environmental benefits result, including lower levels of bleach plant effluent and easier mill closure. The disadvantages are the longer cooking times and lower pulp yields, and, therefore, lower productivity. Polysulfide and AQ address these issues because both improve pulping rates and pulp yields. A comparison has also been made for the kappa numbers resulting from the soda/catalyst pulping of pine for pure DMAQ and the mixture of bisadducts made from BQ (Table 13). It appears that the bisadduct mixture is slightly less active than DMAQ.

### 8.2 Large Scale Pulping Experiments

The data in Table 16 present a comparison of large scale (1 Kg) pulping of southern pine with (1) AQ, (2) the bisadduct of benzoquinone and isoprene, (3) DMAQ, and (4) the semipurified catalyst mixture from an aqueous Diels-Alder between DMBQ and isoprene. Except for the catalyst mixture, most cooks were done in duplicate. Five soda/AQ cooks were conducted; additional soda/AQ pulps were needed to help define the bleaching parameters. The reproducibility of the cooks was good.

The value of the catalyst can be seen from the higher kappa number (37.5) of the control kraft cook that has no catalyst, but was performed under the same conditions as the kraft/catalyst cooks. A 1-kg soda control was not performed; however, based on previous small scale experiments, the kappa number should be about 60. Two kraft cooks were performed at elevated H-factors to get a 31 kappa pulp for comparison to the kraft/catalyst pulps; their cooking time differed by only 3 minutes, and only 10 minutes longer than the 37.5 kappa kraft control. The 28.1 and 33.5 kraft pulps were combined to get the desired 31 kappa pulp.

**Table 14 - Kappa Number Comparison of Polysulfide (1.22%)/Catalyst Pulping of Pine<sup>a</sup>**

Sample #	% Additive	Kappa #	Average K	Std. Dev.	4 Bomb Ave.	Std. Dev.
1	0.025% DMAQ	29.0, 29.0	29.0	0.0	29.4	0.8
2	0.025% DMAQ	28.6, 28.6	28.6	0.0		
3	0.025% DMAQ	30.0, 29.4	29.7	0.3		
4	0.025% DMAQ	31.2, 29.8	30.5	0.7		
5	0.05% AQ	33.1, 33.7	33.4	0.3	30.0	2.4
6	0.05% AQ	29.9, 29.0	29.4	0.5		
7	0.05% AQ	29.2, 29.7	29.4	0.3		
8	0.05% AQ	27.5, 28.0	27.8	0.3		
9	0.025% DMAQ	27.0, 26.8	26.9	0.1	26.8	1.0
10	0.025% DMAQ	25.2, 25.6	25.4	0.2		
11	0.025% DMAQ	28.0, 27.3	27.6	0.4		
12	0.025% DMAQ	27.6, 27.3	27.5	0.2		
13	0.10% AQ	25.5, 25.7	25.6	0.1	24.8	0.8
14	0.10% AQ	24.7, 25.8	25.2	0.6		
15	0.10% AQ	24.9, 24.3	24.6	0.3		
16	0.10% AQ	23.9, 23.7	23.8	0.1		

<sup>a</sup>Cook Set #1, Samples # 1-8, 60 min from 100 °C to 171/172°C, 70 min at 171/172°C; Cook Set #2, Samples # 9-16, 60 min from 100°C to 173/174°C, 70 min at 173/174°C; The difference in the final holding temperature between the two cooks was due to a malfunction of the controller for the oil bath in which the runs were performed.

**Table 15 - Kappa Number Comparison of Soda/Catalyst Pulping of Pine**

Sample #	% Additive	Kappa <sup>a</sup>	Average K	Std. Dev.	Ave. K for Set	Std. Dev.
1	0.05% DMAQ	30.2, 30.0	30.1	0.1	29.6	0.5
2	0.05% DMAQ	30.2, 29.3	29.8	0.7		
3	0.05% DMAQ	29.0, 29.1	29.1	0.0		
4	0.05% Bisadduct	32.4, 31.8	32.1	0.4	30.6	1.3
5	0.05% Bisadduct	29.4, 29.7	29.5	0.2		
6	0.05% Bisadduct	30.2, 30.2	30.2	0.0		
7	0.10% Bisadduct	27.2, 26.8	27.0	0.2	27.4	0.5
8	0.10% Bisadduct	27.9, 27.6	27.7	0.3		
9	0.025% DMAQ	30.3, 29.7	30.0	0.5	31.7	1.5
10	0.025% DMAQ	32.4, 33.2	32.8	0.6		
11	0.025% DMAQ	32.9, 31.6	32.2	0.9		
12	0.025 % Bisadduct	34.5, 35.2	34.9	0.5	34.5	0.5
13	0.025 % Bisadduct	33.5, 34.9	34.2	1.0		
14	0.05 % Bisadduct	31.8, 33.1	32.4	0.9	30.3	3.0
15	0.05 % Bisadduct	28.3, 28.0	28.2	0.2		

<sup>a</sup> Kappas for samples # 1-8 were performed on o.d. pulp, whereas samples # 9-15 were never dried pulp.

Table 16 - Detailed Pulping Results for 1-Kg Pine Cooks<sup>a</sup>

Cook Type	Catalyst Type	Catalyst Applied	Cook H-factor	Kappa Number	Screened Yield (%)	Viscosity mPa•s	Recovered Cat. - % <sup>b</sup>
Soda	AQ	0.10	2090	33.7	45.0	17.3	0.3
		0.10	2097	33.1	43.7		
		0.10	2089	33.1	45.1		
		0.10	2111	31.2	45.4		
		0.10	2114	32.3	44.1		
	Bisadduct	0.05	2124	33.6	45.6	18.2	0.9
		0.05	2106	30.8	43.5	16.0	
	DMAQ	0.05	2106	33.7	45.4	18.5	1.8
		0.05	2108	35.2	45.6	18.1	
	cat. mixture	0.05	2099	34.0	43.9	16.0	2.0
Kraft	AQ	0.10	1214	30.3	46.8	36.7	
		0.10	1192	31.6	47.3	38.2	0.5
	Bisadduct	0.05	1195	31.8	46.1	40.2	1.9
		0.05	1200	30.8	47.0	36.8	
	DMAQ	0.05	1197	32.7	47.2	36.4	
		0.05	1197	31.3	46.5	37.7	2.3
	cat. mixture	0.05	1197	30.8	40.6	33.1	2.5
	none	0.00	1196	37.5	44.1	39.1	
	none <sup>c</sup>	0.00	1389	28.1	45.8	37.9	0.0
	none <sup>c</sup>	0.00	1346	33.5	45.6		
Polysulfide <sup>d</sup>	AQ	0.05	1053	32.2	46.4	29.6	0.3
		0.05	1040	33.0	46.7	31.4	0.1
	DMAQ	0.025	1045	33.0	45.2	31.2	0.3
		0.017	1031	35.9	46.3	31.0	0.4
K-100 kraft <sup>e</sup>	none	0	649	93.4	53.0		
	AQ	0.04	643	87.1	54.8		
	Bisadduct	0.02	647	93.1	53.8		
K-50 kraft <sup>f</sup>	none	0	799	58.0	49.0	38.91	
	AQ	0.04	797	51.6	51.0	38.28	
	Bisadduct	0.02	792	54.2	51.6	37.94	

<sup>a</sup> Unless stated otherwise, the cooks were performed with an active alkali = 18%, sulfidity = 25% for kraft cases, and a final cook temperature = 170°C. <sup>b</sup> The residual catalyst in the pulp was recovered by solvent extraction; % of applied catalyst. <sup>c</sup> The H-factor was modified in an attempt to get a 31 kappa pulp; pulps were combined for viscosity measurement and further studies. <sup>d</sup> PS = 1.22%, active alkali = 19%, sulfidity = 12%. <sup>e</sup> Cook targeted for a kappa number of ~100, active alkali = 15%. <sup>f</sup> Cook targeted for a kappa number of ~50.

The data in Table 16, and the comparisons given in Figures 26 - 28, clearly show (as was the case in the small scale runs) that our catalysts at half the doses are performing as well as AQ for producing 30 kappa pulps. Also, as expected, the presence of a catalyst improved the yield in the 30 kappa kraft case. The 1-kg polysulfide/catalyst cooks were performed in pairs (back-to-back) on the same day with the same 1.3% preprepared polysulfide liquors. The comparisons were done at 1/3-1/2 dose DMAQ relative to AQ. The first and last polysulfide cooks listed in Table 16 were performed as a pair and the other polysulfide cooks as a pair. It is quite clear from the data given in Table 16 and Figure 28 that DMAQ is twice as effective as AQ in the polysulfide cooks, but apparently not three times as effective.

The higher amount of NaOH and longer reaction times used in the soda cooks results in more cellulose degradation and, thus, lower viscosities in comparison to the kraft cooks. A low viscosity means that the polymer being tested has a relatively low degree of polymerization. In general, as the kappa number drops in a given series, the viscosity will too. This trend can explain some of our observations, but fails in some of the other comparisons. A possible area of concern is the low values observed for screened yield and viscosities in the soda and (especially) kraft/ DMAQ-catalyst mixture pulps.

The pulps were extracted and the level of catalyst determined. The values obtained indicate that (1) the bisadduct was aromatized to DMAQ during the cooks and (2) the level of recovered catalyst was significantly higher in the DMAQ cases (DMAQ, bisadduct, and catalyst mixture) than for the AQ cases. The latter result may explain the greater effectiveness of the DMAQ-related catalysts; the catalyst is less degraded during the cook and, thus, the concentration will be higher throughout.

A final set of experiments involved cooking to higher kappa numbers; the results are listed in the bottom of Table 16. Pulps with high lignin content are used in the production of liner board and bag stock.<sup>66</sup> AQ has been reported to be very effective at lowering the kappa number of such cooks by 10-15 units as compared to a kraft control. Our results do not show such a decrease for either AQ or the bisadduct. In addition, unlike the 30-kappa pulp results, the bisadduct (at half the levels of AQ) was not as effective as AQ for these higher kappa pulps. The reasons for these differences is not apparent. It should be noted that time constraints prevented us from performing duplicate high kappa cooks; therefore, the conclusions drawn are tentative at this point.

### 8.3 Bleaching Experiments

An important aspect of developing a new pulping process is to demonstrate the pulps can be easily bleached. Should the latter not be true, the pulping process will have very limited applicability. Consequently, we set out to establish the "bleachability" of the pulps prepared from DMAQ and related catalysts; comparisons would be made to the corresponding AQ pulps. Bleachability relates the amount of bleaching chemicals consumed to reach a certain brightness for a set of pulps. This brightness can be the final brightness or some intermediate brightness. By going to fully bleached pulps, we were able to compare brightness values at many points and generate pulps for strength measurements. The bleachability of the pulps was determined using a D(EOP)DED bleach sequence, in which D = chlorine dioxide ( $\text{ClO}_2$ ), E = extraction with dilute NaOH, and EOP = extraction with dilute NaOH in the presence of oxygen and HOOH. Actually, a subset of terms employed for the bleach sequence are somewhat illogically referred to as:  $D_0(EOP)D_1E_2D_2$ , where  $D_0$ ,  $D_1$ , and  $D_2$  refer to the first, second, and third application of chlorine dioxide, and  $E_2$  is the second extraction stage.

We initially bleached the soda/AQ pulp to a 90 brightness, but backed off with less chlorine dioxide in the last stage to get an 87.5 brightness pulp because we had reached a brightness ceiling at 90. The ceiling is recognized by observing no changes in the final brightness with increased amounts of  $\text{ClO}_2$ ; this is seen in the first data set in Table 17, in which the  $D_2 \text{ClO}_2$  charge was varied between 0.2% - 0.8%.

The data in Table 17, some of which is shown in Figures 29-32, indicate that there were small, but not significant, differences in brightness, viscosities, and chlorine dioxide consumed; in general, the soda/catalyst pulps as a set and the kraft and kraft/catalyst pulps as a set were judged to be equally bleachable. The variability can be judge by comparing the repeat bleaches of the soda/AQ, soda/DMAQ, and kraft/DMAQ pulps with the first bleaches of these pulps; the brightness and viscosity data within a set fall within the repeat's variability ranges. One set of soda bleaching studies employed the same levels of applied chemicals throughout and provided the same final brightness values, except in the case of the soda/catalyst mixture which exhibited low brightness. Another study used a constant kappa factor of 0.20% ClO<sub>2</sub> for each pulp and a noticeable improvement in brightness occurred in the soda/catalyst mixture case, in which the unbleached pulp entered with a somewhat higher lignin content. [The kappa factor relates to applying a certain level of ClO<sub>2</sub>/pulp lignin content and, thus, takes into account the differences in entering kappa numbers of the pulps being compared.]

Two out of the three catalyst mixture pulps gave lower brightness pulps after full bleaching; possibly the unsaturated components in the catalyst mixture are consuming some bleaching chemicals, thus, slightly limiting the amount available chemicals need to remove the lignin. The somewhat lower amount of chlorine dioxide consumed in the soda and kraft AQ cases hints that DMAQ pulps may be slightly harder to bleach. The lower viscosity of the kraft control may be reflecting the longer cooking times that were required to reach the targeted kappa number. A longer cook would likely exhibit more carbohydrate damage.

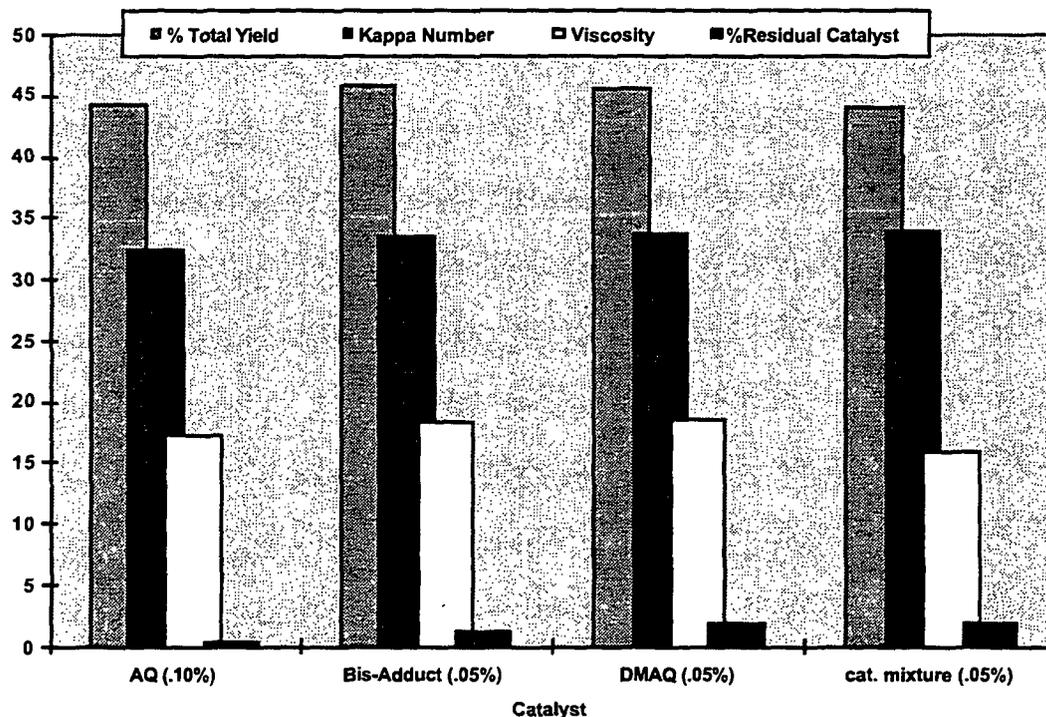


Figure 26 - Comparison of Unbleached, Southern Pine Pulps from 1-Kg Soda/Catalyst Pulping

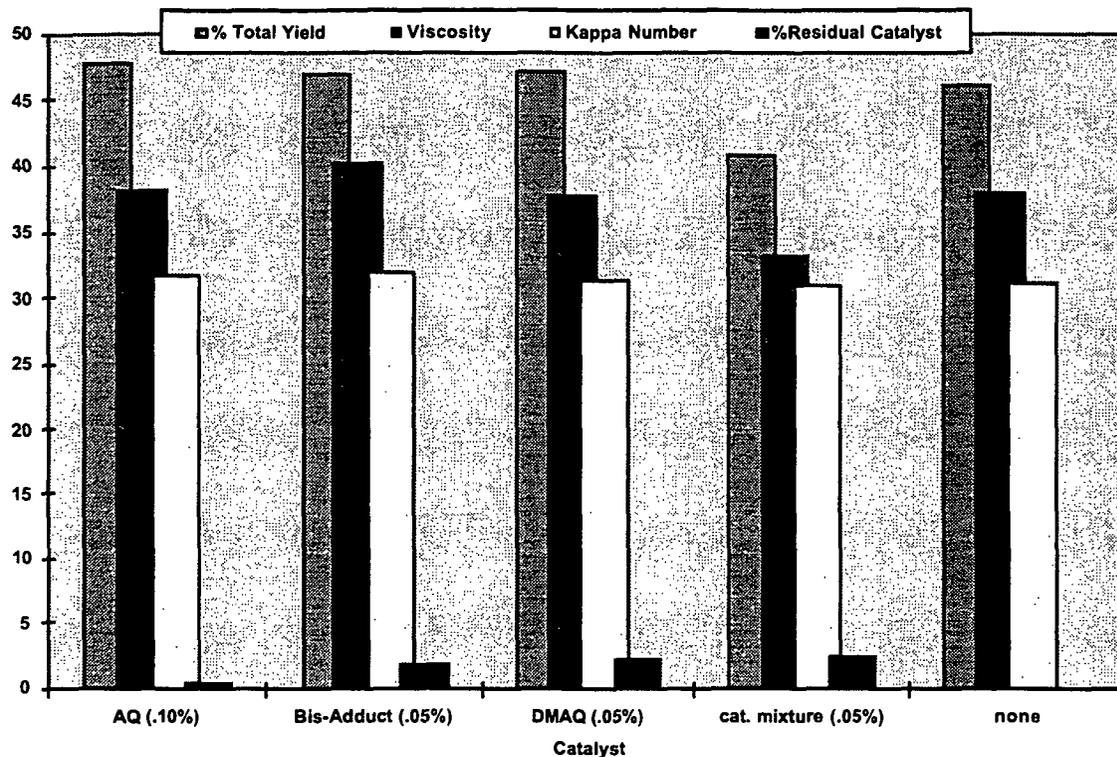


Figure 27 - Comparison of Unbleached, Southern Pine Pulps from 1-Kg Kraft and Kraft/Catalyst Pulping

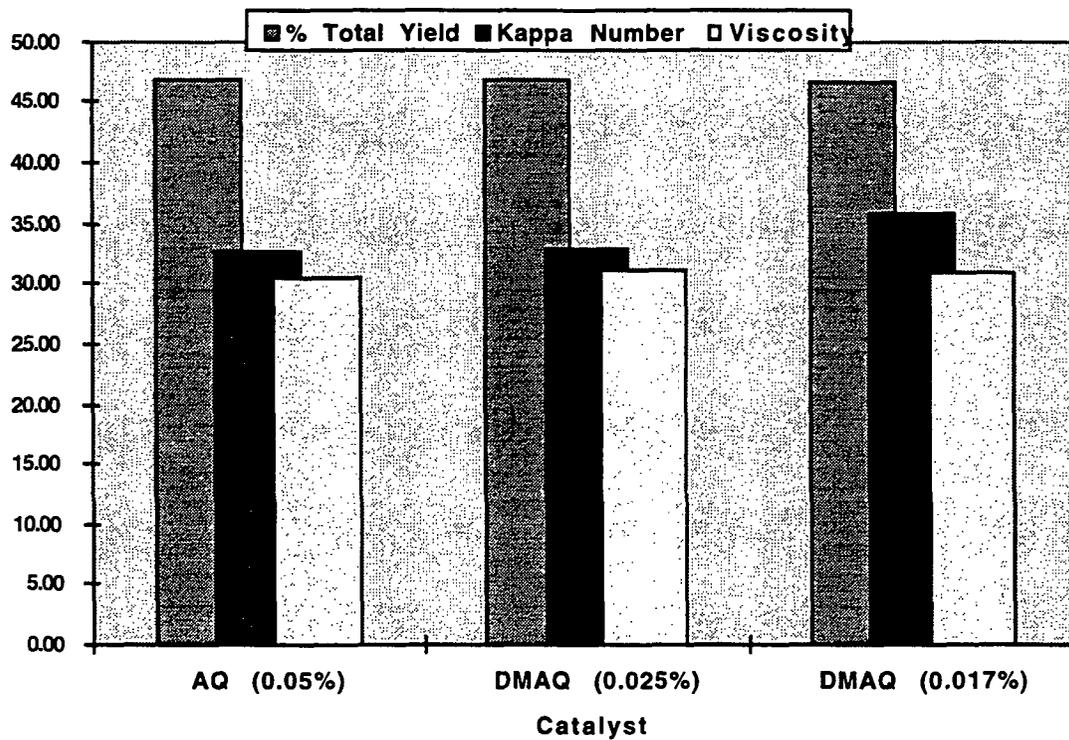


Figure 28 - Comparison of Unbleached, Southern Pine Pulps from 1-Kg Polysulfide/Catalyst Pulping

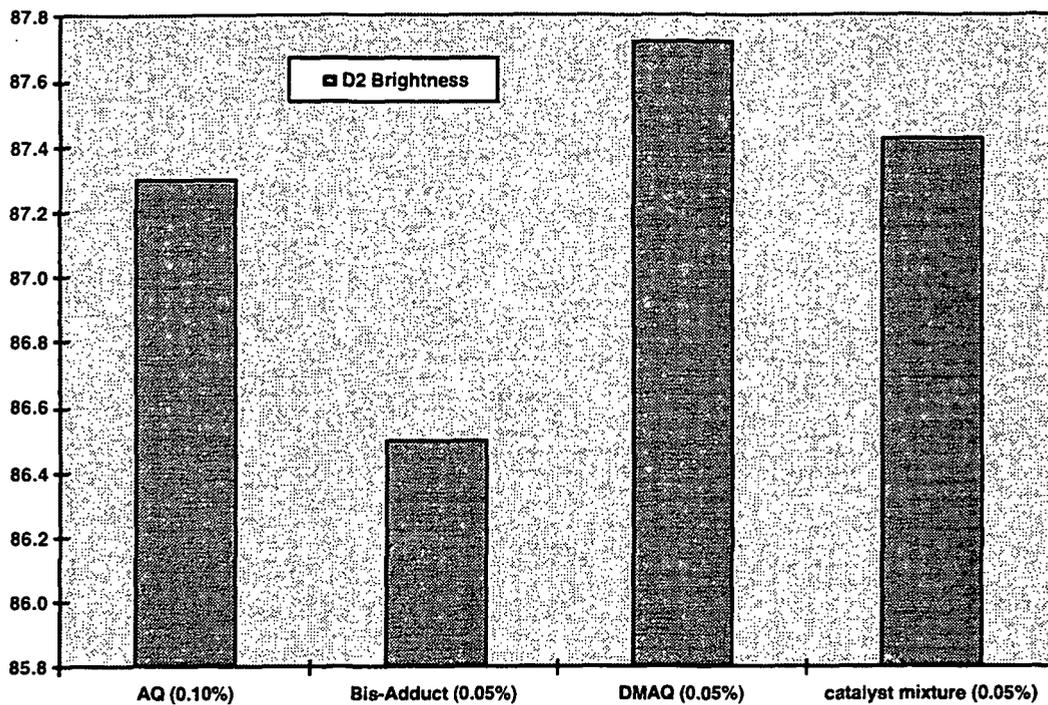


Figure 29 - Soda/Catalyst Pulp D<sub>2</sub> Brightness Comparison for Constant 0.20 Kappa Factor Bleaching

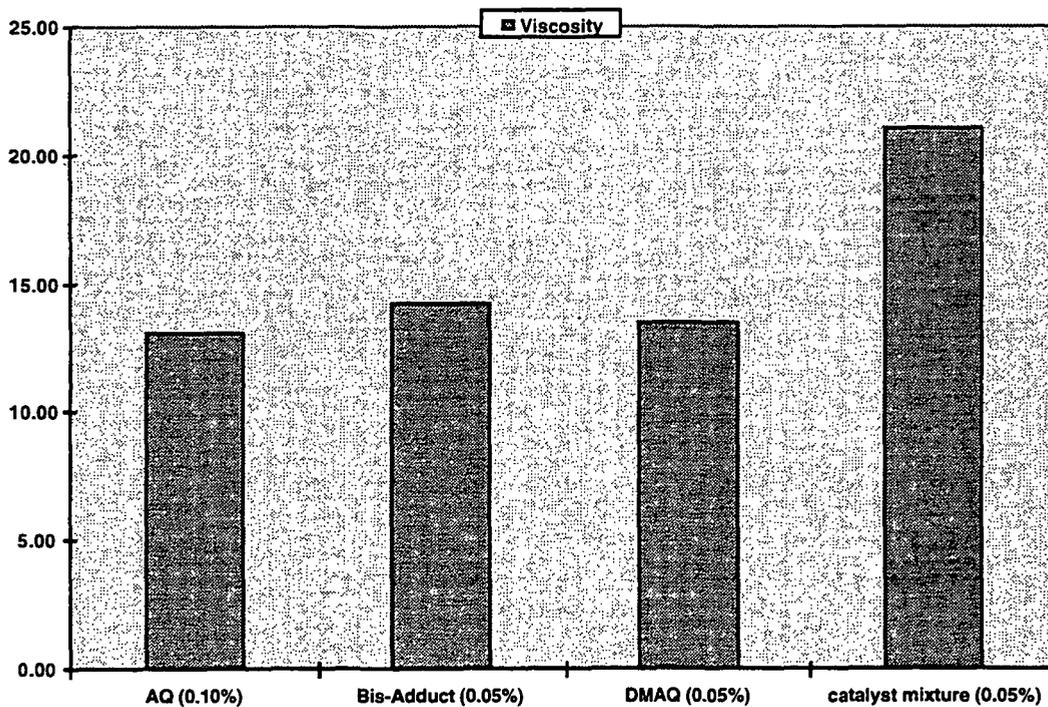


Figure 30 - Soda/Catalyst Pulp D<sub>2</sub> Viscosity Comparison for Constant 0.20 Kappa Factor Bleaching

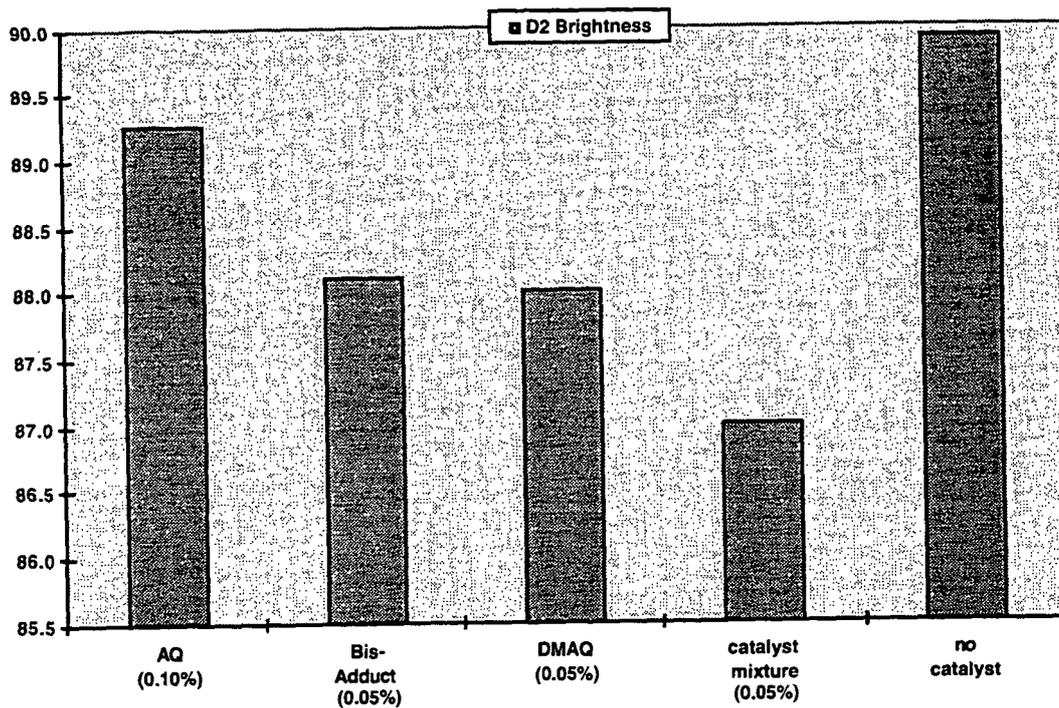


Figure 31 - Kraft Pulp D<sub>2</sub> Brightness Comparison

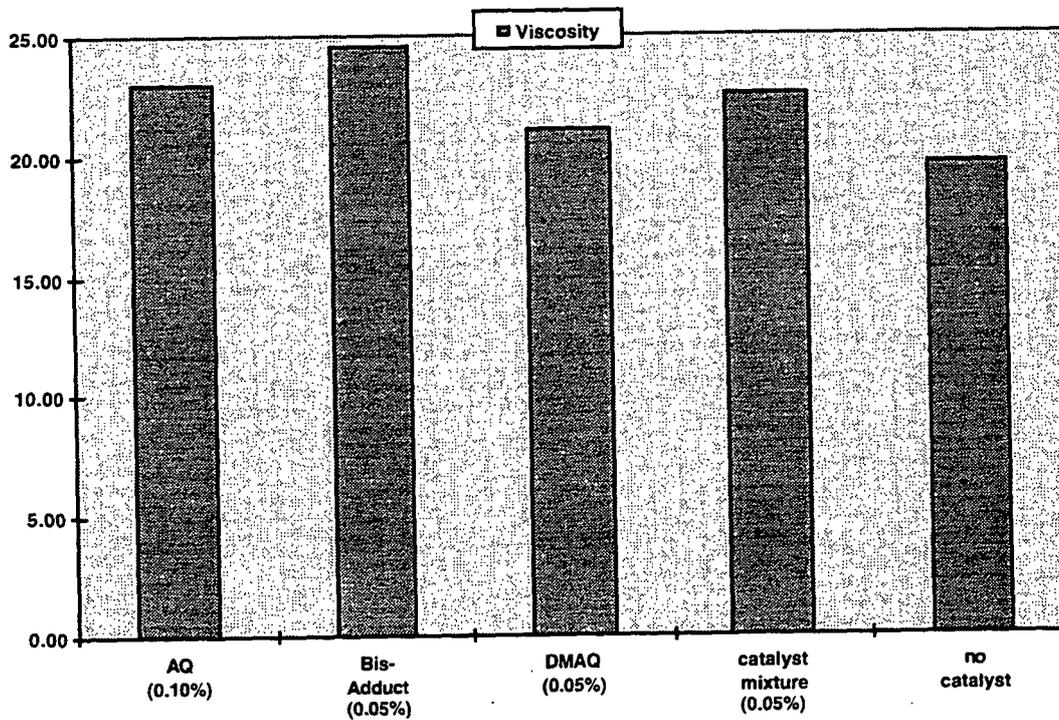


Figure 32 - Kraft Pulp D<sub>2</sub> Viscosity Comparison

Table 17 - Detailed Bleaching Conditions and Results

Cook Type (% catalyst)	D <sub>0</sub>			(EOP)				D <sub>1</sub>			E <sub>2</sub>		D <sub>2</sub>				% ClO <sub>2</sub> used	Visc. mPa*s
	45 min/50°C <sup>a,c</sup>			60 min/0.5% H <sub>2</sub> O <sub>2</sub> <sup>b,c</sup>				90 min/1.0% ClO <sub>2</sub> <sup>b,c</sup>			0.5% NaOH <sup>b-d</sup>		180 min <sup>b,c</sup>					
	Kappa Factor	ClO <sub>2</sub> %	Final pH	NaOH %	Final pH	Bright-ness	Kappa No.	Final pH	Resid. %ClO <sub>2</sub>	Bright-ness	Final pH	Bright-ness	ClO <sub>2</sub> % <sup>e</sup>	Final pH	Resid. %ClO <sub>2</sub>	Bright-ness		
Soda/AQ (0.1%)	0.20	2.38	1.6	3.8	11.9	55.8	4.6	3.2	0.05	83.0	11.9	78.6	0.40	3.4	0.03	89.1	3.70	
[Small scale optimization]								3.2	0.10	83.3	12.0	79.2	0.40	3.4	0.03	89.6	3.65	
								3.2	0.07	82.9	12.1	79.0	0.20	3.2	0.01	87.8	3.50	
													0.80	3.3	0.22	89.1	3.89	
Soda/AQ (0.1%)	0.20	2.38	1.8	3.8	11.6	57.6	4.3	2.8	0.12	82.7	11.2	79.6	0.20	3.1	trace	87.3	3.46	13.1
	0.20 <sup>f</sup>	2.38	1.8	3.8	11.7	59.6	4.2	2.8	0.10	83.8	11.2	80.7	0.20	3.1	0.01	88.0	3.47	14.2
Soda/Bisadduct (0.05%)	0.19	2.38	1.8	3.8	11.6	56.5	5.0	2.9	0.06	82.7	11.2	79.0	0.20	3.0	trace	87.4	3.52	
	0.20	2.56	1.6	4.0	12.0	56.5	6.0	2.9	0.05	82.8	11.3	79.4	0.20	3.4	trace	86.5	3.71	14.2
Soda/DMAQ (0.05%)	0.19	2.38	1.9	3.8	11.6	55.3	5.6	2.7	0.03	80.5	11.2	78.2	0.20	3.0	trace	87.0	3.55	
	0.20	2.56	1.8	4.1	12.0	56.9	4.7	2.9	0.05	81.9	10.7	78.8	0.20	3.2	trace	87.7	3.71	13.5
	0.20 <sup>f,g</sup>	2.67	1.7	4.2	11.6	59.3	4.2	3.0	0.09	84.8	11.1	81.1	0.20	3.2	0.02	88.5	3.76	12.7
Soda/cat mixture (0.05%)	0.18	2.38	1.9	3.8	11.4	53.7	5.6	3.3	0.02	80.8	10.8	77.1	0.20	3.1	trace	84.7	3.56	
	0.20	2.59	1.8	4.1	12.0	57.8	4.6	3.0	0.07	82.2	11.3	80.0	0.20	3.4	0.01	87.4	3.71	14.0
Kraft/AQ (0.1%)	0.20	2.40	2.0	3.8	12.0	59.1	3.9	3.4	0.32	84.2	11.4	83.6	0.20	3.9	0.03	89.3	3.24	23.0
Kraft/Bisadduct (0.05%)	0.20	2.41	1.7	3.8	11.9	56.0	5.1	2.9	0.07	82.7	10.7	78.9	0.20	3.5	trace	88.1	3.53	24.5
Kraft/DMAQ (0.05%)	0.20	2.38	1.8	3.8	12.1	58.5	5.0		0.12	83.0	11.1	79.2	0.20	3.4	0.01	88.0	3.45	21.1
	0.20 <sup>f,g</sup>	2.49	1.9	3.9	11.6	62.1	3.8	3.1	0.21	85.1	10.8	81.7	0.20	3.5	trace	89.7	3.48	22.7
Kraft/cat mixture (0.05%)	0.20	2.34	1.8	3.7	12.4	56.3	5.2	2.6	0.02	80.6	11.0	77.7	0.20	2.9	0.00	87.0	3.52	22.6
Kraft	0.20	2.36	2.0	3.7	12.0	61.2	3.9	3.4	0.16	84.7	11.5	81.5	0.20	3.2	0.01	89.9	3.39	19.7

<sup>a</sup> % residual ClO<sub>2</sub> was trace - 0.01%; <sup>b</sup> 70°C bath temperature; <sup>c</sup> sequence performed at 10% consistency; <sup>d</sup> 1 hour <sup>e</sup> A 0.2% ClO<sub>2</sub> charge was used for the comparison; the brightness ceiling was not reached for the pulps at this ClO<sub>2</sub> level; <sup>f</sup> bleaches done at a later, but same time; <sup>g</sup> employed a different pulp as above - one that had a slightly higher entering kappa number.

## 9.0 PULP STRENGTH COMPARISONS

In a typical papermaking process, bleached pulp is refined prior to application to a paper machine; the degree to which the pulp is refined has an important effect on strength parameters in the resulting sheet. Our refining involved beating nine bleached pulps in a PFI mill at 10% consistency at three different revolution settings. The revolutions were targeted to provide pulps at three different levels of freeness: 300, 400, and 600; the unrefined pulp had a freeness of ~750. The higher the freeness, the more quickly water will drain through a fiber mat. Handsheets made from the beaten and unbeaten pulps were submitted to the Institute's Paper Testing Laboratory for strength tests. In all, forty handsheets were made for each pulp: ten each for three different refining degrees and ten of the unbeaten pulp; roughly half of handsheets were evaluated and another half saved for possible future tests. The data from the refined and unbeaten pulps in each set were used to construct plots that provide strength values at desired freeness values. For each sheet, we determined basis weight, caliper, (and from these two, the density), tear, tensile, burst, and zero span. Five sheets in each set were analyzed and average values determined for each parameter. For some strength tests discussed below, we provide the average values for the five handsheets; in other cases, we compare values for each individual handsheet.

As will be seen below, the strength tests had a considerable amount of scatter. Even so, the average values and trendlines for the various pulps within a set were fairly similar. An exception were the data associated with the soda/AQ and soda/DMAQ fully bleached pulps. These were the first two sets of handsheets made by an inexperienced technician. In fact, it is possible that the scatter throughout the tests was a result of inconsistently prepared handsheets. Many of these handsheets had lower than usual basis weights. Therefore, we repeated the bleaching and strength testing of new soda/AQ, soda/DMAQ, and kraft/DMAQ pulps; handsheets made from these pulps had consistent, desired basis weights. The comparative data for the two new soda pulps are presented separately from the other tests.

### 9.1 Tear -Tensile Comparisons

A frequently used measure of comparative strength properties of pulps involves comparing a plots of tear index vs. tensile index. The indexes are determined by dividing the tear and tensile values by the basis weight of the sheets and multiplying by 100. Plots for the kraft and soda/catalyst sets are shown in Figures 33 and 34. The various data points and trendlines for each pulp type are not easily deciphered from the figures; however, the important point of the data in Figure 33 is that there are basically no differences for the pulps in the kraft set. One expects to see a downward slope in the trendlines; the one positive slope line is for the kraft/DMAQ pulp. A repeat determination of the tear and tensile indexes of a new kraft/DMAQ pulp provided a nearly flat slope in a plot of tear index vs. tensile index.

In the soda set (Figure 34), the two trendlines that are identical are the soda/bisadduct and soda/catalyst mixture; the stronger pulp (upper trendline) is the soda/AQ pulp, while the weaker pulp is the soda/DMAQ pulp. However, a repeat set of tests for these two pulps gave the data in Figure 35. The new tear and tensile indexes are lower in the new set because of the higher handsheet basis weights. More importantly, however, the two pulps gave nearly identical tear index vs. tensile index values at the different freeness points; one soda/DMAQ data point was considered an outlier. The standard deviations of the tensile and tear indexes for the repeat handsheets were 50-60% lower than that of the initial large data set.

Time constraints prevented us from doing a full comparison of all the different pulps. However, one would expect that bisadduct and catalyst mixture pulps would equal that of the DMAQ pulps since the bisadduct goes to DMAQ during cooking and the catalyst mixture's main activity is due to the presence of DMAQ. Also, it is generally accepted that the addition of AQ (and presumably DMAQ) to a kraft pulping system has no adverse effects on strength parameters; in contrast, if the catalyst is used to lower the cook temperature and NaOH content, pulp strength actually improves.

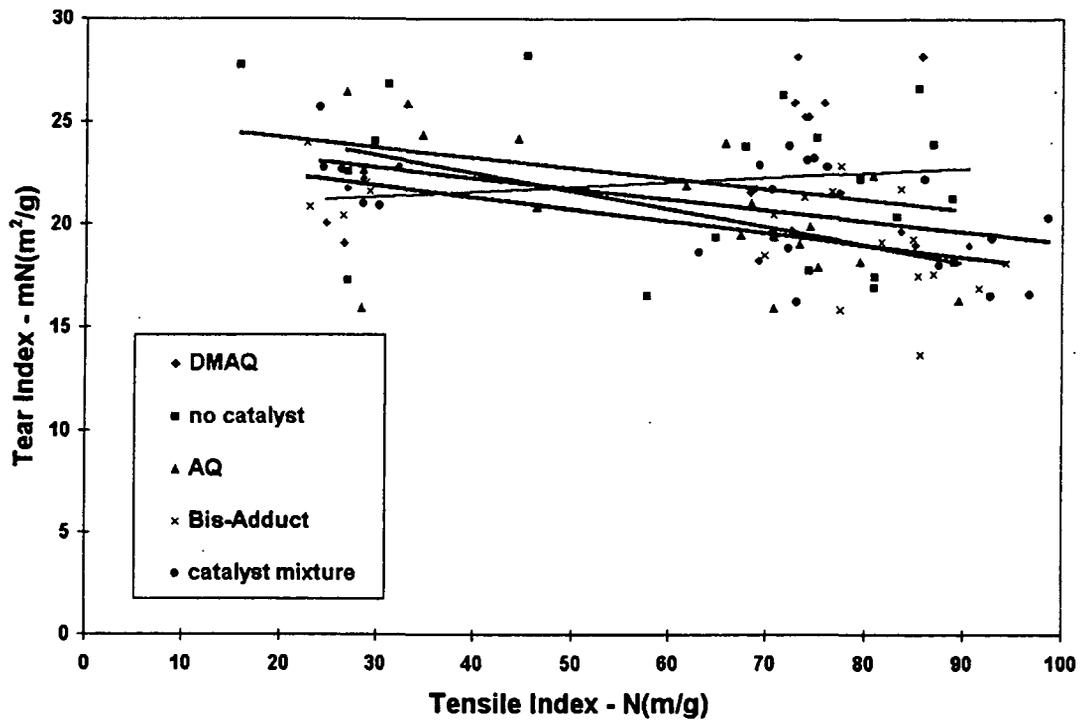


Figure 33 - Comparison of Tear/Tensile Indexes for Kraft and Kraft/Catalyst Bleached Pulps.

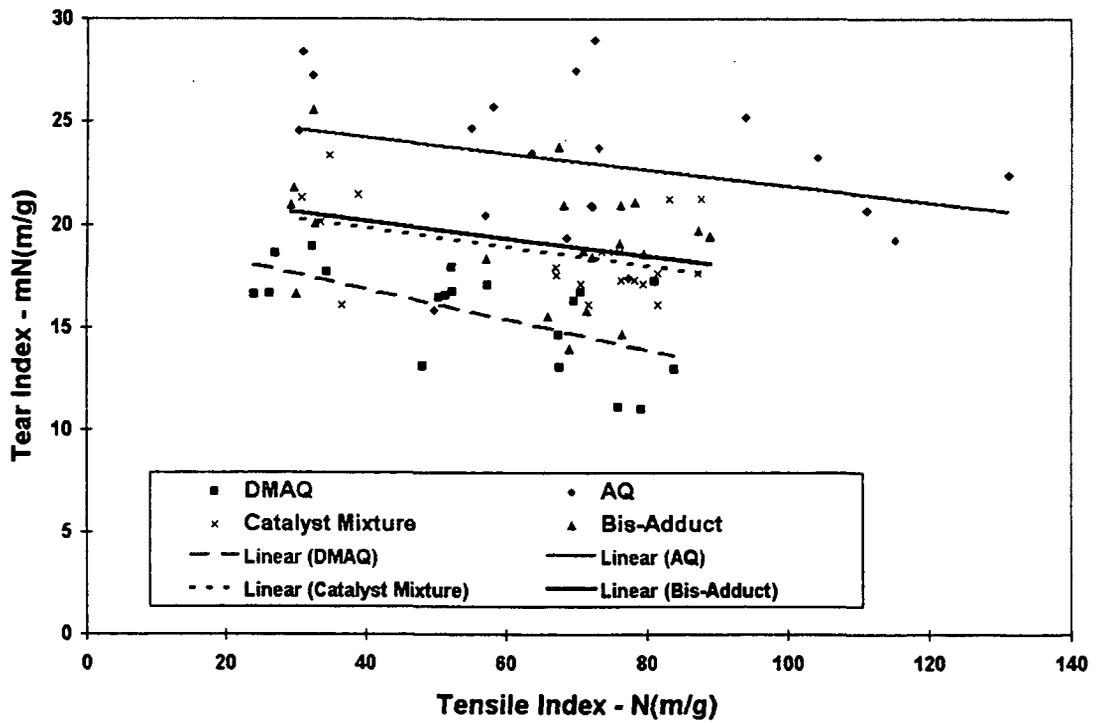


Figure 34 - Comparison of Tear/Tensile Indexes for Soda/Catalysts Bleached Pulps.

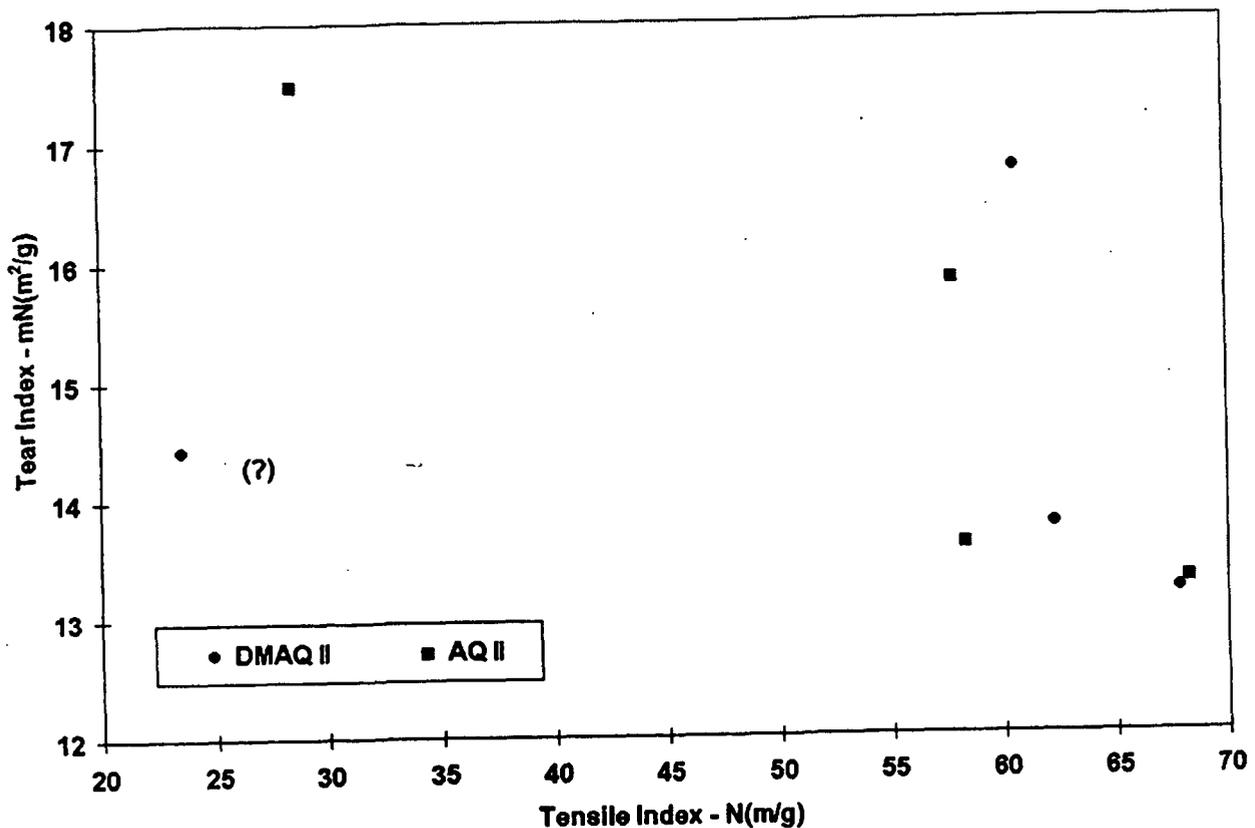


Figure 35 - Comparison of Tear/Tensile Indexes for Two Soda/Catalyst Pulps at Four Freenesses.

### 9.2 Other Strength Comparisons

Table 19 below compares the average density, burst, and zero span values for the nine pulps at 350 and 500 Canadian standard freeness (CSF); viscosity values for the unbeaten pulps are also provided in the table. The three repeat pulps are designated by (II) in the table. One expects the density, burst, and zero span values to decrease at higher freeness values and this is what our data most often shows. Zero span, which is a measure of individual fiber strength, should correlate with the viscosity value. Except possibly for an anomalous low viscosity for the kraft control, the data in the table indicates no real differences in viscosities and zero span indexes. Both values are related to fiber length. In general, the strength values in Table 18 are all within the standard deviation ( $\pm$  values in the table) of one another within the two series. The burst index for the repeat soda/AQ pulp fell much more in line with the other soda pulps. The low densities and high burst indexes for the original soda/AQ pulp further verifies our suspicion that its handsheets were suspect; its data should probably be disregarded.

Table 18 - Comparison of Selected Strength Parameters for Soda/ and Kraft/Catalyst Bleached Pulps

CSF	Density g/cm <sup>3</sup> (± 0.03)		Burst Index (kPa·m <sup>2</sup> /g) (± 0.5)		Zero Span Index N(m/g) (± 10)		Viscosity mPa·s
	350	500	350	500	350	500	
Kraft (no catalyst)	0.69	0.66	7.2	6.2	132	125	19.7
Kraft AQ	0.70	0.69	8.5	7.8	117	124	23.0
Kraft DMAQ	0.67	0.67	8.4	7.8	118	122	21.1
Kraft DMAQ (II)	0.73	0.71	7.6	7.1	128	117	22.7
Kraft Bisadduct	0.70	0.69	7.3	6.3	116	110	24.5
Kraft Cat. Mixture	0.74	0.64	6.6	6.2	126	133	22.6
Soda AQ <sup>a</sup>	0.65	0.66	7.3	7.3	125	119	13.0
Soda AQ (II)	0.70	0.69	6.7	6.0	123	118	14.2
Soda DMAQ	0.71	0.69	6.5	6.1	125	122	13.5
Soda DMAQ (II)	0.70	0.68	6.7	6.2	127	116	12.7
Soda Bisadduct	0.69	0.65	6.8	7.0	108	118	14.2
Soda Cat. Mixture	0.69	0.68	6.5	5.5	112	111	14.0

<sup>a</sup>Several suspicious pieces of data suggest that the handsheets for this pulp are not uniform.

Strength comparisons of the two repeat soda/AQ and DMAQ pulps are shown in Figures 36-39. Very few differences were observed between these two carefully prepared pulps. There appears, however, to be a bad tear value for one of the soda/DMAQ handsheets. This can be seen in the tear vs. tensile comparison (Figure 35); the bad data point was omitted in the tear vs. freeness graph (Figure 36). Trendlines were employed in two cases; however, curved lines appear more appropriate in other cases.

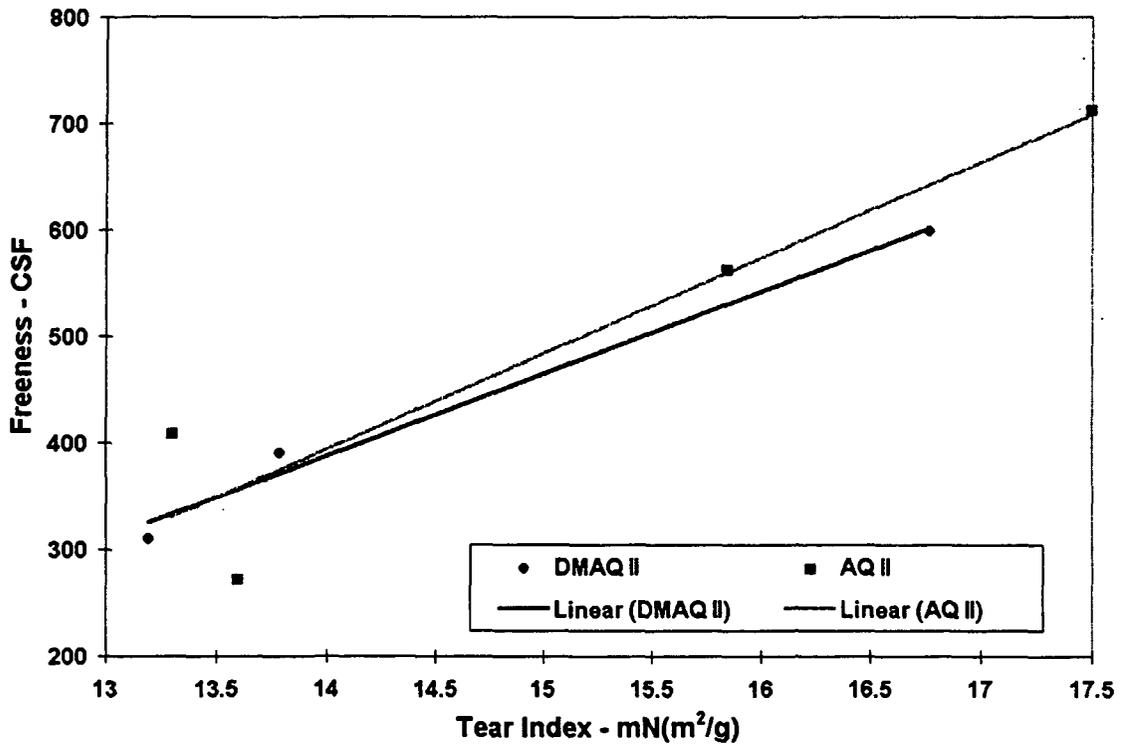


Figure 36 - Comparison of Average Tear Indexes for Soda/AQ Pulps at Four Freenesses and Soda/DMAQ Pulps at Three Freenesses.

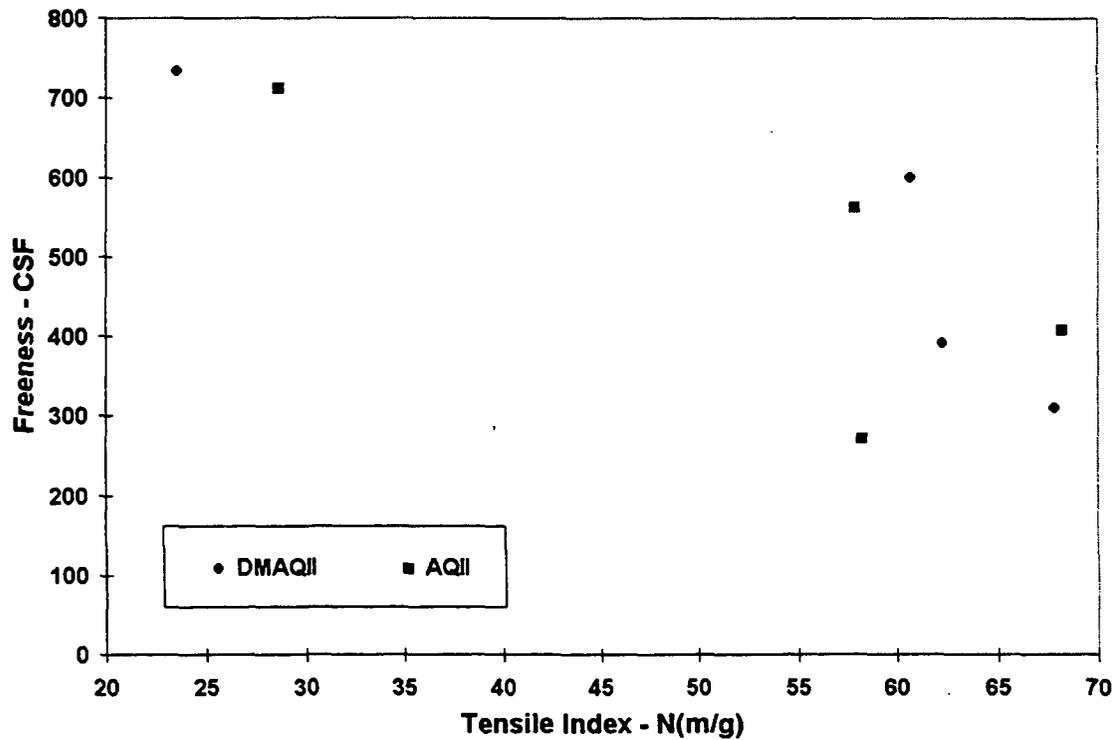


Figure 37 - Comparison of Average Tensile Indexes for Two Soda/Catalyst Pulps at Four Freenesses.

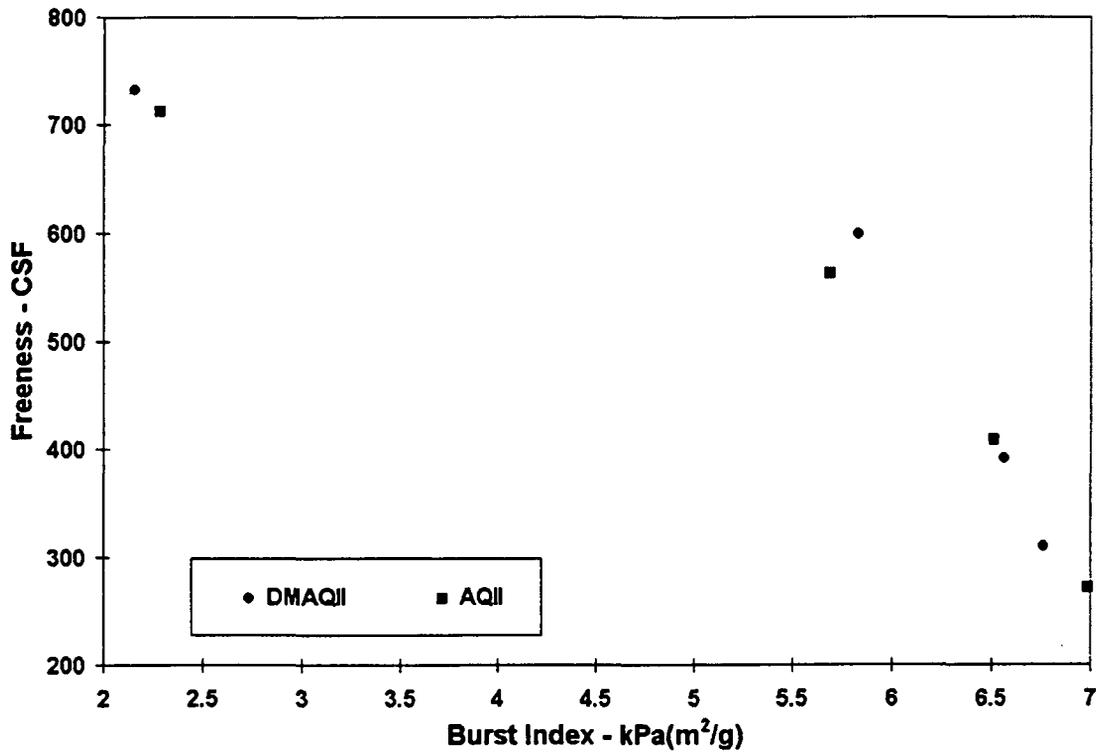


Figure 38 - Comparison of Average Burst Indexes for Two Soda/Catalyst Pulps at Four Freenesses.

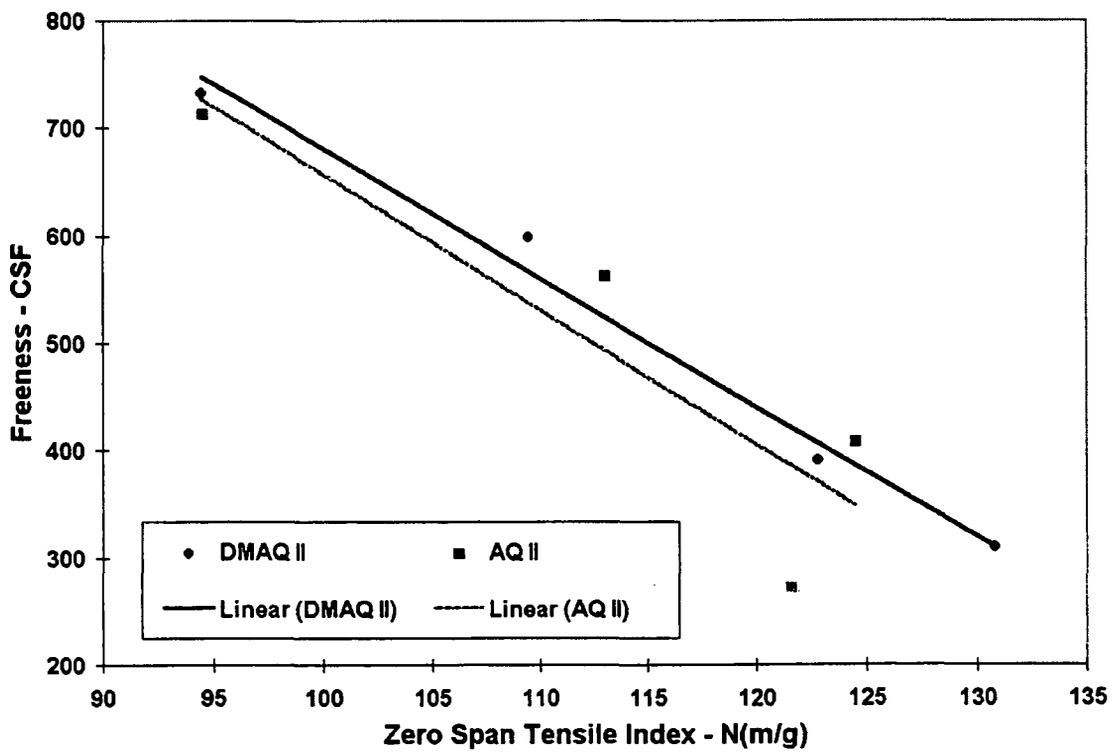


Figure 39 - Comparison of Ave. Zero Span Tensile Indexes for 2 Soda/Catalyst Pulps at 4 Freenesses.

## 10.0 ECONOMIC EVALUATION SUMMARY

In October 1996, a complete revision of our economic summary was written. The conclusions of the report are included here for reference.

A new technoeconomic evaluation of a two stage process for the conversion of lignin into a quinone containing catalyst mixture for the production of alkaline pulp has been completed. This evaluation updates one carried out in 1991. Continuing work at NREL and the IPST has investigated developing a two stage process for the conversion of lignin into a quinone containing catalyst mixture. The first stage of the process oxidizes lignin to give a mixture of catalyst precursors (benzoquinones). In the second stage of the process, the catalyst precursors are converted into the catalyst mixture.

The results of this evaluation give strong indication that low molecular weight (LMW) organosolv lignin could be the lowest cost source of feedstock for the pulping catalyst process, largely because it is obtained directly as a product of the extraction and solvent recovery operations of the pulping process, and could be transferred to a catalyst production process at close to zero cost. A parallel evaluation of possible competing processes based on nonrenewable resources is continuing in order to monitor the performance of a biomass-based process for catalyst production against potential improvements in these existing and developing conventional processes. When compared to existing catalyst production processes, the NREL/IPST process continues to be the lowest cost approach to these materials.

A key aspect of our research program is an ongoing technoeconomic evaluation of the various stages of the process. A brief, preliminary evaluation appeared in 1989, and was followed by a second evaluation in 1991 based on the experimental work to that point. This report incorporates results since that time and describes three base cases for the preparation of catalyst mixtures. One is based on organosolv lignin obtained from the NREL Clean Fractionation process (CF Case). The others (BL Case and VS Case) are based on the use of kraft lignin as a starting material. The primary difference between the cases (apart from the choice of starting material) is in the lignin processing stage. The organosolv case proceeds by separation and use of a LMW lignin fraction, produced directly in solvent recovery operations without special extraction steps, followed by conversion into pulping catalyst.

The BL Case is similar to the CF Case, but uses lignin derived from kraft black liquor as the starting material. The other black liquor case (VS Case) assumes a conversion of the lignin into a crude mixture of discrete intermediates, including vanillin, syringaldehyde, and other small lignin fragments, as the lignin processing stage. This approach was evaluated because laboratory results indicated that either vanillin or syringaldehyde could be converted to the corresponding benzoquinone in higher yield than LMW lignin itself.

All cases describe large-scale, stand-alone plants, sized to supply pulping catalyst by distribution to a significant part of the entire pulping industry, and are based on built-up process flow diagrams, principal stream material balances, and preliminary major equipment design. Capital investment and cost of production summaries were then prepared for each case.

The evaluation concludes the following:

1. If key assumptions described in the report are met, a lignin to pulping catalyst process still appears to be one of the most economic approaches yet developed. Laboratory scale pulping results have shown that the catalyst mixture is as active as a catalyst as commercial grade pulping catalyst with.
2. The most efficient, lowest cost process route from lignin to pulping catalyst appears to be lignin derived from Clean Fractionation. But there is an important proviso: LMW lignin must be

available directly from the pulping process, without further fractionation. A large scale, integrated operation producing cellulose as its primary product from Clean Fractionation, and using a portion of the lignin for catalyst production could be an important approach. Substantial coproduct credits could be taken in such an operation. Such accounting is very commonly used in the chemical industry.

3. A large scale, centralized operation using lignin derived from kraft black liquor could also produce pulping catalyst at a competitive price using ultrafiltration as a process for separating the lignin from the black liquor. However, lack of access to important (most likely proprietary) data from the pulp and paper industry regarding costs, material balances, etc., add uncertainty to the absolute costs of this process.
4. The total amortized manufacturing cost of pulping catalyst from organosolv lignin (CF Case) could be as low as \$1.11/lb, while one based on kraft black liquor without an intermediate conversion to a V/S mixture (BL Case) could be as low as \$1.33/lb.
5. An organosolv-based coproduct route could be a simple, direct way to get started in the pulping catalyst from lignin business. However, it is reasonable to argue that research on pulping catalyst from kraft black liquor lignin should continue as a back-up possibility since organosolv pulping processes are not yet commercial in the United States. In the short term, interaction with an industrial partner to demonstrate this process at a mill site using kraft lignin should be pursued. Such a joint operation would help verify the projections made in this report and develop the necessary material and energy balance information needed for the process. In parallel, for the longer term, more investigation of the integrated pulp and catalyst operation should be continued, using a portion of the lignin generated in the process as the ultimate source.
6. Conversion of lignin to an intermediate mixture of V/S (VS Case) does not appear to be a viable route for the production of pulping catalyst unless methodology can be developed that improves the conversion of kraft lignin to a V/S mixture, or until it can be determined whether other monomeric components present in the V/S mixture can be used as starting materials for preparation of benzoquinones.
7. The amount of raw materials ( $\text{NO}_2$ ,  $\text{HOOH}$ , isoprene), their efficiency of use, and hence, their cost contribution in each of the base cases has a significant impact on the amortized production cost of the catalyst. Improvements in these processes through research using the sensitivity analyses as guides will improve the product cost outlook.
8. Support for further research on coproduction of organosolv cellulose pulp and its associated LMW lignin should be sought from industrial developers of organosolv pulping. This study shows the potential promise of attractive profitability of a pulping catalyst-organosolv pulp coproduct manufacturing operation.
9. When compared to other existing routes to pulping catalysts (specifically AQ), the lignin based process still appears competitive if certain process performance goals are met. It appears that the IPST/NREL pulping catalyst-from-lignin process might have to meet a competitive production cost performance target as low as \$1.00/lb. Apparently the pulping industry can afford to pay in the range of \$2.00/lb, but there is a good chance that the market can supply their needs with no significant reduction of this price, and IPST/NREL's pulping catalyst from lignin process might have a good chance of participating successfully.

## 11.0 APPENDIX

### 11.1 Work Outline For Final Phase Of Project And Milestones

At the beginning of the final phase of the project, the following summary and work plan was developed with the DOE program manager and the DOE Golden Field Office. Each of the objectives outlined in this agreement, save for the mill test, have been completed. As negotiated with the program manager in July 1997, the pulping, bleaching, and paper results were judged to be sufficiently credible for industrial evaluation.

#### **Project Summary: Sulfur-Free Pulping**

**Objective:** Produce low cost pulping catalysts from lignin that can be employed in conventional kraft pulping operations to increase productivity and lower energy costs and negative environmental impacts, particularly sulfur emissions.

**Approach:** Using guidance from the industrial project advisory committee to the Institute of Paper Science and Technology, a two phase approach was undertaken. The first phase involved proof-of-concept analyses of the prospects for employing lignin as a feedstock for conversion into the pulping catalysts rather than petrochemical and other non-renewable resources (small/lab scale: 1 - 100g, when referring to catalyst production; 10-20g wood/run for pulping studies). The second phase involves selecting the best routes to produce the pulping catalysts that could be employed at a larger scale (0.5 - 1 lb runs when referring to catalyst production; 200 - 500 g wood/run for pulping runs) and supply sufficient process data such that the economics for producing the catalyst justify industrial investment in demonstration projects.

**Targets:** Amortized production cost of catalyst: less than \$1.50/lb. Overall yield of the two process steps : 20 - 30%. Pulp yields: 45%; kappa numbers: 20 - 30.

**Impacts:** **Energy:** The project is forecast to reduce energy consumption in the pulp and paper industry by about 0.07 quads/year in addition to that currently saved by intermittent current use in U. S. mills. **Environmental:** Use of catalyzed pulping processes will directly address a primary problem for the pulp and paper industry - bleach plant effluent. Pulping catalysts allow more efficient removal of lignin from wood. Subsequent purification will be easier and release fewer effluents.

**Results:** Work in phase I is essentially complete. Phase II efforts in the following specific issues need to be addressed in order to reduce the selling price to the target values:

<u>Item</u>	<u>Impact on cost</u>
Process optimization	60%
Increased catalyst performance	15%
Defining scaling parameters	25%
Adequate pulp performance	Must occur for product to be viable

All efforts are directed towards addressing the items listed above with the greatest effort on increasing process optimization since that has the greatest impact on price and hence the viability of this process to industry.

#### Projected Milestones and Explanation

**Process Optimization Milestones.** These are directed at achieving our target cost goal of less than \$1.50/lb. This cost goal is equivalent to the overall yield of product necessary from the two steps of the process, lignin oxidation and olefin addition, i. e., if we meet certain minimum yield requirements in these steps, the cost of catalyst will be within our target range. Our current projections indicate that we will realize this cost goal if the overall yield of the two steps is in the 20 - 30% range.

1) Assess performance of lignin oxidation technology.

Three approaches to the lignin oxidation have been developed: fragmenting lignin into smaller pieces, introducing necessary chemical functionality into the lignin side chain to improve oxidation performance, and investigating new oxidation methodology. Subtasks include the following:

- Screening of oxidation/olefin addition techniques: This work will continue the effort in optimization and understanding of the process of using NO<sub>2</sub> as the oxidant. This work will be important for the determination of the best method for producing larger amounts of catalyst. New oxidation methodology, identified as possibly cost effective, but not yet tested, will be investigated.
- Screening of different lignin sources: This work will examine alternate lignin sources for their suitability as starting materials for catalyst production. Organosolv lignins, lignin from early cooks (from removal of black liquor at different times during pulping), and extracted lignin will be studied. The last source is not commercial and of lower priority. However, it could offer a highly reactive lignin that should be investigated.

Since there are a number of different specific parameters to be tested with regard to the general milestone, success will be achieved if a given oxidation technique gives a process that advances our progress toward the economic target value. The quantitative measure of success will be whether the oxidation technique examined gives an overall yield for the process of 20-30%, which is equivalent to our cost target of \$1.00 - \$1.50/lb. The cost for this task will be \$310K.

2) Assess methods to fragment lignins to simple monomers.

Part of the IPST work of phase I included studying new methodology for converting lignin to smaller fragments. Catalytic versions of these reactions will be studied and could allow more efficient use of a greater proportion of the lignin. There is an additional possibility that the technology used for this fragmentation could also oxidize the lignin in the same step. Both of these possibilities could lead to a lower overall process cost. Work areas include:

- Screening of different lignin fragmentation methods: Other simple, cost-effective methods for converting lignin into smaller fragments more amenable to conversion into benzoquinones will be investigated.

Yield increases from the oxidation of smaller fragments will be measured against the costs of processing the smaller fragments. The final determination will be based on whether a given approach moves us closer to our target values, both in overall yield and cost. The cost for this task will be \$80K.

**Improved Catalyst Performance and Scaling Parameter Milestones.** These address whether the catalyst performs well under normal pulping conditions, the properties of the pulp, and scale up of both the catalyst preparation and pulping runs. The measure of success will be a comparison of properties. Properties equivalent to or better than those observed from conventional processes will define a successful result.

1) Assessment of catalyst performance under kraft conditions.

We will continue to investigate the performance of the catalyst mixtures prepared by this process. A focus will be on reproducibility and scaleup of the pulping runs. Work will include:

- Performance of the catalyst mixtures under kraft conditions
- Performance of the catalyst mixtures at larger pulping scales
- Performance of the catalyst mixtures in other pulping processes, such as ASAQ and ASAM

Success of the tests will be determined by comparison with processes using pure AQ and those using no catalyst. Two direct measurements will determine success or failure. Pulp yield and kappa number will be determined, and values equal to or better than those obtained from runs catalyzed with pure AQ will be considered a success. Pulp yields of 45% and kappa numbers of 20 - 30 will be targets. The cost for completion of this task will be \$110K.

2) Assess bleaching performance and paper properties of pulps derived using catalyst mixture.

Several aspects of pulp properties will be examined and includes:

- examining kappa number reductions and brightness of the pulps from our catalyst mixture process, compared to AQ pulps, towards chlorine dioxide, ozone, oxygen, and peroxide.
- examining pulp strength properties, both before and after bleaching.

Success will be measured by comparison to samples produced from uncatalyzed pulping runs and runs catalyzed by pure AQ. A successful process will be indicated by samples that exhibit qualities equal to or greater than those exhibited by conventionally prepared samples for a given application (because of the large differences in properties required for different grades of paper made from market pulp). The cost for this task will be \$80K.

3) NREL/IPST begin catalyst testing in mill operation.

This milestone marks the best estimate as to when we see the project winding down (mid FY97). The implications of this milestone are that we have prepared sufficient catalyst for testing, and that an industrial partner has found its performance sufficiently promising to test it in the mill.

**Economic Evaluation Milestone.** The evaluation will include: projections of costs for several oxidation approaches under investigation, two olefin addition approaches, the cost of process improvements, mass balances and flow sheets. The report will verify the results of the earlier report (1991), indicate the cost targets necessary for a competitive lignin based process, and indicate those areas where improvement will be necessary. The cost for completion of this task will be \$20K.

1) Completion of new economic evaluation of process.

Negotiations between NREL and the DOE program manager in May 1997 added the following adjusted milestones:

Completion of bleaching, pulping and paper properties determination	August 1997
Completion of oxide studies	August 1997
Draft final report including results from oxidation and pulping studies and best economic projections	September 1997

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