

ABSTRACT

CUI, Yu. Delignification of Kraft-AQ Southern Pine Pulp with Hydrogen Peroxide Catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$. (Under the direction of Dr. Chen-Loung Chen and Dr. Josef G. Gratzl)

Over the years, hydrogen peroxide has been used to improve the brightness of pulp at the end of a bleaching sequence. However, the degree of delignification achieved by a hydrogen peroxide stage is usually modest. That is because in alkaline condition the hydroperoxy anion reacts with chromophores in pulp as a nucleophile that does not oxidize residual lignin to a significant extent. In order to enhance the reactivity of hydrogen peroxide as an oxidant, a binuclear manganese complex $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ was added. As a result, the degree of delignification was significantly improved, while at the same time, the strength properties of the pulp were better preserved compared traditional in hydrogen peroxide delignification.

In order to better understand the mechanism of this delignification process, lignin model compound oxidation and kinetics of pulp delignification were studied. In addition, residual lignin was isolated from the pulp before and after delignification and then characterized by GPC, FTIR, and $^1\text{H}\text{-}^{13}\text{C}$ 2D NMR. Shown by the model compound study, hydrogen peroxide is able to oxidize 1-(3,4-dimethoxyphenyl)ethanol, *E*-diphenylethene, and 1-(3,4-dimethoxyphenyl)-1-

propene to a considerable extent when catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$, indicating that the reactivity of hydrogen peroxide as an oxidant is significantly improved. Indeed, as shown by the kinetic study of pulp delignification, the degree of delignification as well as the rate of delignification were greatly improved when the catalyst was applied. In addition, the catalyzed delignification process benefits from the concerted reaction mechanism that regulates the formation of hydroxyl radicals responsible for the severe damage to the fibers. As a result, the strength properties were well preserved. Shown by the characterization of residual lignin before and after the delignification, residual lignin was oxidized to a good extent which accounts for the significant degree of delignification. The process simulation of this catalyzed delignification process by WinGEMS4.0 showed that this process was profitable if the cost of the catalyst was kept below \$330/kg.

**Delignification of Kraft-AQ Southern Pine Pulp with Hydrogen Peroxide
Catalyzed by Mn(IV)₂-Me₄DTNE**

By

Yu Cui

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Department of Wood and Paper Science

Raleigh

2000

Approved by

Dr. Adrianna G. Kirkman

Dr. Carol A. Haney

Dr. Josef S. Gratzl

Dr. Chen-Loung Chen

Chair of Advisory Committee

Co-Chair of Advisory Committee

Dedicated to my wife and parents, for their love and support.

BIOGRAPHY

The author was born on June 13, 1970 in Wuhan, China. Although he went to a local school, the author was carefully educated and strictly disciplined by his dedicated father who greatly influenced his life and personality. At the age of 17, the author left home for the Beijing Institute of Technology where he received his Bachelor's degree in chemical engineering with honor in 1991, and his Master's degree in the same discipline three years after.

Like many other Chinese college graduates who sought further education abroad, the author went to the United States in 1994. He chose to go to the North Carolina State University just outside the well-known Research Triangle Park, where he spent two years in the chemistry department and found himself interested in the wood chemistry. He then switched to the Department of Wood and Paper Science to pursue a Ph.D. degree under the direction of Dr. Josef S. Gratzl and Dr. Chen-Loung Chen.

The author is married to formal Miss Wei Zhou. Besides chemistry, he likes to spend time listening to music, classical and rock 'n roll. He also enjoys travelling with his wife and playing badminton.

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The author wishes to reserve this second paragraph of the acknowledgement to his family, although his gratitude to them is greater than words can express. He wishes to thank his parents who never ceased loving and supporting him, and to thank his brother for his unselfish support and brotherhood that they both cherish. Finally, the author wishes to thank his wife for her love and encouragement that helped him out countless times, and for many hard times made easy.

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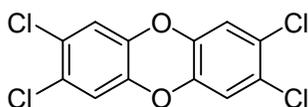
INTRODUCTION

I. Environmental Challenge to the Pulp and Paper Industry

Kraft pulping has been and will continue to be the predominant pulping method. In spite of numerous advantages, such as superior pulp strength properties, flexible raw materials, and mature chemical and energy recovery process, kraft pulping suffers a severe disadvantage of high content of residual lignin. Residual lignin in kraft pulp is notoriously resistant to further kraft pulping reaction during which lignin is degraded by alkaline hydrolysis, while in the meantime carbohydrates are unavoidably degraded through the peeling reaction mechanism ^[1]. Therefore, kraft pulping must be terminated at a certain point in order to avoid severe damage to the fibers, and the residual lignin remaining in the kraft pulp must be removed by oxidative degradation.

Removal of residual lignin in pulp by oxidative degradation (usually referred as “pulp bleaching” in the pulp and paper industry) traditionally has been accomplished by bleaching sequences employing elemental chlorine (Cl_2) and/or chlorine dioxide (ClO_2) ^[2]. In spite of its excellent effectiveness and selectivity in delignification, elemental chlorine is largely responsible for the formation of a wide variety and a large amount of chloro-organics such as polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) ^[3-6]. Some of these chlorinated dioxins and furans found in the typical bleaching effluent, for example, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (1) (2,3,7,8-TCDD) (See Figure 0.1.) are

recognized carcinogens and/or mutagens [7-9]. The public awareness of this issue had grown rapidly and the impact of the pulp and paper industry on the environment has spread globally during the past several decades [10-14]. Consequently, the environmental regulations on the pulp and paper industry enforced by the government have been becoming dramatically stricter. Recently, the United States Environmental Protection Agency has issued so called “Cluster Rule” to regulate the air emission and effluent discharge of the pulp and paper industry [15]. In many Scandinavian and Western European countries, the environmental regulations are even harsher. It therefore became urgent for the pulp and paper industry to develop and implement environmentally friendly bleaching technology. Driven mainly by this environmental pressure, the development of environmentally friendly bleaching technologies utilizing oxygen-based chemicals has been and will continue to be one of the major technical advances in the pulp and paper industry.



1

Figure 0.1. Chemical structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD)

Under the environmental pressure, “elemental chlorine free” (ECF) bleaching was developed. The idea of ECF bleaching is to substitute chlorine

dioxide for elemental chlorine as principle bleaching chemical. Although chlorine dioxide significantly reduces the amount of 2,3,7,8-TCDD (1) formed during the bleaching process to the “undetectable” level, other AOXs are still found in the bleaching effluents. It is therefore desirable to completely eliminate chlorine-containing chemicals including chlorine dioxide from bleaching processes to achieve “totally chlorine free” (TCF) bleaching in order to completely eliminate the formation of chloro-organics during the bleaching process. The exclusion of chlorine containing chemicals offers another incentive of facilitating closure of the water loop of the bleaching processes. Thus, the application of TCF bleaching technology will lead to elimination of the discharge of bleaching effluents and dramatic reduction of fresh water consumption. Among the technologies aiming at ECF or TCF bleaching, oxygen and hydrogen peroxide bleaching processes were developed and have been widely implemented by the industry due mainly to the environmental advantages of not generating the chloro-organics in the bleaching processes. However, oxygen based chemicals are generally less effective delignifying agents than chlorine and chlorine dioxide because of their lower reactivity towards the residual lignin and the relatively high extent of undesired degradation of carbohydrates i.e. lower selectivity. Therefore, the research toward activation of oxygen and hydrogen peroxide and improvement of their selectivity has become very significant, and remains challenging.

II. Activation of Oxygen Based Bleaching Chemicals

Many research activities have been devoted to the enhancement of residual lignin removal by oxygen without severe degradation of carbohydrates. Among many processes developed recently, the laccase-mediator system is one of the best understood. It has been found that laccase alone is incapable of degrading lignin but promotes its dehydrogenative polymerization ^[16]. Interestingly however, when applied together with a cosubstrate or “mediator”, such as 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonicacid) diammonium salt **(2)** (ABTS) or 3-hydroxy-1,2,3-benzotriazin-4-one **(3)** (HOBT) ^[17], (see Figure 0.2.) laccase is able to selectively degrade lignin to a significant extent ^[18,19] as well as to catalyze oxidation of nonphenolic benzyl alcohols to the corresponding aldehydes ^[20]. The mechanism of the laccase-mediator system has been intensively studied and clarified by our research group ^[21]. Although laccase-mediator system offers many advantages, such as lower operating temperature, less oxygen consumption, and milder pH requirement, the commercialization of the laccase-mediator system is not considered practical at the present time because of the high cost of laccase and the mediators, and other technological difficulties ^[22]. While there have been many attempts to seek inexpensive mediators and decreasing the cost of laccase, mimicking the behaviors of laccase-mediator systems is likely more cost effective and therefore is a highly desired alternative.

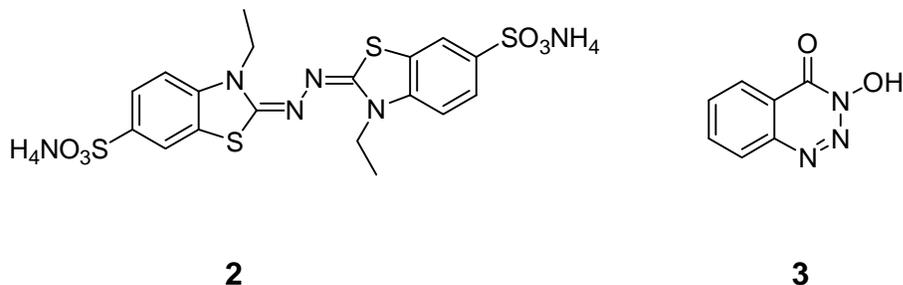


Figure 0.2. Chemical structure of commonly used mediators, 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) (**2**), and 3-hydroxy-1,2,3-benzotriazin-4-one (HOBT) (**3**) for laccase-mediator-system catalyzed oxygen delignification.

The purpose of this research is to improve delignification with hydrogen peroxide and its selectivity by applying a binuclear manganese complex, $[\text{LMn(IV)}(\mu\text{-O})_3\text{Mn(IV)}](\text{ClO}_4)_2$ (**4**) (Figure 0.3.) where L=1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (abbreviated as $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ hereafter) as catalyst. In this study, the catalyst was made *in situ* from its more stable precursor $\text{LMn(III)}(\mu\text{-O})_2(\mu\text{-OAc})\text{Mn(IV)}](\text{ClO}_4)_3$ (**5**). The chemical structure of the precatalyst is shown in Figure 0.3.

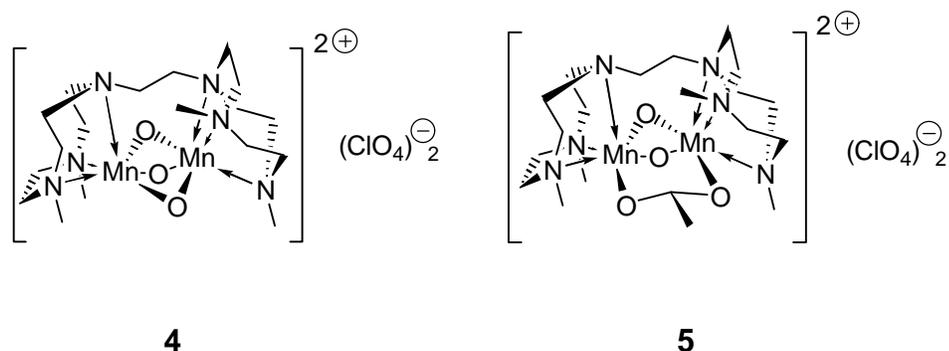
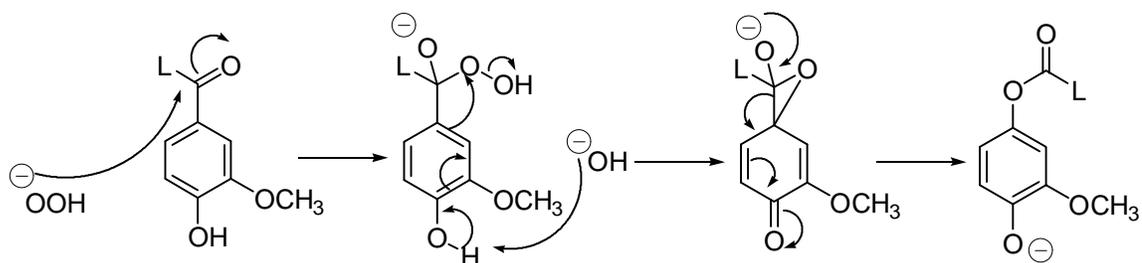


Figure 0.3. Chemical structure of [LMn(IV)(μ -O)₃Mn(IV)](ClO₄)₂ (**4**), and [LMn(III)(μ -O)₂(μ -OAc)Mn(IV)](ClO₄)₃ (**5**), where L=1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane

III. Hydrogen Peroxide as a Bleaching Agent

Hydrogen peroxide has long been used in alkaline condition only as a bleaching agent to boost the brightness of pulp at the end of the bleaching sequences, rather than being used as a delignifying agent to remove residual lignin from chemical pulp. This is because hydrogen peroxide dissociates in alkaline condition to yield hydroperoxy anion that mainly reacts with chromophores such as carbonyls conjugated with aromatic rings as a nucleophile rather than oxidizes other functional groups in residual lignin ^[23,24] to achieve a significant degree of delignification. This reaction is often referred as the Dakin reaction (See Scheme 0.1.). Regardless of the formation of esters which lead to further hydrolytic degradation of residual lignin, the degree of degradation observed is modest because the presence of carbonyls conjugated with aromatic rings in the residual lignin is not abundant.

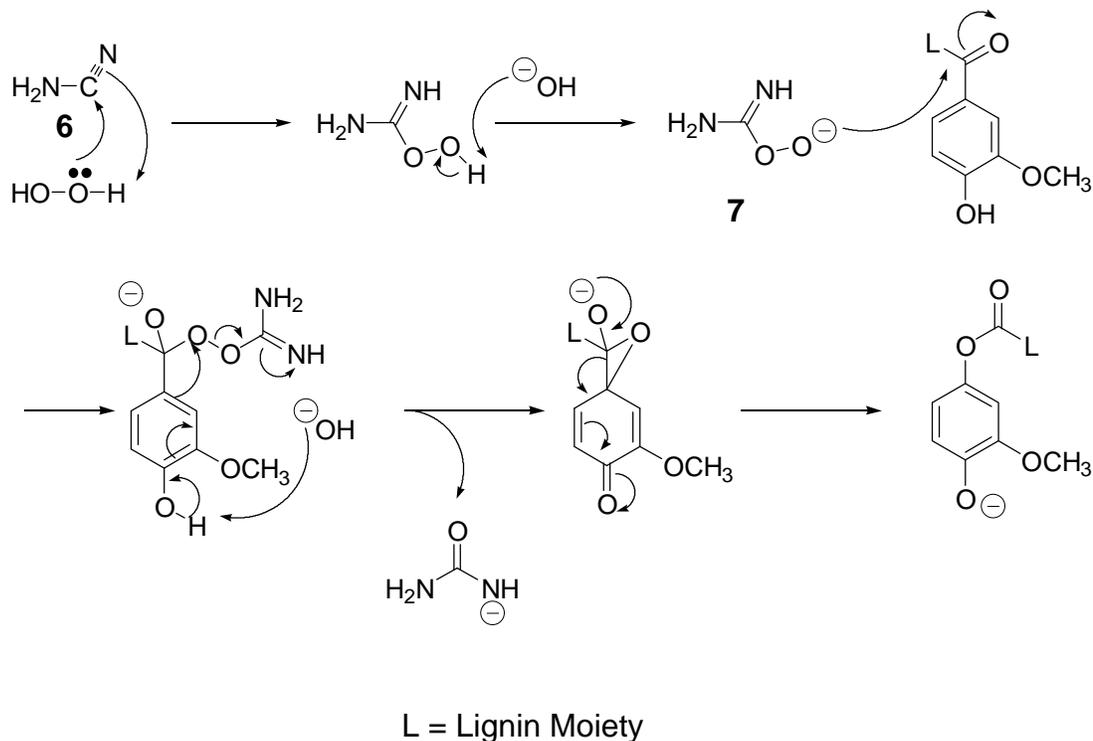


L =Lignin Moieties

Scheme 0.1. Perhydroxy anion reacts with chromophores in residual lignin as a nucleophile via Dakin reaction.

IV. Activation of Hydrogen Peroxide

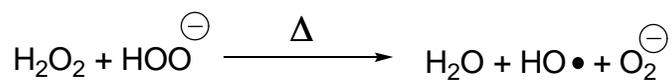
Recently, there have been several research activities in activating hydrogen peroxide by applying nitrilamine (**6**) (also named cyanamide) which reportedly increases the brightness improvement and the amount of residual peroxide at the end of bleaching ^[25, 26]. However, the degree of delignification achieved was still modest. This is because the active specie of this process, the amino-imino peracid anion (**7**) reacts with residual lignin in such a way that is virtually identical to that of hydroperoxy anion through Dakin reaction (See Scheme 0.2.). Although the reactivity of the hydrogen peroxide as a nucleophile is improved, its reactivity as an oxidant remains unchanged.



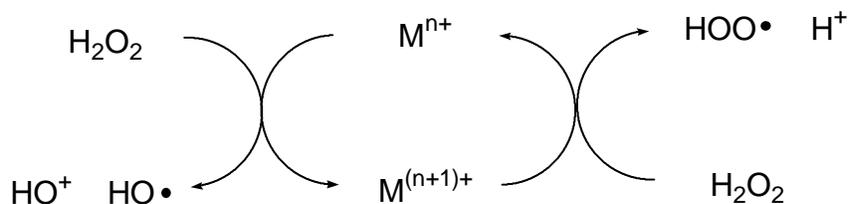
Scheme 0.2. Nitrilamine (**6**) activated hydrogen peroxide bleaching via Dakin reaction of lignin moiety with amimo-imino peroxide anion (**7**)

As a result, hydrogen peroxide is considered as a delignifying agent only at high temperatures, frequently at 100°C ^[27-29] and above when the hydroxyl radical is responsible for the oxidation of residual lignin. Conducting hydrogen peroxide delignification at high temperatures is not only energy demanding but also raises other concerns. At high temperature, the decomposition of hydrogen peroxide due to the thermally induced disproportionation (See Scheme 0.3.) becomes significant. The adventitiously present transition metal ions not only accelerate the decomposition of hydrogen peroxide but also promote the formation of hydroxyl radicals (See Scheme 0.4.) ^[30, 31]. The resulting hydroxyl

radicals vigorously attack carbohydrates when their concentration reaches a critical level causing serious degradation of carbohydrates. Therefore, a certain amount of chelants such as ethylenediaminetetraacetic acid (EDTA) ^[32] or diethylenetetraaminepentaacetic acid (DTMPA) ^[33], must be added to control the transition metal profile in the reaction media so that the decomposition of hydrogen peroxide is minimized, and the formation of hydroxyl radicals are controlled. Currently, achieving a relatively high degree of delignification of kraft pulp with hydrogen peroxide at relatively low temperatures (approximately 60~80°C which normally does not require massive extra heating to achieve) is still challenging.



Scheme 0.3. Thermally induced disproportionation of hydrogen peroxide



Scheme 0.4. Transition metal ion induced decomposition of hydrogen peroxide and the formation of hydroxyl radicals.

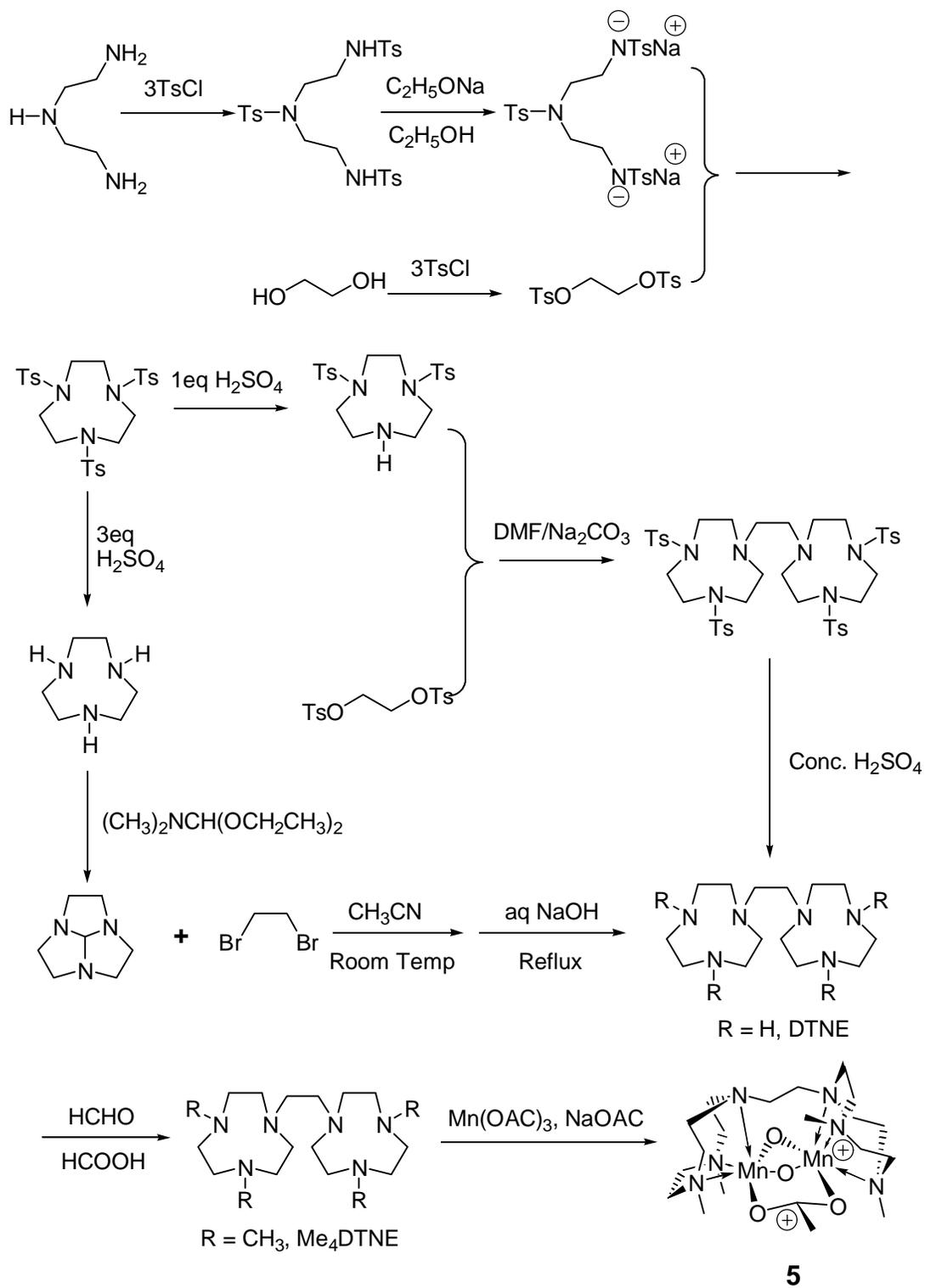
V. Goal of the Research

The goal of this research is to improve the reactivity of hydrogen peroxide as an oxidant to such an extent that it is able to oxidize some functional groups present in residual lignin such as α -hydroxyl groups and conjugated C-C double bonds at relatively low temperatures. At the same time, the formation of hydroxyl radicals is regulated in such a way that carbohydrates are mostly preserved during the delignification process. The delignification is to be accomplished in the presence of the binuclear manganese complex **4** that resembles the behavior of the laccase-mediator systems. Therefore, in addition to a high degree of delignification, better selectivity of the delignification will also be achieved.

Although the synthesis of binuclear manganese complexes has been reported in mid eighties (see Scheme 0.5.), the research activities in this kind of complexes were mainly driven by scientific curiosity^[34-36] for their theoretical importance. It was not until the late nineties that $[\text{LMn(IV)}(\mu\text{-O})_3\text{Mn(IV)}](\text{ClO}_4)_2$ (**4**), where $\text{L}=1,2\text{-bis}(4,7\text{-dimethyl-1,4,7-triazacyclonon-1-yl})\text{ethane}$, was considered as a catalyst in delignification of chemical pulp with hydrogen peroxide^[37-40]. However, the mechanism of this catalytic process was not well understood, nor was the kinetics of delignification studied.

In order to better understand the mechanism of this process, 1-(3,4-dimethoxyphenyl)ethanol (**8**) (often called *O*-methylvetraylalcohol), *E*-

diphenylethene (**9**) (often called *trans*-stilbene), and 1-(3,4-dimethoxyphenyl)-1-propene (**10**) (often called *O*-methylsuganol, mixture of *E*- and *Z*-isomers, mole ratio 85:15) were chosen as the model compounds to investigate the oxidative degradation of residual lignin in chemical pulps with hydrogen peroxide catalyzed by Mn(IV)₂-Me₄DTNE [38, 39]. In the light of the model compound studies, the kinetics of delignification was studied [40], followed by the isolation of the residual lignin by cellulolytic hydrolysis from pulp before and after delignification [41]. The degraded lignin fragments were also precipitated from the spent bleaching liquor by hydrochloric acid. These lignin samples were characterized by FTIR, GPC, elemental analysis, and NMR in order to elucidate the structural changes of lignin during the hydrogen peroxide delignification catalyzed by Mn(IV)₂-Me₄DTNE. Furthermore, the modeling and simulation of this process using WinGEMS4.0 was performed and the economic feasibility is evaluated.



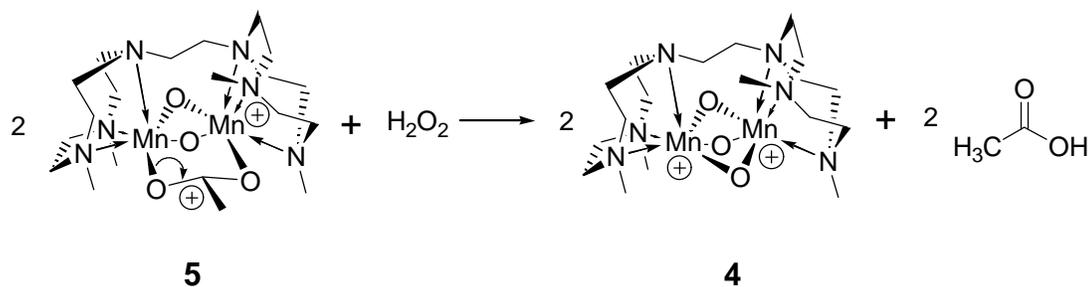
Scheme 0.5. The synthesis of the [LMn(III)(μ-O)₃(μ-OAc)Mn(IV)](ClO₄)₂ **5**

CHAPTER ONE

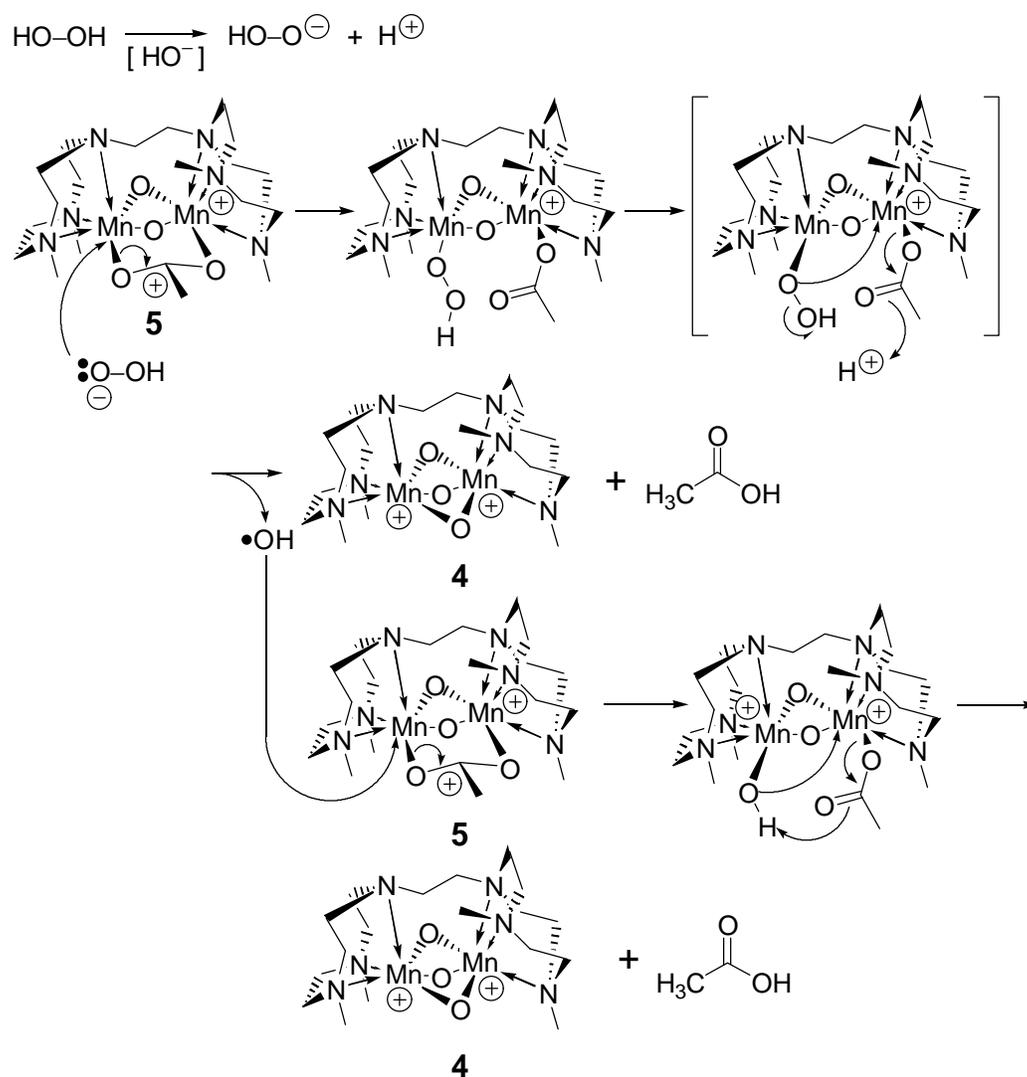
OXIDATION OF LIGNIN MODEL COMPOUNDS WITH HYDROGEN PEROXIDE CATALYZED BY Mn(IV)₂-Me₄DTNE

I. Conversion of the Precatalyst to the Catalyst

In this study, the catalyst **4** was synthesized *in situ* by oxidation of its more stable precursor [LMn(III)(μ -O)₂(μ -OAc)Mn(IV)](ClO₄)₂ (**5**) with hydrogen peroxide^[36,40] (Scheme 1.1). Two mole equivalents of precatalyst **5** are oxidized by one mole equivalent of hydrogen peroxide to give **4** and acetic acid, each in one mole equivalent (Scheme 1.2). This process probably involves nucleophilic substitution of the -O-C(CH₃)-O- group in the Mn(III) nucleus of **5** by hydrogen peroxide with concomitant transfer of a 3d_(x²-y²) electron from the e_g(σ^*) set in the Mn(III) to the -O-O- bond of the resulting -Mn(III)-O(H)-OH moiety, producing **4**, acetic acid and hydroxyl radical, one molar equivalent each. The hydroxyl radical immediately oxidizes the Mn(III) of the second molar equivalent of **5** to Mn(IV) through a concerted reaction involving a transfer of an electron in the 3d_(x²-y²) orbital of the e_g(σ^*) set in the Mn(III). This orbital is the highest occupied molecular orbital (HOMO) of the Mn(III) nucleus. The hydroxyl group is now bonded to the new Mn(IV) in the form of ligand binding that substitutes the acetyl ligand binding. The subsequent elimination of a molar equivalent of acetic acid from the intermediate yields the second molar equivalent of **4**.



Scheme 1.1. The formation of [LMn(IV)(μ-O)₃Mn(IV)](ClO₄)₂ (**4**) from [LMn(III)(μ-O)₂(μ-OAc)Mn(IV)](ClO₄)₃ (**5**) upon mixing with hydrogen peroxide



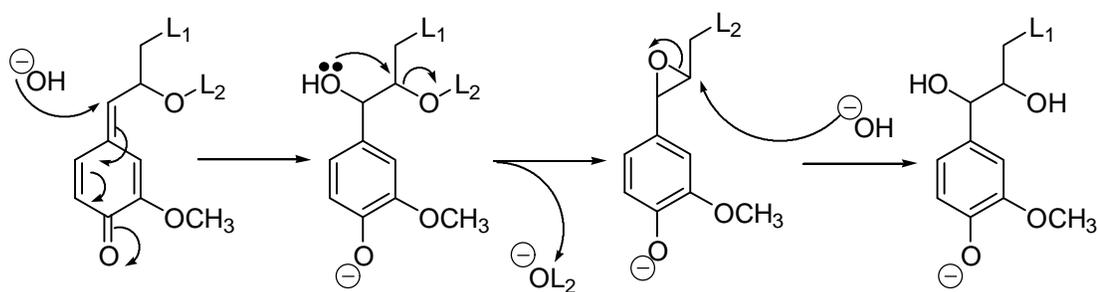
Scheme 1.2. Formation of the catalyst **4** from the precatalyst **5**

II. Presence of α -Hydroxyl Groups, and Conjugated C-C Double Bonds in Residual Lignin of Kraft-AQ Pulp

During the alkaline pulping process, due to the cleavage of α - and β -aryl ether linkages in lignin, residual lignin is expected to have more free phenolic groups and less α - and β -aryl ether linkages^[42-45]. In addition, the degradation of lignin during the pulping reaction is always accompanied by the condensation of lignin which is responsible for the formation of diphenylmethane linkages^[46-50]. Furthermore, it is possible that residual lignin is covalently bonded to carbohydrates^[51-55], which means that residual lignin cannot be completely removed unless the lignin-carbohydrate bonds are selectively cleaved. Consequently, residual lignin that survives the alkaline pulping reaction is very resistant to further hydrolytic degradation reaction. As a result, degradation of residual lignin must be achieved by oxidation followed by hydrolysis. Among the functional groups present in the residual lignin, hydroxyl groups and C-C double bonds conjugated with aromatic rings are susceptible to oxidation.

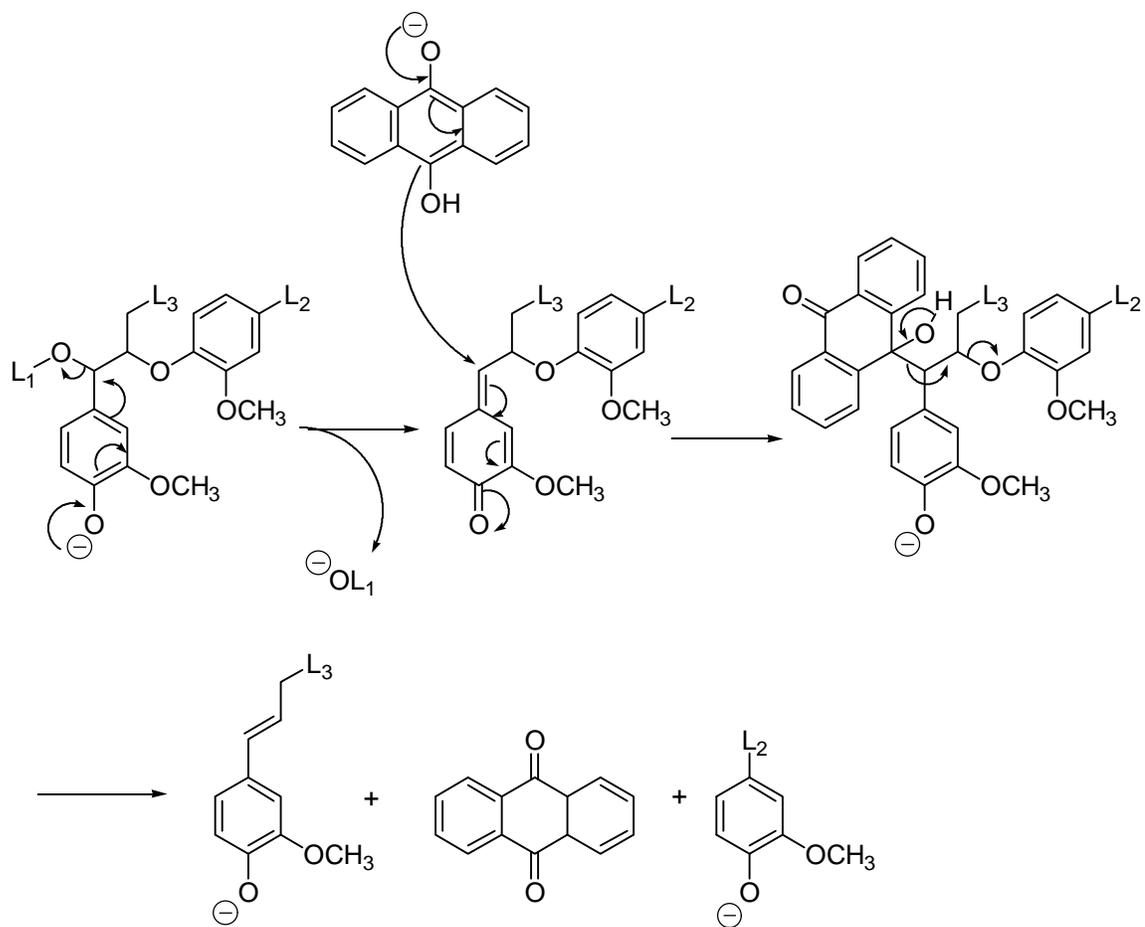
During the kraft pulping process, hydrosulfide anions and hydroxy anions compete for the quinonemethide intermediates. Although they are less reactive than hydrosulfide anions, hydroxy anions still have plenty of chances to attack the quinonemethide intermediates (see Scheme 1.3.). As a result of the subsequent reactions, α -hydroxyl groups are present in the residual lignin of alkaline pulp. In addition, during the alkaline-AQ process, dissociated AHQ attacks the α -C of the

quinonemethide intermediate ^[56]. The resulting adduct undergoes a fragmentation reaction to give AQ and a lignin fragment bearing conjugated C-C double bonds (see Scheme 1.4.). Furthermore, conjugated C-C double bonds in the form of stilbene and styrene type structures are also present in the residual lignin of kraft pulp, as a result of the cleavage of the β -5, and the γ - γ linkages during the pulping reaction (See Scheme 1.5, and 1.6.).



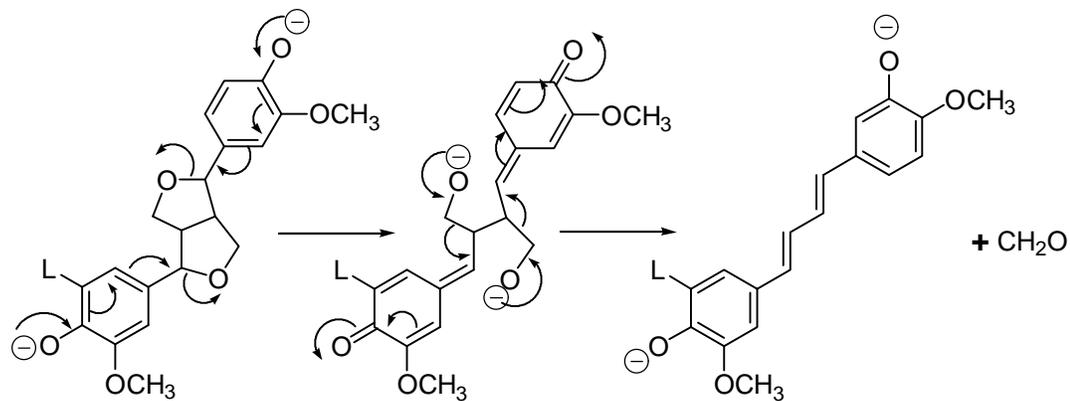
L₁, L₂ = Lignin Moieties

Scheme 1.3. The formation of the α -hydroxyl groups in the residual lignin during kraft pulping process.



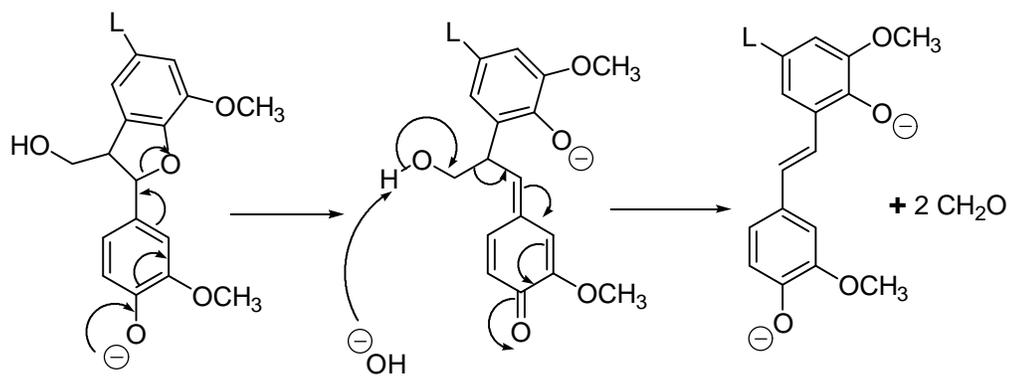
L₁, L₂, and L₃ = Lignin Moieties

Scheme 1.4. The formation of conjugated C-C bonds in the residual lignin during alkaline-AQ pulping



L = Lignin Moiety

Scheme 1.5. The formation conjugated C-C double bonds in the form of stilbene in the residual lignin during kraft pulping

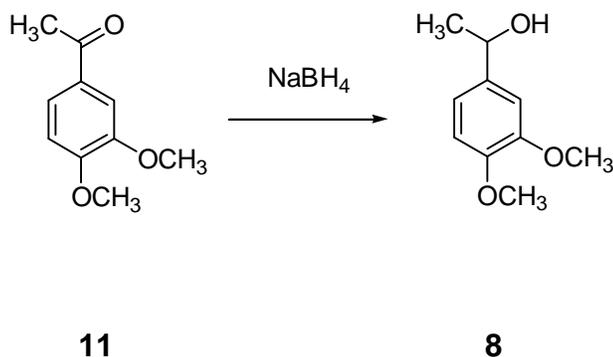


L = Lignin Moiety

Scheme 1.6. The formation conjugated C-C double bonds in the form of styrene in the residual lignin during kraft pulping

III. Oxidation of Lignin Model Compounds ^[39, 40]

Lignin model compounds are frequently used to simplify the investigation of the reactivity of lignin because of the difficulty associated with the structural characterization of lignin. In this study, 1-(3,4-dimethoxyphenyl)ethanol (**8**), *E*-diphenylethene (**9**), and 1-(3,4-dimethoxyphenyl)-1-propene (mixture of *E*, *Z* isomers in mole ratio of 85:15) (**10**) were chosen to represent the nonphenolic α -hydroxyl, conjugated C-C double bond and stilbene functionalities in the residual lignin. 1-(3,4-dimethoxyphenyl)ethanol was synthesized from 3,4-dimethoxyacetophenone (**11**) by NaBH₄ reduction ^[57] (See Scheme 1.7.). *E*-diphenylethene and 1-(3,4-dimethoxyphenyl)-1-propene were purchased from Aldrich without any further purification.



Scheme 1.7. Synthesis of 1-(3,4-dimethoxyphenyl)ethanol (**8**) from 3,4-dimethoxyacetophenone (**11**) by NaBH₄ reduction

As expected, hydrogen peroxide was found incapable of oxidizing **8**, **9**, or **10** when applied alone. Upon the catalysis by $[\text{LMn(VI)}(\mu\text{-O})_3\text{Mn(VI)}](\text{ClO}_4)_2$ (**4**), however, these substrates were readily oxidized to a significant extent. Shown in the Figure 1.1 is the disappearance of 1-(3,4-dimethoxyphenyl)ethanol (**8**) during the catalyzed oxidation. Model compounds **9** and **10** showed similar behaviors during the oxidation (see Figure 1.2, and 1.3). Since hydrogen peroxide was used in great excess (100 equivalents), the reactions are first order with respect to the substrates (See Figure 1.4, 1.5, and 1.6.). The reaction rate constants are listed in the Table 1.1. The activation energy of the oxidation reactions of **8**, **9**, and **10** was calculated according to Arrhenius equation as 23.8, 59.1, and 52.9kJ/mole·K respectively (See Figure 1.7.). It has been found that typical organic reactions have activation energies in the range of 50-150kJ/mole·K ^[58]. The activation energies of all the oxidation reactions studied fall within or even below the low end of this range, an indication of reducing of activation energy by the catalyst.

The oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**8**) and 1-(3,4-dimethoxyphenyl)-1-propene (**10**) with hydrogen peroxide catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ resembles the oxidation with laccase-mediator system (LMS) with ABTS as mediator ^[59]. The oxidation of **8** leads mostly to its corresponding ketone, 3,4-dimethoxy- acetopnenone **11** in a yield of approximately 35-50 mol% depends on the reaction temperature within 15 minutes (Scheme 1.8). The substrate **8** also underwent dehydration during the gas chromatographic analysis to give (3,4-dimethoxyphenyl)ethene (**12**) (Scheme 1.9.). The oxidation of *E*-diphenylethene

(9) provided *E*-diphenyletheneoxide (13) in approximately 50% yield (Scheme 1.10). However, in the case of oxidation of 10, a mixture of 1-(3,4-dimethoxyphenyl)propane-1,2-epoxide (14), 1-(3,4-dimethoxyphenyl) propane-1,2-diol (15), and 3,4-dimethoxybenzaldehyde (16) was identified (Scheme 1.11.) as the reaction product. Yields of the products vs. reaction time are listed in Table 2.

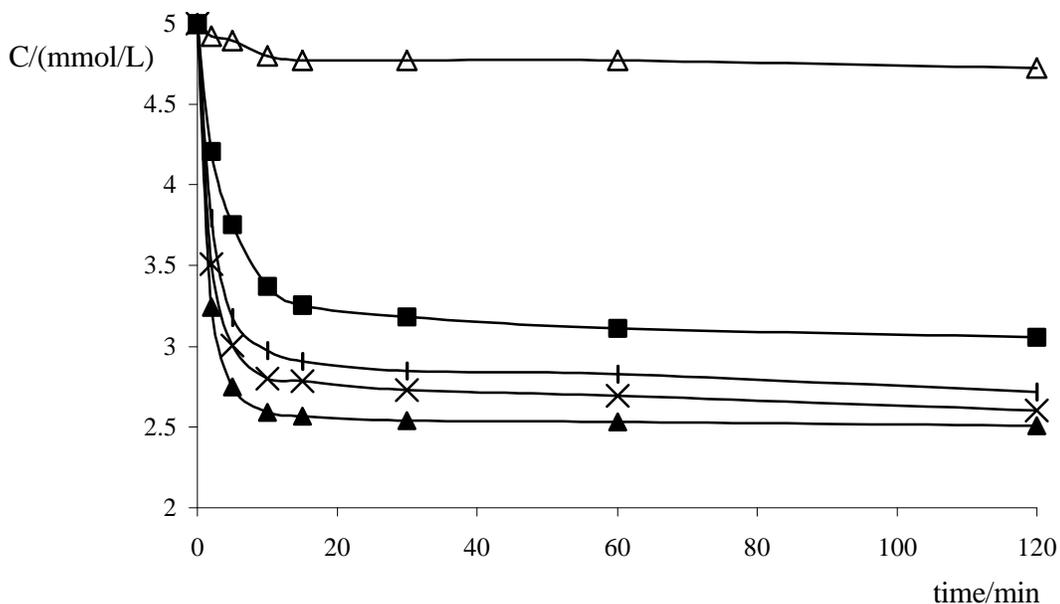


Figure 1.1. The disappearance of the 1-(3,4-dimethoxyphenyl)ethanol (8) upon the oxidation with hydrogen peroxide catalyzed by [LMn(IV)(μ -O)₃Mn(VI)](ClO₄)₂ (4) at ■ 30°C, ◆ 40°C, X 50°C, ▲ 60°C. Δ oxidation with hydrogen peroxide without catalyst at 60°C.

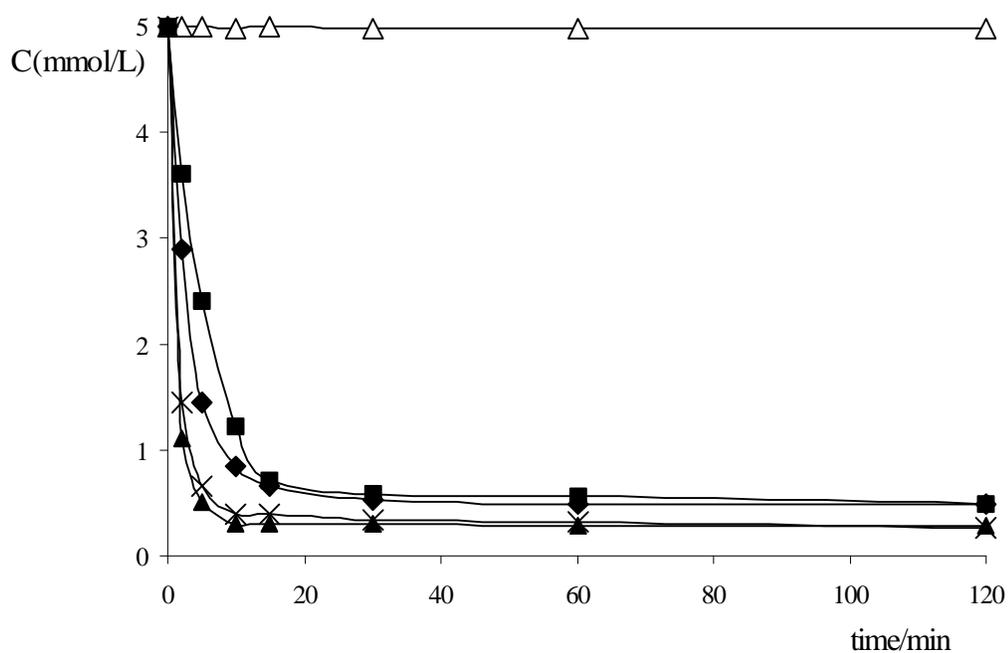


Figure 1.2. The disappearance of the 1-(3,4-dimethoxyphenyl)-1-propene (**10**) upon the oxidation with hydrogen peroxide catalyzed by $[\text{LMn(IV)}(\mu\text{-O})_3\text{Mn(VI)}](\text{ClO}_4)_2$ (**4**) at ■ 30°C, ◆ 40°C, X 50°C, ▲ 60°C. △ oxidation with hydrogen peroxide without catalyst at 60°C.

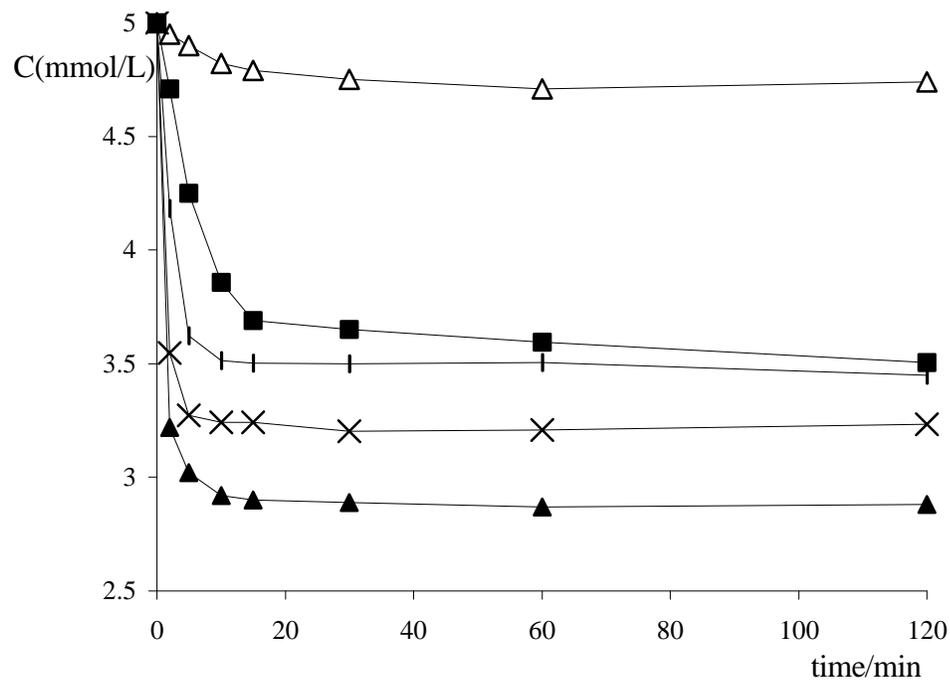


Figure 1.3. The disappearance of the **E**-diphenylethene (**9**) upon the oxidation with hydrogen peroxide catalyzed by $[\text{LMn(IV)}(\mu\text{-O})_3\text{Mn(VI)}](\text{ClO}_4)_2$ (**4**) at ■ 30°C, ◆ 40°C, X 50°C, ▲ 60°C. △ oxidation with hydrogen peroxide without catalyst at 60°C.

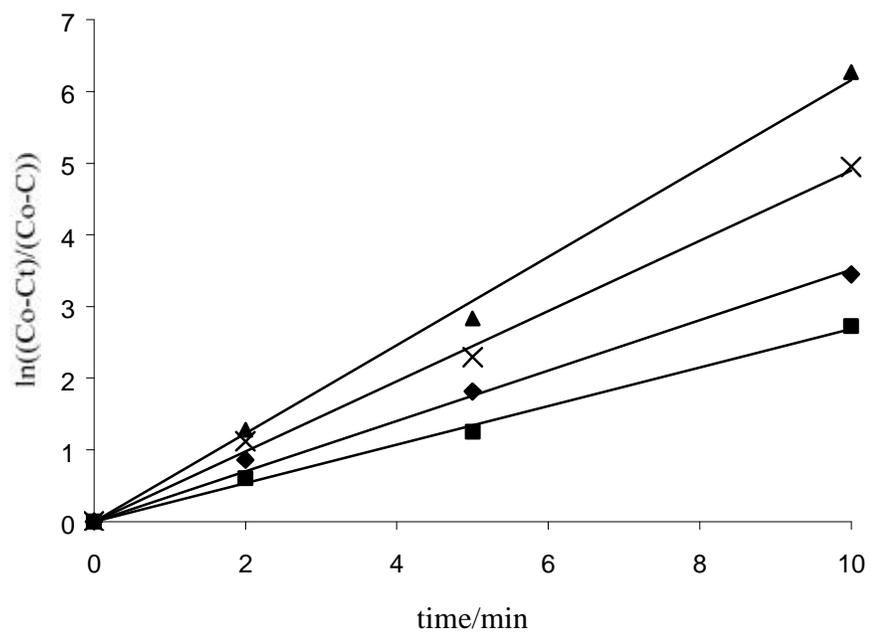


Figure 1.4. *Pseudo*-first-order oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**8**) with hydrogen peroxide catalyzed by Mn(IV)₂-Me₄DTNE (**4**) at ■ 30°C, ◆ 40°C, X 50°C, ▲ 60°C.

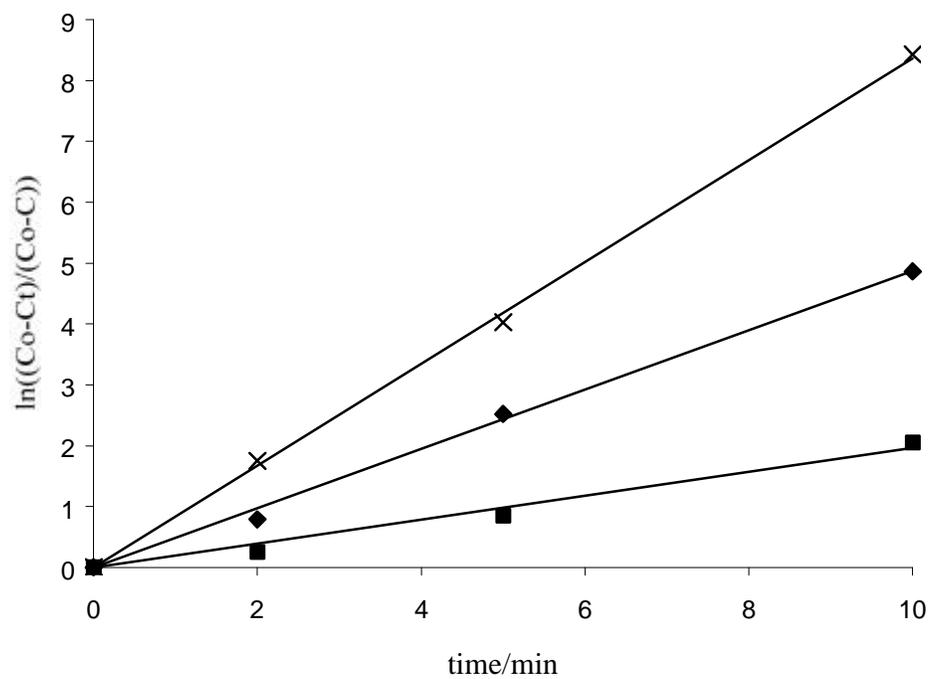


Figure 1.5. *Pseudo*-first-order oxidation of E-diphenylethene (**9**) with hydrogen peroxide catalyzed by Mn(IV)₂-Me₄DTNE (**4**) at ■ 30°C, ◆ 40°C, and X 50°C.

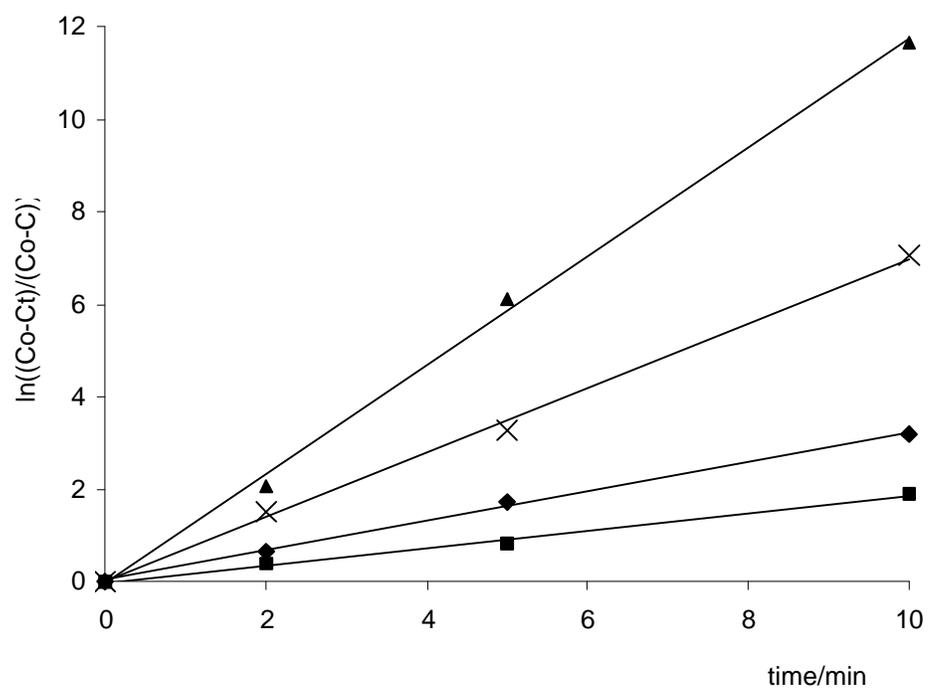
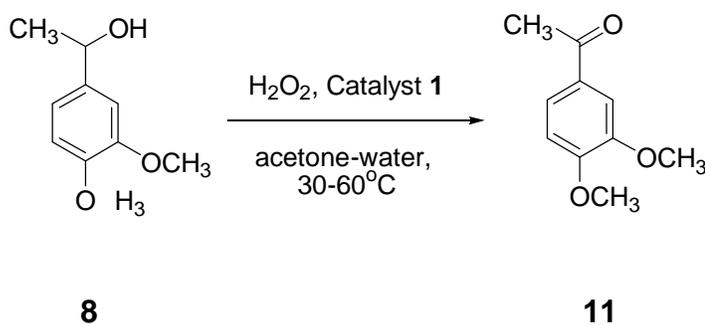


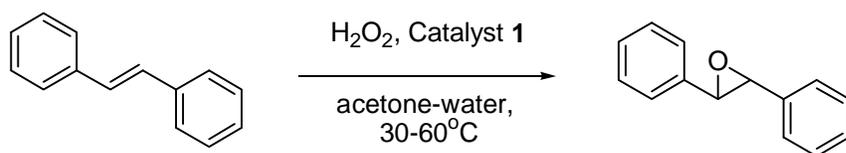
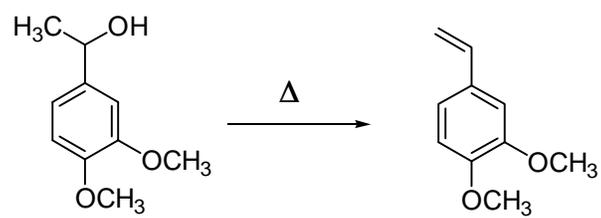
Figure 1.6. *Pseudo*-first-order oxidation of 1-(3,4-dimethoxyphenyl)-1-propene (**10**) with hydrogen peroxide catalyzed by Mn(IV)₂-Me₄DTNE (**4**) at ■ 30°C, ◆ 40°C, X 50°C, ▲ 60°C.

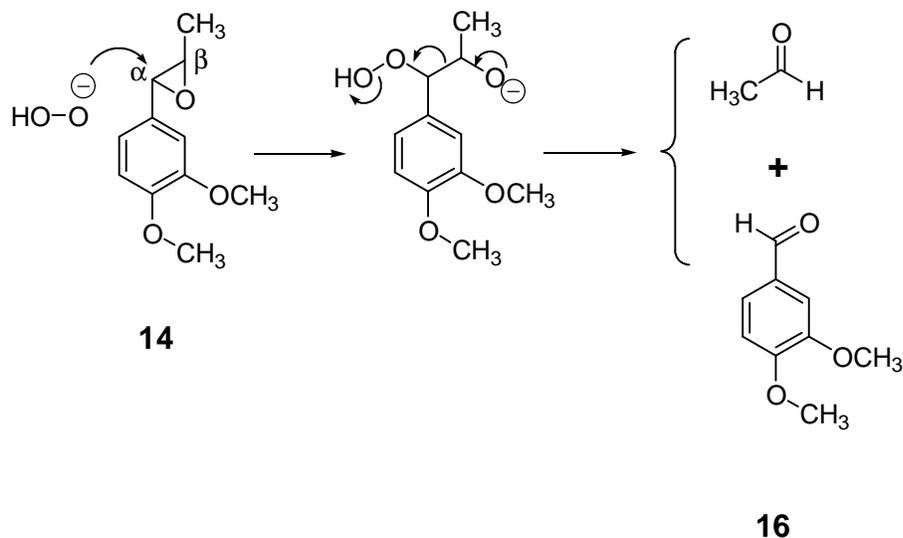
Table 1.1. *Pseudo*-first-order reaction rate constants of the oxidation reactions of 1-(3,4-dimethoxyphenyl)ethanol (**8**), *E*-diphenylethene (**9**), and 1-(3,4-dimethoxyphenyl)-1-propene (**10**) with hydrogen peroxide catalyzed by [LMn(IV)(μ -O)₃Mn(VI)](ClO₄)₂ (**4**) at various temperatures.

Temperature (°C)	Reaction Rate Constant (sec ⁻¹)		
	1-(3,4-dimethoxyphenyl)ethanol (8)	<i>E</i> -diphenylethene (9)	1-(3,4-dimethoxyphenyl)-1-propene (10)
30	16.2	11.8	10.8
40	21.0	28.7	19.2
50	29.4	50.2	42.0
60	37.2	102.5	70.2



Scheme 1.8. Oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**8**) with hydrogen peroxide catalyzed by [LMn(VI)(μ -O)₃Mn(VI)](ClO₄)₂ (**4**).





Scheme 1.12. The formation of 3,4-dimethoxyacetophenone (**16**) from (3,4-dimethoxyphenyl)-1,2-epoxide (**14**).

One of the advantages of the $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ catalyzed reactions is the fast reaction rate which is highly desired in terms of its potential commercialization. The oxidation almost completes in 15 minutes. In the light of the results from the model compound studies, hydrogen peroxide catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ is expected to be capable of rapidly oxidizing the α -hydroxyl groups and conjugated C-C double bonds in the residual lignin of chemical pulps. Under alkaline condition, the resulting carbonyls and epoxides are very susceptible to further nucleophilic attack which leads the residual lignin to further degradation and fragmentation, thus becoming soluble in the reaction media. A high degree of delignification would therefore be achieved, hopefully at relatively low temperatures.

Table 1.2. Yield of products of the oxidation reaction of 1-(3,4-dimethoxyphenyl)-1-propene (**10**) with hydrogen peroxide catalyzed by [LMn(IV)(μ -O)₃Mn(IV)](ClO₄)₂ (**4**) at 50°C as a function of reaction time.

Reaction Time (min)	Yield (%)		
	1-(3,4-dimethoxyphenyl)propo-1,2-epoxide (14)	1-(3,4-dimethoxyphenyl)propo-1,2-diol (15)	3,4-dimethoxybenzaldehyde (16)
2	47.4	1.6	1.5
10	1.5	34.0	24.2
120	1.4	37.9	24.3

IV. Conclusions

Hydrogen peroxide is found unreactive to 1-(3,4-dimethoxyphenyl)ethanol (**8**), *E*-diphenylethene (**9**) or 1-(3,4-dimethoxyphenyl)-1-propene (**10**) when applied alone. The reactivity of hydrogen peroxide as an oxidant is considerably improved upon the application of the catalyst. All the reactions studied readily proceed to a good extent. The catalyzed oxidation of 1-(3,4-dimethoxyphenyl)-ethanol (**8**) yields 3,4-dimethoxyacetophenone as product. The catalyzed oxidation of *E*-diphenylethene (**9**) yields the corresponding epoxide as product. In the case of 1-(3,4-dimethoxyphenyl)-1-propene (**10**) a mixture of the corresponding epoxide, diol and 3,4-dimethoxybenzaldehyde was identified as reaction product. All the reactions studied follows first order kinetics with respect to substrates.

CHAPTER TWO

DELIGNIFICATION OF KRAFT-AQ SOUTHERN PINE PULP WITH HYDROGEN PEROXIDE CATALYZED BY Mn(IV)₂-Me₄DTNE

I. Comparison of Catalyzed and Uncatalyzed Delignification

The model compound study provides us a great deal of insight into the lignin reaction during the catalytic delignification process. The reactivity of hydrogen peroxide as an oxidant is considerably improved by the catalyst to such an extent that it is able to oxidize α -hydroxyl groups and the conjugated C-C double bonds in the residual lignin. In order to confirm the results from the model compound study, the delignification kinetics of a kraft-AQ southern pine pulp was studied. The pulp was subjected to acid treatment in order to minimize the free metal content. The kappa number, viscosity, and GE brightness was 31.6, 31.1mPa.s, and 24.2 respectively after the acid treatment. This pulp was then subjected to hydrogen peroxide delignification, with and without the catalyst. The degree of delignification was quantified by kappa number, and the carbohydrate preservation was evaluated by viscosity of the pulp. The effect of varying consistency or alkaline charge on the degree of delignification, as well as the resulting pulp quality was also studied.

In order to compare the catalyzed and uncatalyzed delignification, the degree of delignification and selectivity, kappa number, viscosity, and GE brightness of the pulps obtained by catalyzed and uncatalyzed delignification are summarized in Table 2.1.

Table 2.1. The physical properties of the pulp obtained by catalyzed and uncatalyzed delignification ¹⁻⁷.

Pulp Samples	Delignification		Viscosity (mPa·s)	GE Brightness
	Kappa Number	Degree of Delignification		
Original Pulp	31.6	----	31.1	24.2
Uncat. Delig. (80°C)	23.6	25%	21.6	40.8
Uncat. Delig. (50°C)	26.3	16%	24.3	38.1
Cat. Delig. (80°C)	16.8	46%	20.1	44.7
Cat. Delig. (60°C)	19.2	39%	21.4	46.4
Cat. Delig. (50°C)	19.9	37%	21.5	45.1

¹ Acid wash at 10% consistency, 2.0pH, 70°C for 30minutes

² Pulp consistency: 10% in alkaline solution

³ NaOH charge: 2% NaOH on pulp (O.D.)

⁴ Starting pH 11.5, ending pH 10.9

⁵ H₂O₂ charge: 4% on pulp (O.D.)

⁶ Catalyst charge: 60 ppm on pulp (O.D.)

⁷ Reaction time: 120 min.

In the absence of Mn(IV)₂-Me₄DTNE, the pulp was treated with 2% NaOH and 4% hydrogen peroxide at 10% consistency and 80°C for two hours. As expected, the degree of the delignification was modest. At 80°C, the kappa number of the pulp dropped from 31.6 to 23.6 (about 25% delignification), and the brightness of the pulp increased from 24.2 to 40.8 (a 67% increase). However, the viscosity of the pulp dropped sharply from 31.1 to 21.6 mPa·s (or 31%). Upon the addition of Mn(IV)₂-Me₄DTNE at 60ppm on pulp (O.D.) under the same conditions, the degree of the delignification was significantly improved

(from ~25% to ~46%). The kappa number was brought down to 16.8, almost 7 units further decrease compared to uncatalyzed delignification. It is noteworthy that the kappa number dropped to about 18 in only 20 minutes in the presence of $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ then decreased slowly and eventually leveled off. In addition, applying of the catalyst also resulted in a moderate increase in GE brightness of about 4 points compared to uncatalyzed delignification (totally ~20 points, an 85% increase). Considering the much higher extent of decrease in the kappa number, we postulate that the catalyst mainly improved the reactivity of hydrogen peroxide as an oxidant, while it retained its reactivity as a nucleophile. The increase of the brightness was mostly attributed to the higher degree of delignification rather than decomposition of the chromophores alone. As a result, the brightness stability should be considerably improved. In addition, the degree of carbohydrate degradation was evaluated by viscosity of the pulp before and after the catalyzed and uncatalyzed delignification. In general, the viscosity of the pulps obtained by catalyzed delignification was 7-11% lower than that of the pulps obtained by uncatalyzed delignification. The difference in the viscosity of the pulp obtained by catalyzed and uncatalyzed delignification decreases with increasing temperature, 21.5 vs. 24.3mPa.s at 50°C and 20.1 vs. 21.6mPa.s at 80°C. The viscosity of the pulps from the catalyzed delignification also decreased slightly with increasing temperature, 21.5 vs. 20.1mPa.s (a 6% decrease) from 50°C to 80°C. However, in the case of uncatalyzed delignification, the decrease in viscosity is rather large, 24.3 to 21.6mPa.s (an 11% decrease) from 50°C to 80°C. Catalyzed delignification showed better carbohydrate preservation, and

produced pulps with significantly lower kappa than did uncatalyzed delignification. The rather slight difference in the viscosity among the pulps from the catalyzed delignification implies that hydrogen peroxide is more reactive toward residual lignin in the presence of the catalyst.

II. Kinetics of Mn(IV)₂-Me₄DTNE Catalyzed Hydrogen Peroxide Delignification

Preliminary experiments indicated that delignification of pine kraft pulp at 10% consistency gives the optimum result at 2% NaOH and 4% H₂O₂ charge (all on O.D. pulp). Therefore, the kinetic study was carried out at this condition at 50, 60, and 80°C. At these temperatures, the delignification proceeded readily within 30 minutes (initial phase), then slowed down and eventually leveled off (residual phase) (See Figure 2.1.). As expected, the delignification followed the first order kinetics with respect to kappa number in the initial phase. The delignification rate constants were 0.17, 0.18, and 0.21 min⁻¹ at 50, 60, and 80°C, respectively, at the initial phase (See Figure 2.2.). The rate of delignification then significantly slowed down after 30 min at all the temperatures studied, probably due to deactivation of the catalyst. These results were consistent with those of model compound studies, suggesting that delignification proceeded in a way that is similar to the oxidation of lignin model compounds. It is more than likely that a significant degree of oxidation of the residual lignin in pulp occurred. Hydrogen peroxide catalyzed by Mn(IV)-Me₄DTNE oxidized the α -hydroxyl groups (Scheme

2.1.) and C-C double bonds conjugated with the aromatic rings (Scheme 2.2.) in the residual lignin. The oxidation and the subsequent fragmentation was almost completed within 30 minutes (See Figure 2.1.), and the following dissolution of the lignin fragments was responsible for the slower minor delignification afterwards. The activation energy of the delignification was 7.16kJ/(mole-K) (See Figure 2.3.), calculated according to Arrhenius Equation, suggesting that the dependence of the rate of delignification on temperature was moderate because the activation energy of the delignification decreased considerably upon the addition of the catalyst. As a result, the rate of delignification is satisfactory at temperatures as low as 50°C.

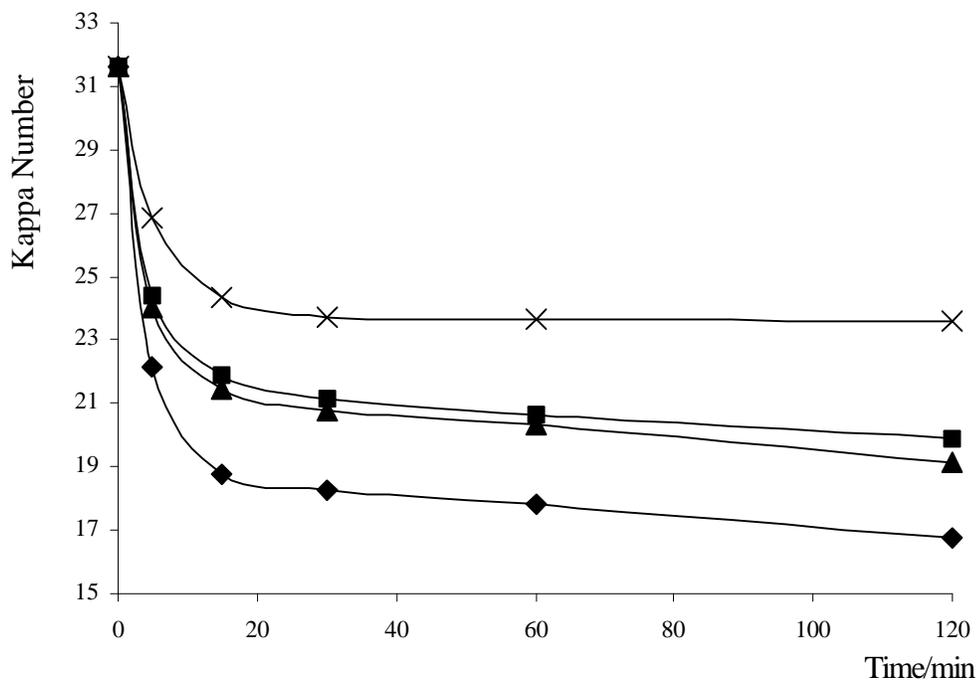


Figure 2.1. Comparison of uncatalyzed delignification at 80°C with catalyzed delignification at 50, 60, and 80°C in alkaline solution (Uncatalyzed delignification at X 80°C. Consistency, 10% in alkaline solution; NaOH charge, 2% on pulp (O.D.); H₂O₂ charge, 4% on pulp (O.D.). Catalyzed delignification at ■ 50°C, ▲ 60°C, ◆ 80°C. Consistency, 10% in alkaline solution; NaOH charge, 2% on pulp (O.D.); H₂O₂ charge, 4% on pulp(O.D.); Catalyst charge, 60 ppm on pulp (O.D.).

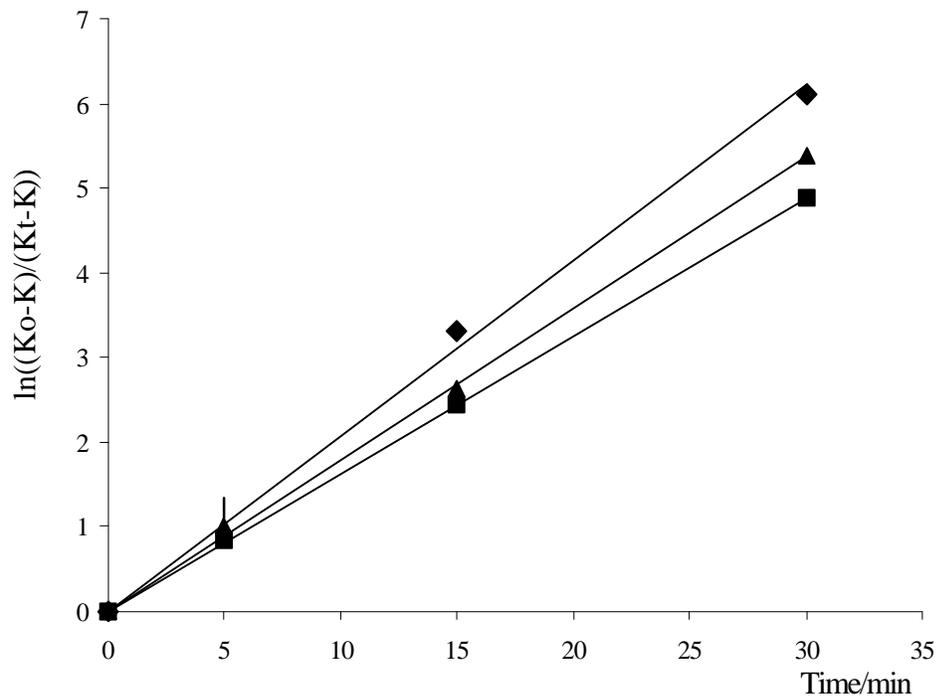


Figure 2.2. The *pseudo*-first order delignification with hydrogen peroxide catalyzed by Mn(IV)-Me₄DTNE at 50, 60, and 80°C in alkaline solution (◆ 80°C, ▲ 60°C, ■ 50°C). Consistency, 10% in alkaline solution; NaOH charge, 2% on pulp (O.D.); H₂O₂ charge, 4% on pulp(O.D.); Catalyst charge, 60 ppm on pulp (O.D.).

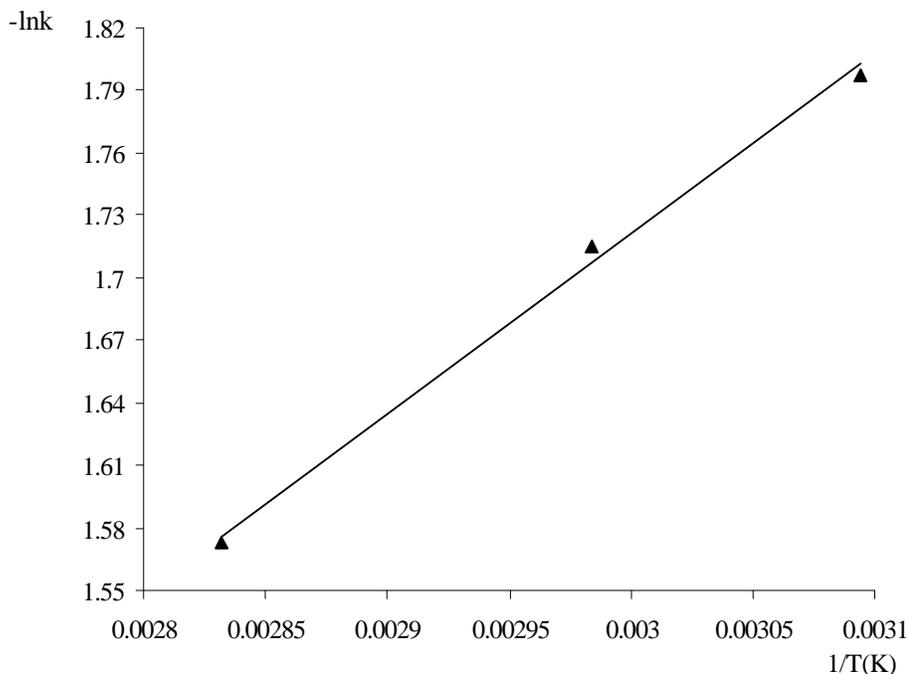
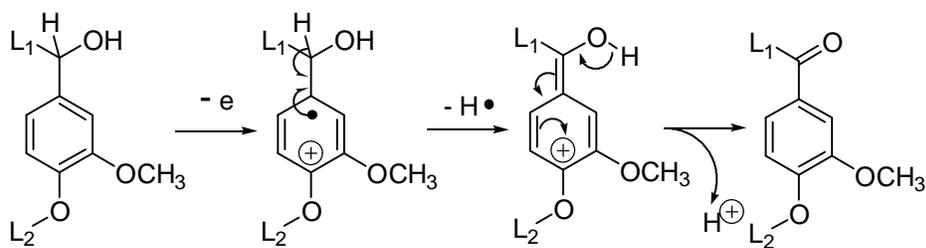


Figure 2.3. The temperature dependence of the rate of delignification: activation energy of the Mn(IV)-Me₄DTNE-catalyzed delignification with hydrogen peroxid in alkaline solution. Consistency, 10% in alkaline solution; NaOH charge, 2% on pulp (O.D.); H₂O₂ charge, 4% on pulp (O.D.); Catalyst charge, 60 ppm on pulp (O.D.).

III. Concerted Reaction Mechanism that Regulates the Formation of Hydroxyl Radicals

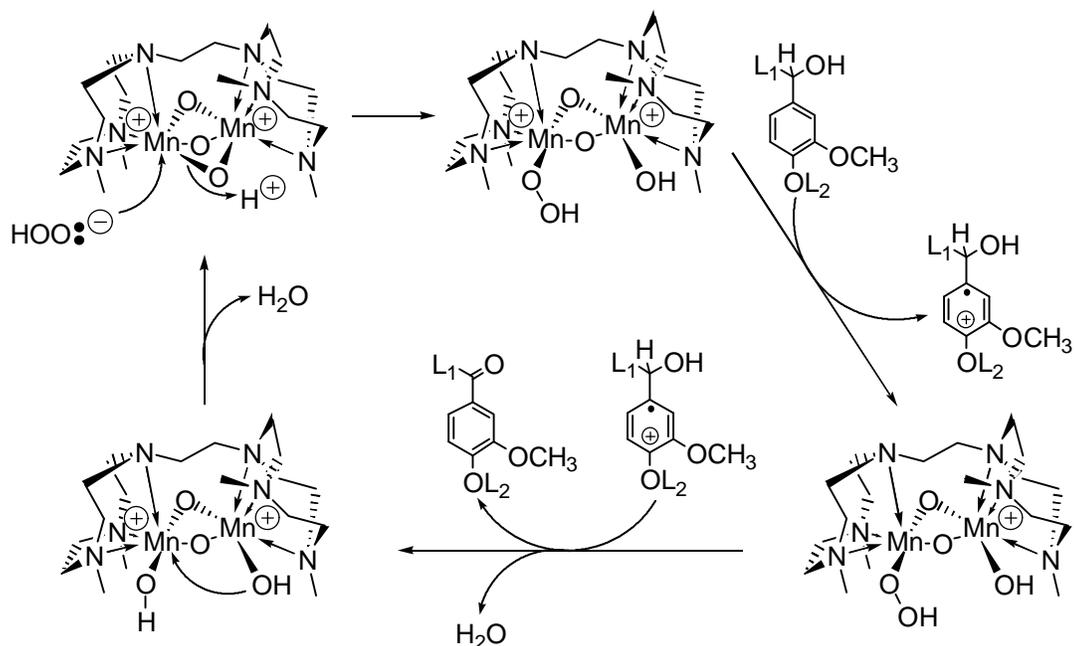
Shown in the Scheme 2.1. is the mechanism of the oxidation of α -hydroxyl groups with hydrogen peroxide in the presence of Mn(IV)₂-Me₄DTNE. The lignin molecule bearing α -hydroxyl groups gives up one electron to the catalyst to form the cation radical. The hydrogen atom at the α -position is taken by the hydroxyl radical simultaneously with its release from the catalyst (See Scheme 2.2.). As a

result, oxidation takes place to yield α -carbonyl. The reaction differs from the normal step-wise reactions in such a way that no reaction intermediate such as hydroxyl radical is actually formed within the reaction media. The reaction goes through a concerted reaction mechanism. So that, hydroxyl radicals which are primarily responsible for the degradation of carbohydrates do not have a chance to accumulate in the reaction media. As a result, the carbohydrates in the pulp will be well protected from hydroxyl radicals. The degradation of carbohydrates indicated by the decrease of viscosity is mainly due to the peeling reactions ^[1] which are unavoidable at the alkaline condition. Scheme 2.2. also shows the catalytic cycle of $Mn(IV)_2$ - Me_4DTNE during the delignification process.

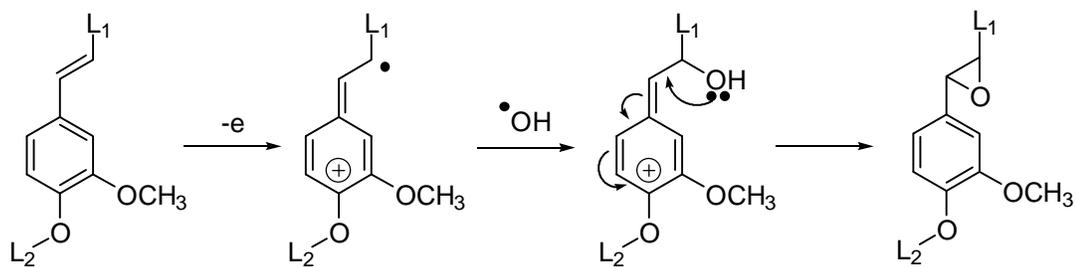


L_1 and L_2 = Lignin Moieties

Scheme 2.1. The oxidation of α -hydroxyl group in residual lignin with hydrogen peroxide catalyzed by $Mn(IV)_2$ - Me_4DTNE under alkaline condition.

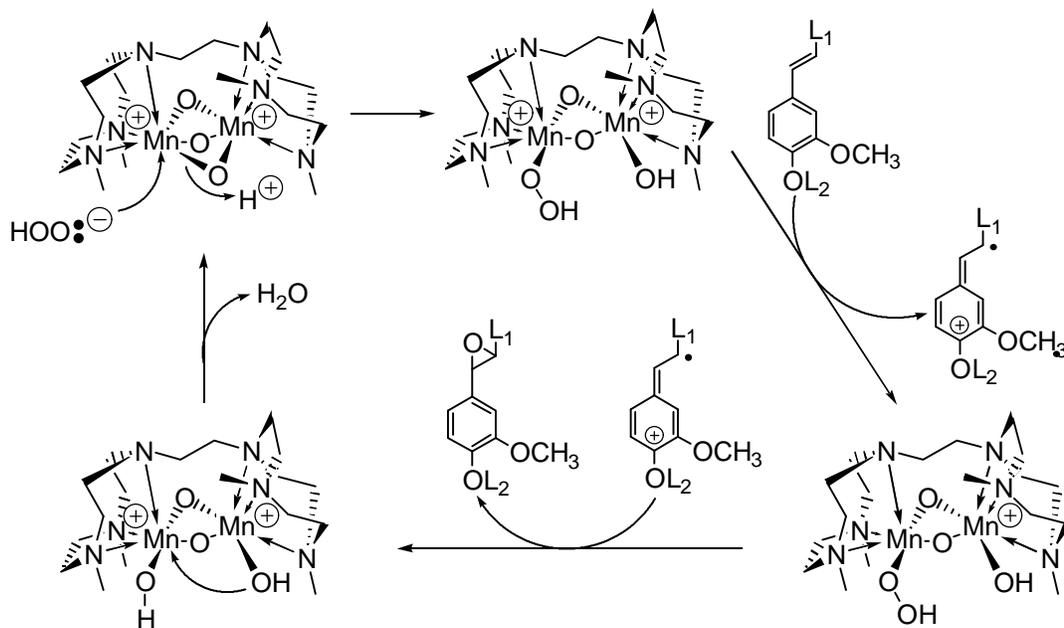


Scheme 2.2. The catalytic cycle of $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ in the oxidation of α -hydroxyl groups during the delignification



L_1 and L_2 = Lignin Moieties

Scheme 2.3. The oxidation of C-C double bond conjugated with aromatic rings in residual lignin with hydrogen peroxide catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ under alkaline condition

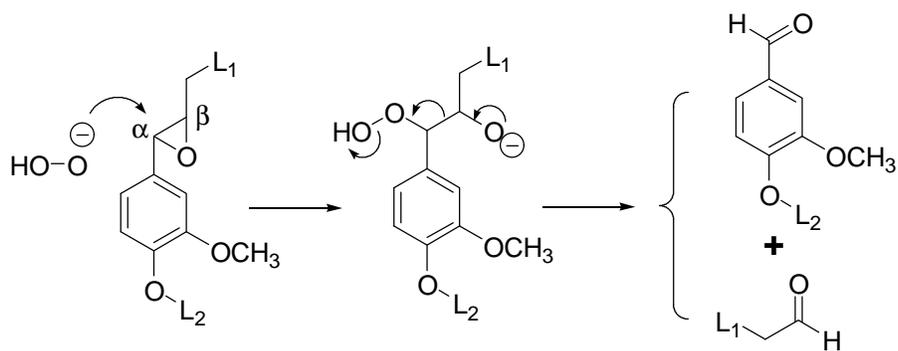


Scheme 2.4. The catalytic cycle of Mn(IV)₂-Me₄DTNE in the oxidation of conjugated C-C double bonds during the delignification

Similarly, the oxidation of conjugated C-C double bonds follows the concerted reaction mechanism as shown in scheme 2.3. and 2.4. The catalytic process benefits greatly from the concerted reaction mechanism which regulates the formation of the hydroxyl radicals. Therefore, there are no excessive hydroxyl radicals floating around to attack the carbohydrates. As a result, fibers are better preserved and enhanced selectivity is achieved.

Shown by the studies described above, the reactivity of hydrogen peroxide as an oxidant is significantly improved in such a way that the α -hydroxyl groups

and the C-C double bonds were oxidized to the corresponding carbonyls and epoxides. The carbonyls will undergo Dakin reaction described before (See Scheme 0.1.), which leads to the formation of esters susceptible to alkaline hydrolysis. Epoxide, on the other hand, will undergo further fragmentation reactions (See Scheme 2.5.), which will lead to the cleavage of C_{α} - C_{β} bond in residual lignin.



L_1 and L_2 = Lignin Moieties

Scheme 2.5. Further reactions responsible for delignification after epoxidation of C-C double bonds.

IV. Effect of Varying Alkaline Charge or Consistency on Degree of Delignification, and Pulp Properties

Increasing the initial concentration of NaOH would increase the concentration of the dissociated hydrogen peroxide, i.e. hydroperoxide anion, the

nucleophile responsible for the brightness improvement. Consequently, it is expected that the higher starting concentration of NaOH will lead to higher ending brightness. Indeed, as shown in Figure 2.4., the ending brightness was 46.4 if NaOH charge was 2%, while the ending brightness was 41.6 if the initial NaOH charge was 1% at 60°C. Further increase of the alkaline charge will not increase the brightness considerably. The increasing alkaline charge also had a slight effect on delignification and viscosity (See Figure 2.4.).

Surprisingly, pulp consistency had only a slight effect on the degree of delignification (See Figure 2.5.), if any. After 2 hours of delignification with 2% NaOH, 4% hydrogen peroxide, and catalyst charge of 60ppm at 60°C, the ending kappa numbers were 18.8, 19.2, and 21.3 for the pulp with beginning consistency of 5, 10, and 15% respectively. Apparently, the difference is far from remarkable. The brightness improvement appeared to be lower at higher consistency, despite the slightly higher degree of delignification. This might be attributed to the solubility of the lignin fragments resulting from the oxidative degradation. The effect of chromophores becomes important because a smaller amount of liquor is available to solublize the lignin fragments at higher consistency.

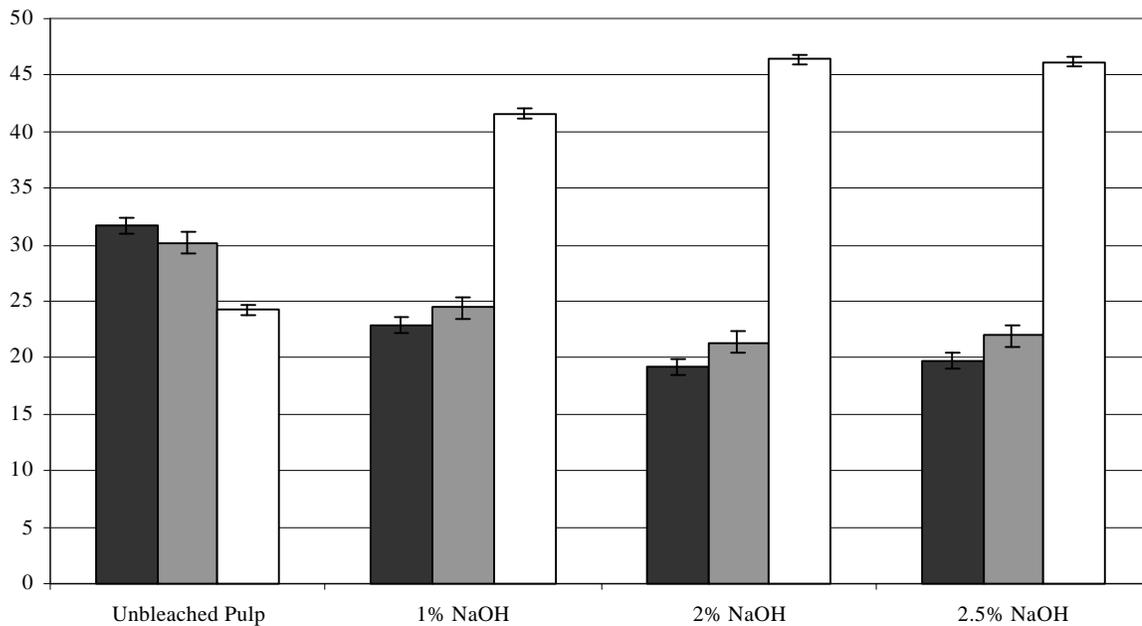


Figure 2.4. The effect of varying alkaline charge on the delignification, GE brightness, and viscosity. NaOH charge, 2% on pulp (O.D.); H₂O₂ charge, 4% on pulp (O.D.); Mn(IV)-Me₄DTNE catalyst charge, 60 ppm on pulp (O.D.); Reaction temperature, 60°C; Reaction time, 120 min. ■ Kappa number, ■ viscosity, □ GE brightness.

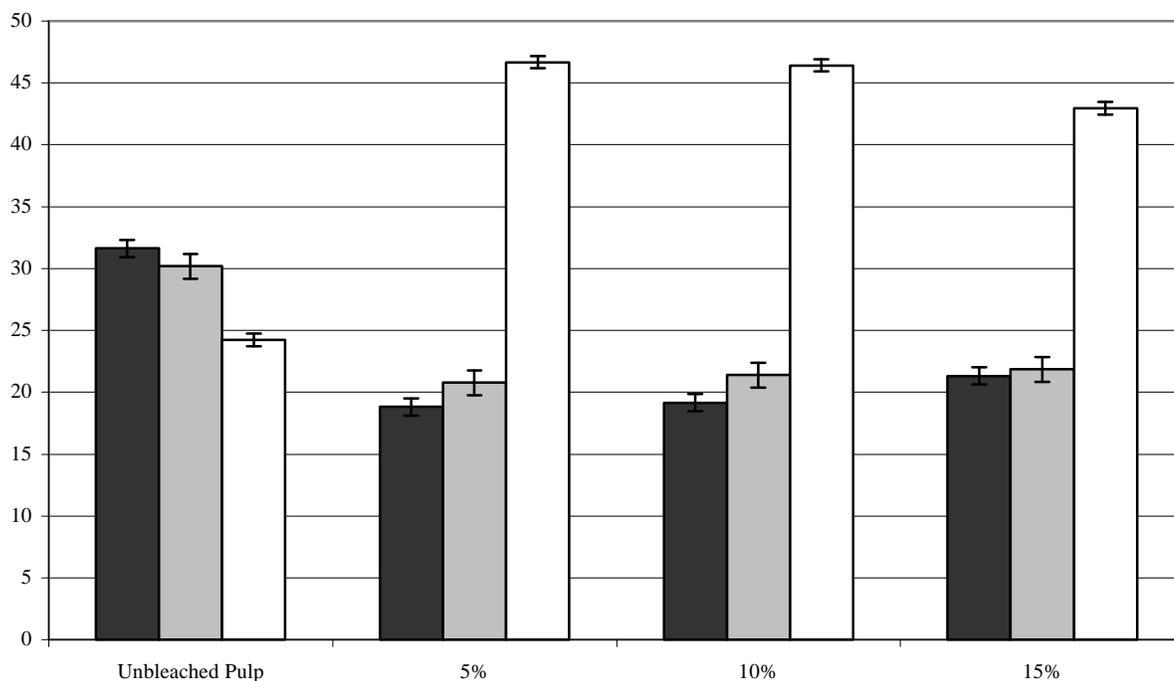


Figure 2.5. The effect of varying pulp consistency in alkaline solution on the delignification, GE brightness, and viscosity. NaOH charge, 2% on pulp (O.D.); H₂O₂ charge, 4% on pulp (O.D.); Mn(IV)-Me₄DTNE catalyst charge, 60 ppm on pulp (O.D.); Reaction temperature, 60°C; Reaction time, 120 min. ■ Kappa number, ■ viscosity, □ GE brightness.

V. Conclusions

Hydrogen peroxide delignification catalyzed by Mn(IV)₂-Me₄DTNE is superior to traditional hydrogen peroxide delignification. The rate of the delignification and the degree of delignification are significantly improved upon the addition of the catalyst. More importantly, the strength properties of the pulp

are better preserved in the presence of the catalyst which regulates the formation of hydroxyl radicals responsible for the excessive damage to the fibers. The catalyzed delignification follows first order kinetics and mostly completes within 30 minutes.

CHAPTER THREE

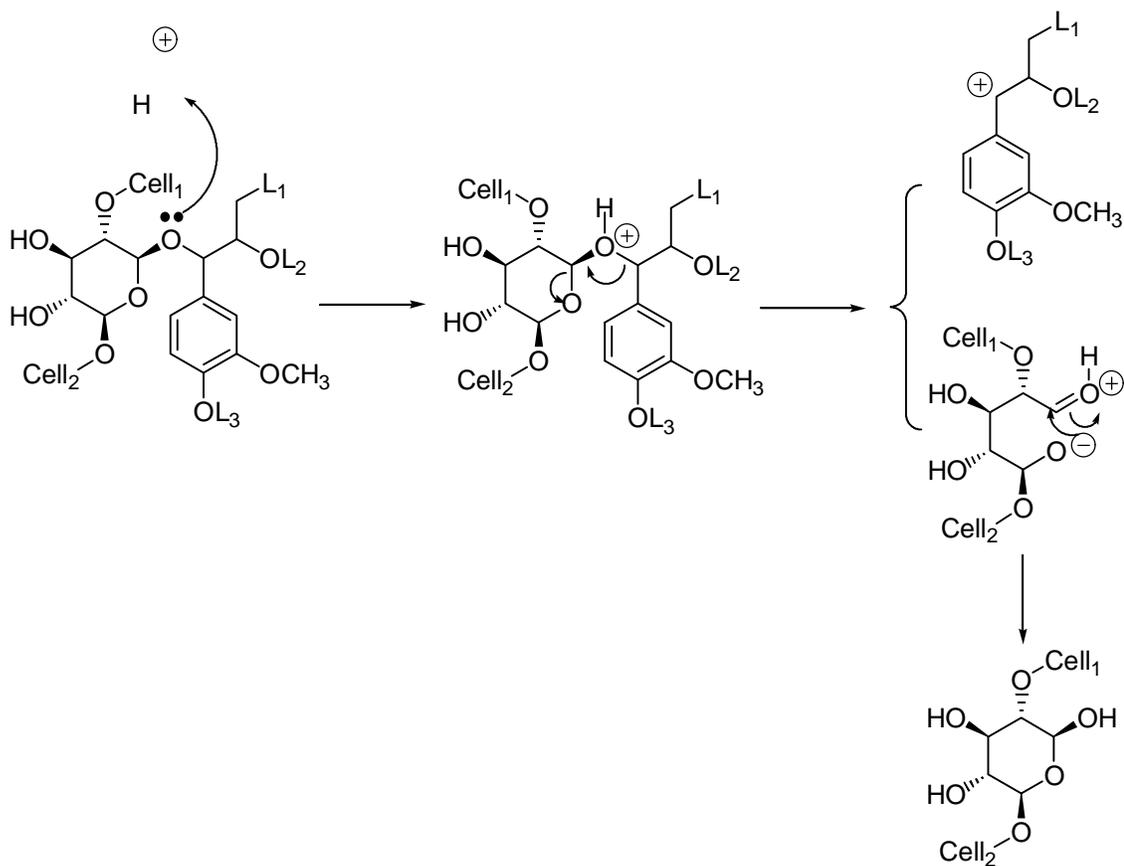
ISOLATION AND CHARACTERIZATION OF LIGNIN FROM PULP AND SPENT BLEACHING LIQUOR

I. Isolation of Lignin Fragment and Residual Lignin from Spent Bleaching Liquor and Pulp

Lignin fragments dissolved in the spent bleaching liquor were recovered by precipitation with hydrochloric acid under vigorous stirring at pH 2 ^[60]. Carbohydrate contamination is minimized at this pH considering that hydrolysis takes place to further degrade the carbohydrate fragments dissolved in the spent bleaching liquor.

Residual lignin was isolated from the pulp by selective hydrolysis of carbohydrates with cellulolytic enzyme (cellulase in this study). This method was developed by Pew and Weyna ^[61, 62], and further modified by Chang ^[63]. In pH 4.5 acetate buffer solution at 45°C, cellulase selectively hydrolyzes the carbohydrates to soluble fragments and leaves lignin behind. Enzymatic hydrolysis is known to well preserve the structure of residual lignin especially the lignin-carbohydrate complexes (LCC) ^[51, 52], compared to acidic hydrolysis where the ether linkage of the lignin-carbohydrate complexes is believed to undergo hydrolytic cleavage (See Scheme 3.1.). However, residual lignin prepared by enzymatic hydrolysis frequently suffers relative high enzyme contamination especially when isolated from bleached or semi-bleached pulp ^[64]. Therefore, all residual lignin preparations isolated by enzymatic hydrolysis were treated with alkali at 70°C for 48 hr, in order to eliminate amino acids and minimize enzyme contamination. Shown by elemental analysis, the nitrogen contents of all the

residual lignin samples are rather considerable, however less than 4%, see Table 3.1., indicating that the enzymatic contamination in the residual lignin samples is present at an acceptable level.



L_1 and L_2 = Lignin Moieties,
 Cell_1 and Cell_2 = Carbohydrates Moieties

Scheme 3.1. The cleavage of lignin-carbohydrate ether bond at the acidic condition.

Table 3.1. Elemental Analysis of Lignin Samples ¹⁻⁶

Samples	C%	H%	N%	S%
Lignin Sample 1	49.47	4.78	1.71	1.10
Lignin Sample 2	49.58	5.13	3.20	1.15
Lignin Sample 3	51.82	5.02	<0.02	<0.02
Lignin Sample 4	48.17	4.20	ND ⁶	0.66
Lignin Sample 5	49.82	5.33	ND	1.75

¹ Lignin Sample 1, isolated from original pulp by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr

² Lignin Sample 2, isolated from pulp of catalyzed delignification by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr. Condition of delignification: 60°C, 10% consistency, 2% NaOH, 4% H₂O₂, and 60ppm catalyst on pulp (O.D.)

³ Lignin Sample 3, from pulp of uncatalyzed delignification by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr. Condition of delignification: 60°C, 10% consistency, 2% NaOH, 4% H₂O₂ on pulp (O.D.)

⁴ Lignin Sample 4, from spent catalyzed bleaching liquor isolated by HCl precipitation.

⁵ Lignin Sample 5, from spent uncatalyzed bleaching liquor isolated by HCl precipitation

⁶ ND = Not Detected

II. Gel Permeation Chromatography of Lignin Samples

Gel Permeation Chromatography (GPC), often referred as Gel Filtration Chromatography (GFC) or Size Exclusion Chromatography (SEC), is a chromatographic separation technique of macromolecules by the difference in their molecular size ^[65]. It has long been used to determine the molecule mass distribution of lignin sample ^[66, 67]. Frequently, a linear correlation can be achieved between the normal logarithm of average molecular mass and the elution volume. A working curve can be obtained using samples of known

molecular mass, then the average molecular mass of unknown samples can be determined by their elution volumes. However, an assumption must be made that the unknown sample molecules are of the same or similar shape as that of the known sample molecules by which the working curve is obtained. As a result, GPC provides more reliable information in terms of relative average molecular mass of samples of similar origin than the absolute molecular weight of certain samples.

As shown by the GPC chromatogram (See Figure 3.1.) the difference in average molecular mass among the residual lignin samples was far from dramatic, indicating that molecular mass was not an important factor that affects the reactivity of the residual lignin in this case. Other factors such as the functional groups present in the residual lignin play far more important roles. However, the molecular mass of the residual lignin from the unbleached pulp is the lowest among the residual lignin samples. This is an indication that the condensation reaction of lignin occurred during delignification, and to a slightly greater extent when delignification is catalyzed, which is suggested by the fact that lignin sample 2 has slightly higher molecular weight than does lignin sample 3. The GPC curve of the lignin sample 2 shows an exclusion at elution volume 8mL well ahead of the major peak at 15mL indicating that the phenolic residual lignin fragments may undergo dehydrogenative polymerization during the catalyzed delignification.

It is also noteworthy that lignin recovered from spent catalyzed bleaching liquor (elution volume 15.5mL) has lower average molecular mass than does the lignin recovered from spent uncatalyzed bleaching liquor (elution volume 15.3mL) (See Figure 3.2). Although the difference is rather slight, it was repeatedly observed indicating that when catalyzed by $Mn(IV)_2$ -Me₄DTNE, hydrogen peroxide is capable of degrading residual lignin to fragments of lower average molecular mass.

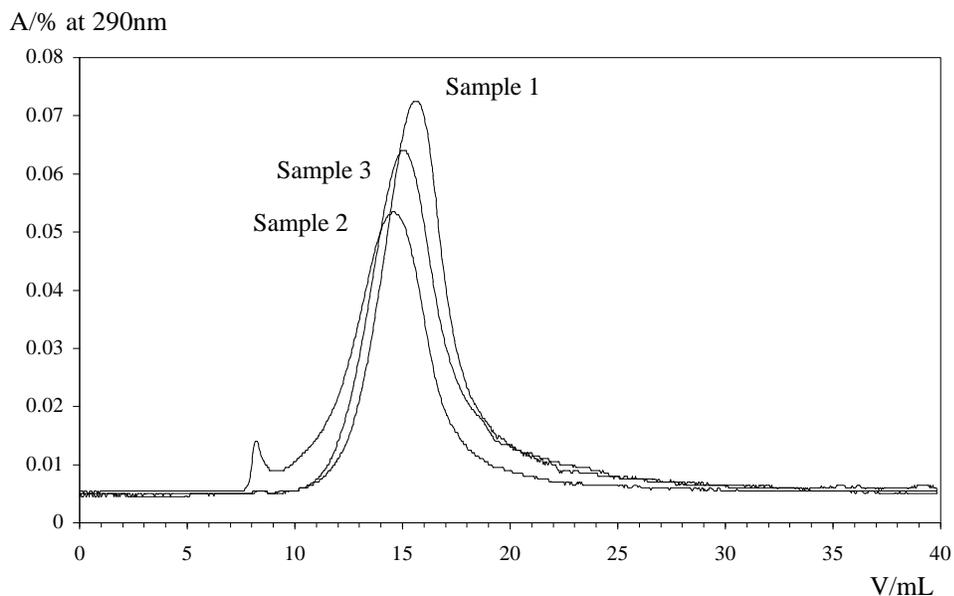


Figure 3.1. Gel permeation chromatogram of residual lignin samples ¹⁻³.

¹ Lignin Sample 1, isolated from original pulp by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr

² Lignin Sample 2, isolated from pulp of catalyzed delignification by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr. Condition of delignification: 60°C, 10% consistency, 2% NaOH, 4% H₂O₂, and 60ppm catalyst on pulp (O.D.)

³ Lignin Sample 3, from pulp of uncatalyzed delignification by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr. Condition of delignification: 60°C, 10% consistency, 2% NaOH, 4% H₂O₂ on pulp (O.D.)

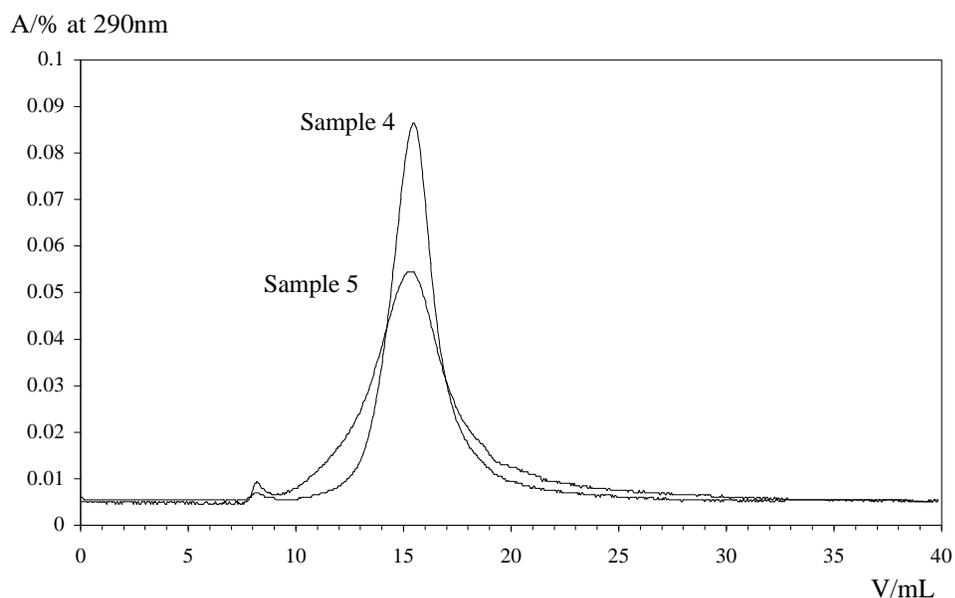


Figure 3.2. Gel permeation chromatogram of lignin samples recovered from spent bleaching liquor ¹⁻².

¹ Lignin Sample 4, from spent catalyzed bleaching liquor isolated by hydrochloric acid precipitation.

² Lignin Sample 5, from spent uncatalyzed bleaching liquor isolated by HCl precipitation

III. Infrared Spectroscopy Study of Lignin Samples

FTIR (Fourier Transform Infrared Spectroscopy) has long been used in lignin characterization ^[66]. Generally, FTIR spectra in the near-infrared region (4,000-10,000 cm^{-1}) consist entirely of overtones and combinations of primary bands within the mid-IR region. For macromolecules like lignin the excessive overlapping of bands produces a diffuse absorption continuum with few characteristic features, making unequivocal assignment practically impossible. In addition, very little information is available from the FTIR spectra in the far-

infrared region ($50\text{-}500\text{cm}^{-1}$). Therefore, FTIR data were acquired only at the mid-infrared region ($440\text{-}4,000\text{cm}^{-1}$).

Although the spectra of all lignin samples showed strong absorption at 3400 , 2900 , and 1600cm^{-1} (See Figure 3.3.), subtle difference among the spectra was indeed observed. A distinct overtone between $2800\text{-}2400\text{cm}^{-1}$ was observed in the spectrum of sample 2, suggesting the presence of the carboxylic acid in the residual lignin that was isolated from the pulp after catalyzed delignification. The spectrum of sample 2 also showed a strong absorption at 1680cm^{-1} suggesting the presence of the carbonyls possibly conjugated with aromatic rings in the residual lignin after the delignification catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$. A more detailed assignment of the FTIR signals of lignin sample is available at a review written by Faix ^[68].

As mentioned before, structural changes within the lignin molecule is far beyond the information provided by FTIR. Consequently, thorough structural characterization with $^1\text{H}\text{-}^{13}\text{C}$ correlation 2D NMR is required in order to acquire more structural information of these lignin samples.

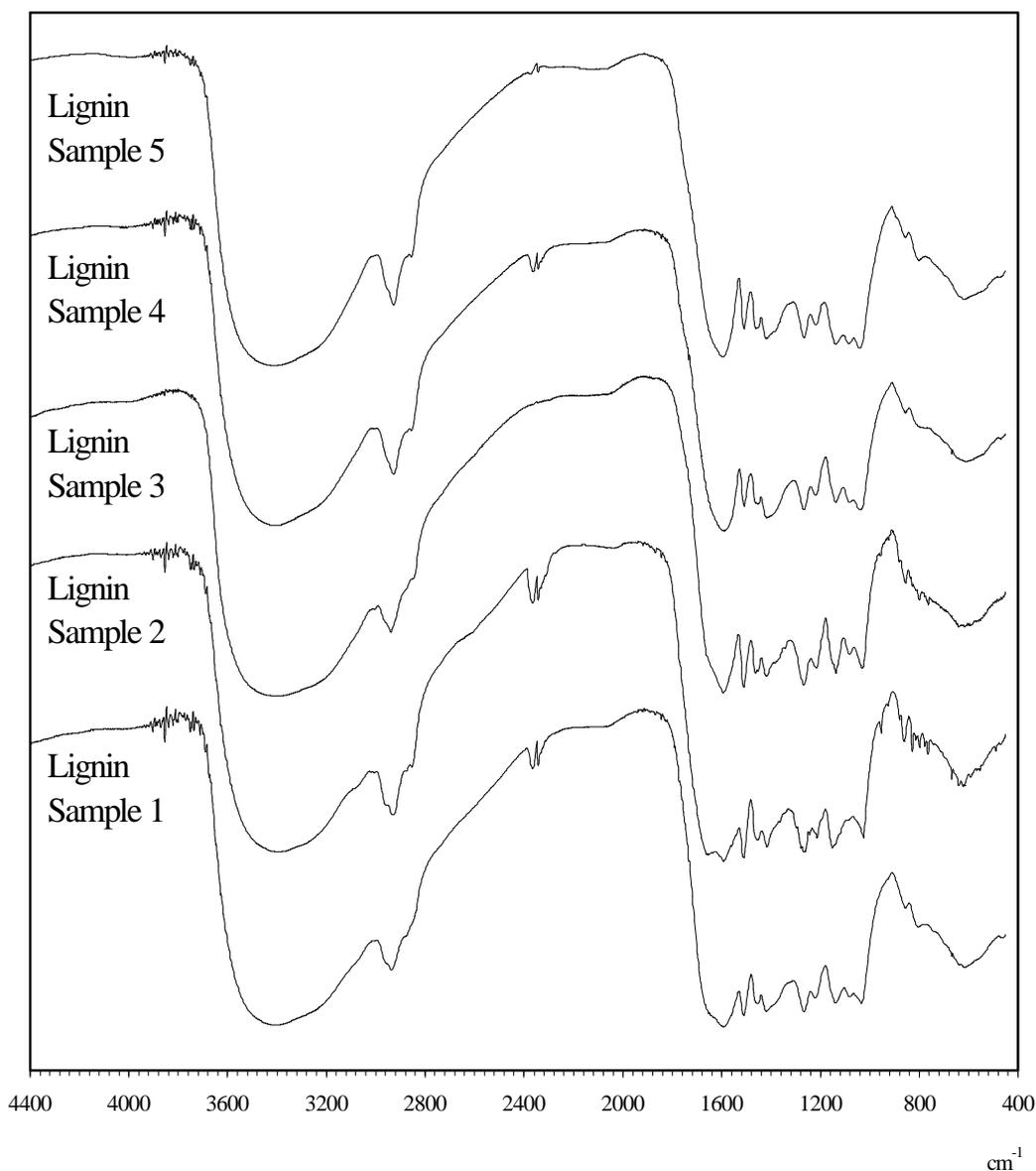


Figure 3.3. The FTIR spectra of the lignin samples ¹⁻⁵.

¹ Lignin Sample 1, isolated from original pulp by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr

² Lignin Sample 2, isolated from pulp of catalyzed delignification by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr. Condition of delignification: 60°C, 10% consistency, 2% NaOH, 4% H₂O₂, and 60ppm catalyst on pulp (O.D.)

³ Lignin Sample 3, from pulp of uncatalyzed delignification by cellulase hydrolysis in pH4.5 acetate buffer at 45°C, 4x48hr. Condition of delignification: 60°C, 10% consistency, 2% NaOH, 4% H₂O₂ on pulp (O.D.)

⁴ Lignin Sample 4, from spent catalyzed bleaching liquor isolated by HCl precipitation.

⁵ Lignin Sample 5, from spent uncatalyzed bleaching liquor isolated by HCl precipitation

IV. ^1H and ^{13}C Correlation NMR Spectroscopy

1. ^1H NMR in lignin characterization

NMR has been a powerful method to characterize structure of organic molecules. Its first appearance as ^1H NMR was only modestly successful in lignin characterization however, due mainly to the polymeric and heterogeneous nature of lignin, and the low resolution of early generation NMR spectrometers. ^1H spectrum of a small organic molecule generated by a 100MHz spectrometer easily provides a great deal of valuable structural insight, but even with today's state-of-art 750MHz spectrometers, ^1H NMR spectrum of lignin sample would be still rather uninformative^[69]. Severe overlapping of signals makes it impossible to obtain any in-depth structural information.

2. ^{13}C NMR in lignin characterization

The natural abundance of ^{13}C nuclei is only 1.1% of that of ^{12}C , and its NMR sensitivity is only about 1.6% of that of ^1H , which means that the overall sensitivity of ^{13}C is only 1/5700 of that of ^1H . The acquisition of ^{13}C NMR spectroscopic data had long be considered impossible because the early NMR technology required a large amount of sample and a prohibitively long time to overcome the extremely low sensitivity of ^{13}C . The phenomenal advances in Fourier transform NMR (FT-NMR) in the seventies paved the way to obtaining

natural abundance ^{13}C NMR, and thus, opened another door to lignin characterization. In fact, ^{13}C NMR offers a number of advantages over ^1H NMR. ^{13}C NMR data are obtained along the carbon backbone of a molecule, and therefore, ^{13}C NMR provides information about virtually all carbons in the molecule, and more importantly, without the complication of spin-spin coupling, thank the proton decoupling technique, and the extremely low probability of two ^{13}C nuclei adjacent to each other in the same molecule. As a result, ^{13}C NMR was once considered the most reliable and comprehensive technique of lignin characterization ^[70, 71] until the emergence of ^1H and ^{13}C correlation 2D NMR.

3. ^1H and ^{13}C correlation 2D NMR in lignin characterization

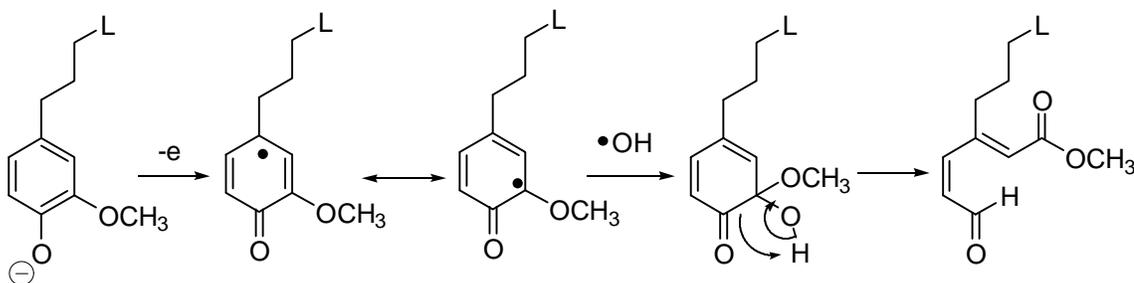
It is not until the late nineties that ^1H and ^{13}C correlation 2D NMR was used for lignin characterization because of the lack of awareness, and mostly the limited access of lignin chemists to the high performance NMR equipment. Recently, the burst of the interest in 2D NMR characterization of lignin has led to fruitful insight into the structure of native lignin as well as residual lignin. Very much like the ^{13}C NMR did a decade ago when it became available to lignin chemists.

The conventional 1D NMR is actually two-dimensional in terms of Cartesian coordinates. The second dimension is peak intensity while the first dimension is chemical shift. The so-called 2D NMR is actually three-

dimensional, although it is frequently presented as a contour slice through “stacked peaks”. Indeed, the 2D designation in NMR does not refer to Cartesian coordination, but refers to the number of Fourier transformations resulting in the final spectrum, in other words to the number of frequency axes.

There are many different kinds of 2D NMR experiments. Among the most popular experiments are Correlated Spectroscopy (COSY) or Homonuclear Correlated Spectroscopy (HOMOCOR), Heteronuclear Chemical Shift Correlation (HETCOR), or Heteronuclear Correlated Spectroscopy (HETERO-COSY) or Chemical Shift Correlation MAP (CSCM), and NOSEY (Nuclear Overhauser and Exchange Spectroscopy). The idea of ^1H and ^{13}C correlation 2D NMR is to correlate the peaks of a ^1H spectrum with the peaks of a decoupled ^{13}C spectrum. Thus, it shows the specific protons attached to each ^{13}C . The ^1H spectrum is presented on the vertical axis and the ^{13}C spectrum is presented on the horizontal axis. The ^1H - ^{13}C correlation is shown by a crosspeak contour at the intersection of a horizontal line drawn from a proton peak or multiplet and a vertical line drawn from a ^{13}C peak. It is not intended to assign all the signals present in the spectra in this thesis. (For a comprehensive assignment of 2D NMR signals of lignin, see Ph.D. thesis by Capanema ^[72]) However, the spectra of residual lignin before and after the catalyzed delignification does provide evidence of lignin degradation during the delignification process.

As observed in the HMQC spectrum of residual lignin isolated from the unbleached pulp (Figure 3.4.), all typical lignin signals, such as signals in the aliphatic region, oxygenated aliphatic region and aromatic region are present. In sharp contrast, the lignin signals in the aromatic region in the HMQC spectrum of residual lignin isolated from pulp delignified with catalyzed hydrogen peroxide (Figure 3.5.) mostly disappeared, indicating that the extensive cleavage of aromatic rings occurred during the catalyzed delignification. The cleavage of aromatic moiety is believed to be via oxidative ring cleavage occurring after the coupling of the hydroxyl radical and the radical originated from phenolic lignin moieties, see Scheme 3.2. The cleavage of aromatic moieties was in addition to the oxidative cleavage of lignin side chain suggested by the signals of decreased intensity in the oxygenated aliphatic region. As a result, the degree of delignification was considerably improved.



L = Lignin Moiety

Scheme 3.2. The cleavage of aromatic moieties in residual lignin with hydrogen peroxide catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$.

V. Conclusions

Shown by the lignin characterization by GPC, FTIR, and NMR, residual lignin in kraft pulp undergoes significant degree of oxidative degradation during the hydrogen peroxide delignification catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$. Most remarkable is the oxidative cleavage of aromatic rings. This cleavage is believed to occur to phenolic lignin moieties as shown in Scheme 3.2. In addition, evidence has been found to support the assumption that cleavage of the side chain also occurs. As a result, exceptional delignification is achieved.

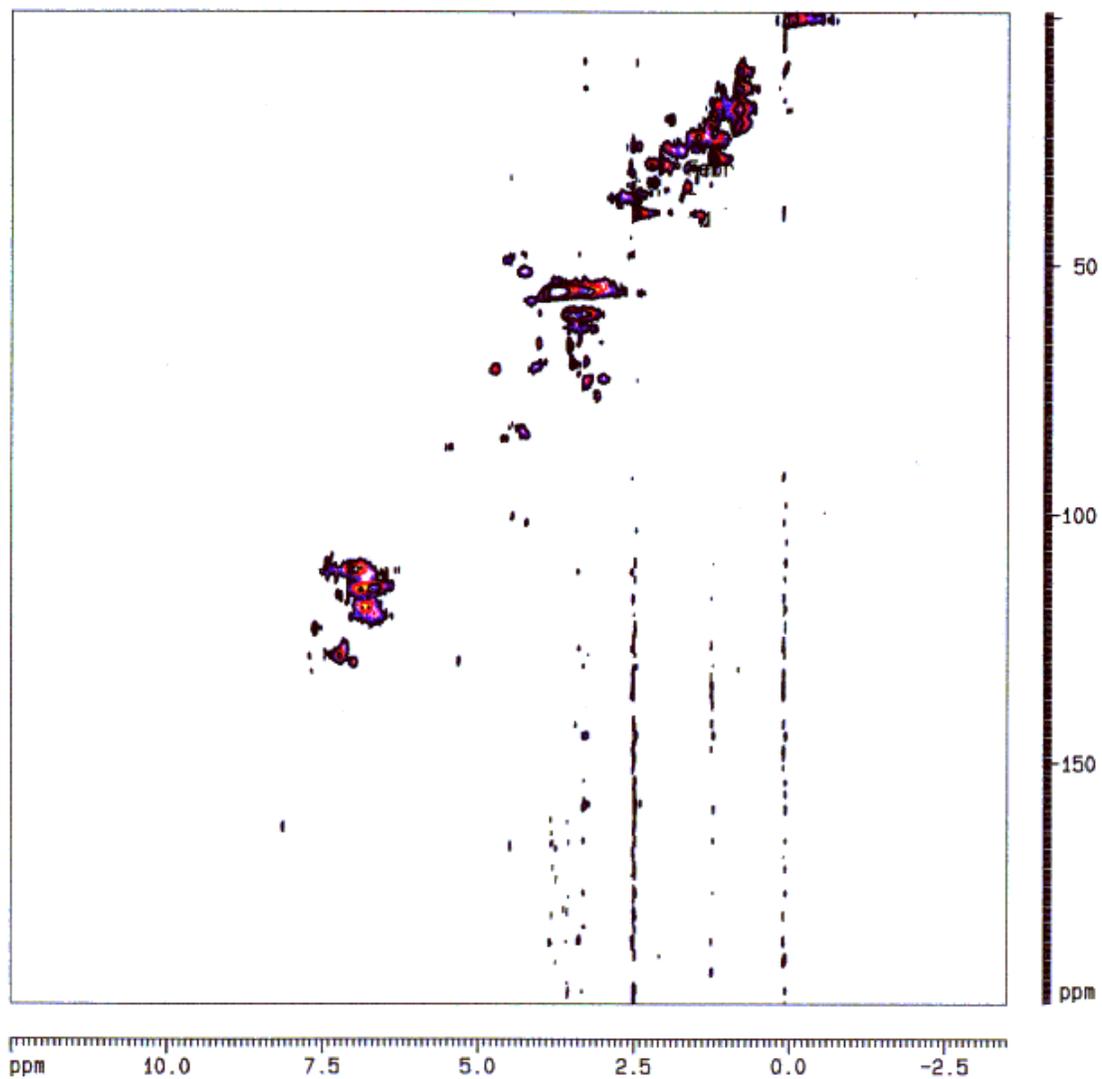


Figure 3.4. HMQC spectrum of residual lignin isolated from unbleached pulp by cellulase hydrolysis.

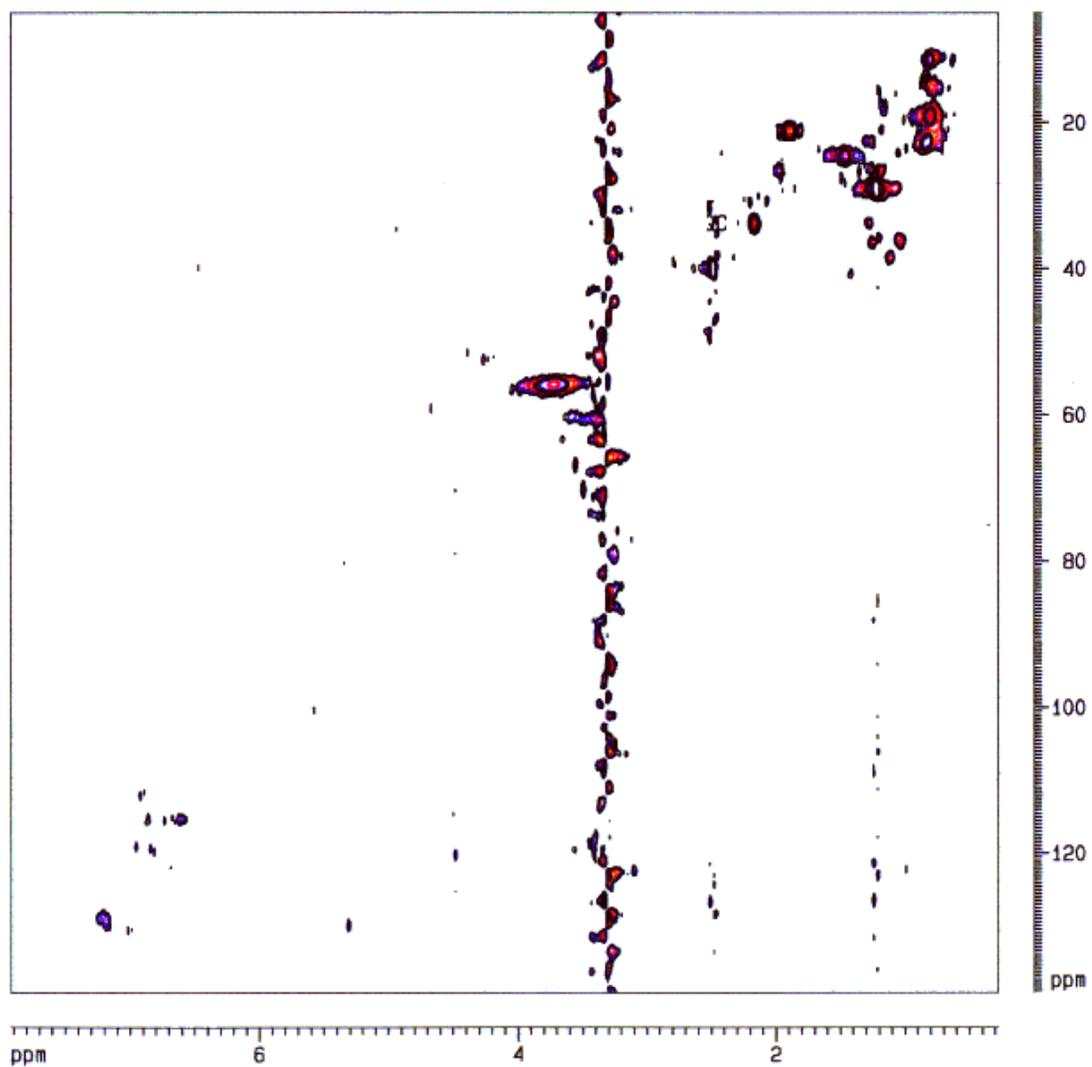


Figure 3.5. HMQC spectrum of residual lignin isolated from pulp delignified with catalyzed hydrogen peroxide by cellulase hydrolysis

CHAPTER FOUR

MODELING AND SIMULATION OF HYDROGEN PEROXIDE DELIGNIFICATION CATALYZED BY $Mn(IV)_2-ME_4DTNE$ USING WINGEMS4.0

I. Process Modeling and Simulation of Pulp and Paper Industry

1. Process Modeling and Simulation ^[73]

Establishing mathematical relationships between causes and effects, usually referred as “modeling” does not require specifying the path that causes the effects. Therefore, models take on a variety of forms, such as statistical models, linear programming models, and process simulation models, depending on the objectives in their development and use. Although frequently used interchangeably with “process modeling”, the term “process simulation” is often viewed as a special type of modeling with a distinct purpose to describe the physical and/or chemical path or process that causes the effects. As a result of the recent burst of computing and information technology, and the growing awareness of its importance, process simulation aided by computers has been enjoying increasing popularity and is becoming indispensable in the pulp and paper industry.

2. Commercial Simulators/Applications

There are currently three common commercial software applications specifically dealing with process simulation in pulp and paper industry, GEMS (General Energy and Material Balance System), MAPPS (Modular Analysis of Pulp and Paper System, available only under the name of IDEAS), and

MASSBAL. GEMS and MAPPS are solved iteratively, namely modules are solved in a specific sequence until successive iterations yield results that fall within a range specified by the users. With MASSBAL however, all equations are linearized, set up as a matrix and solved simultaneously. Computing technology had long been the major threshold of process simulation. If the simulation is to be solved iteratively, it requires computation to be performed at fast speeds. If the simulation is to be solved simultaneously, it requires extensive computer memory. Computing technology has been advancing at a rate that no one has ever imagined. As a result, none of these requirements seems to be difficult to achieve presently.

3. GEMS and WinGEMS4.0 ^[74]

GEMS is an acronym for General Energy and Material Balance System. It is a modular program designed to perform mass and energy balance calculations which are grouped in the modules called blocks. Apart from many generic blocks, GEMS has a wide selection of blocks designed specifically for simulation of pulp and paper process.

GEMS was originally developed by L. Edward and his coworkers in the early seventies, when the program was run on a mainframe computer using punch cards for input. It was then ported to the personal computers to become PCGEMS in mid eighties. It was not until the early nineties, that a simulation

services provider, Pacific Simulation, developed WinGEMS which is the Microsoft Windows version of GEMS. WinGEMS allows interaction between the user and the program. Therefore, it is user-friendly and much more preferred format of GEMS. WinGEMS4.0 is the latest version of WinGEMS. The following reports the simulation study of delignification of kraft-AQ southern pine pulp with hydrogen peroxide catalyzed by Mn(IV)-Me₄DTNE.

II. Process Simulation of Hydrogen Peroxide Delignification Catalyzed by $Mn(IV)_2$ -Me₄DTNE Using WinGEMS4.0

The purpose of this simulation is to understand the impact of upgrading the traditional hydrogen peroxide delignification to the catalyzed hydrogen peroxide delignification on the entire pulping, bleaching, and recovery processes. In addition, the economic feasibility of the catalyzed process is to be evaluated. Two cases are employed in this simulation. The base case simulates the pulping, bleaching, and recovery process using traditional hydrogen peroxide delignification, see Appendix I for block diagram. The alternative case is to simulate the pulping, bleaching, and recovery process using catalyzed hydrogen peroxide delignification, see Appendix II for block diagram.

1. Common Features of the Two Cases

The simulated TCF pulp mill features a continuous digester. In both cases, chips are fed to the digester at 78.75mt/hr OD (2100ODT/day). Pulping is carried out at liquor to wood ratio of 2.9:1, and an active alkali charge of 16.9% on OD wood as Na₂O. The sulfidity is 28%, the reduction efficiency is 86.61%, and the causticizing efficiency is 81.9%. The brown stock is produced at 37.42mt/hr OD (997.97ODT/day), which corresponds to a yield of 48%, at Kappa number 30. The bleached pulp was produced at 35.23mt/hr OD (939.5ODT/day), which corresponds to a yield of 45%, at Kappa number 10. In both cases, the

pulp is bleached with an O stage followed by an E stage. After an acid wash process, the base case goes through a chelating process followed by a P stage. However, the alternative case skips the chelating process and goes directly through a P stage catalyzed by Mn(IV)₂-Me₄DTNE. In other word, the base case has a bleaching sequence of OE(AQ)P, in the alternative case, the P stage is catalyzed by Mn(IV)₂-Me₄DTNE, and the bleaching sequence is OEAP^{Mn}, where P^{Mn} stands for hydrogen peroxide delignification catalyzed by Mn(IV)₂-Me₄DTNE. The general technical data of both cases are summarized in Table 4.1.

Table 4.1. General operation parameters of the base case and the alternative case.

Pulping	Chip Furnished	2100 ODT/day
	Brown Stock	997.9 ODT/day
	Pulping Yield	48%
	Bleached Pulp	939.5 ODT/day
	Bleaching Yield	45%
	Brown Stock Kappa	30
	Bleached Pulp Kappa	10

To be continued.

Table 4.1. continued.

White Liquor	Flow	127 mt/hr, 598.5 gal/min
	Temperature	87.8°C
	AA on Wood as Na ₂ O	16.9%
	Sulfidity	28%
	Reduction Efficiency	86.61%
	Causticizing Efficiency	81.90%
	Liquor to Wood Ratio	2.9
Recovery Boiler	% Solid Fired	75
O Stage	Temperature	90°C
	NaOH Charge	1.5% on OD pulp
	O ₂ Charge	2.4% on OD pulp
	Consistency	13.6%
	Delignification	40%
E Stage	Temperature	80°C
	NaOH Charge	2% on OD
	Consistency	11.1%
	Delignification	10%
A Stage	Temperature	80°C
	H ₂ SO ₄ Charge	2%
	Consistency	11.1%

In both cases, the O stage is run at 90°C, 13.6% consistency, and 1.5% (on OD pulp) NaOH charge, to achieve 40% delignification. The oxygen charge is 2.4% on OD pulp. The E stage is run at 80°C, 11.1% consistency, and 2% NaOH charge, to achieve 10% delignification. The A stage is run at 80°C, 11.1% consistency, 2% H₂SO₄ charge. Both cases use a counter current washing sequence. The P stage uses fresh water and the washing filtrate from the P stage washer is recycled and reused as shower flow of E stage washer. The washing filtrate from E stage washer is reused as the shower flow of O stage washer whose washing filtrate is reused as the shower of brown stock washer. The acidic washing filtrate from the AQ stage (in base case) and the A stage (in alternative case) washer is not recycled but discharged due to the concern of lignin precipitation. They all use fresh water as shower flow.

2. Difference Aspects between Traditional P Stage and P^{Mn} Stage

The most important difference between the traditional P stage and P^{Mn} stage is that the P^{Mn} stage is operated at a much lower temperature that does not require extra heating process to achieve. As a result of the lower operating temperature, the decomposition of hydrogen peroxide due to the thermally induced disproportionation is greatly reduced. Consequently, the amount of hydrogen peroxide charged can be substantially lower. Traditionally, a P stage usually follows a Q stage when chelants, such as EDTA or DTMPA, are applied to bind to adventitiously present transition metal ions, in order to control the

transition metal profile. In the base case, the Q stage is run at 80°C, 11.1% consistency, 2% H₂SO₄ charge on OD pulp, and 0.14% EDTA on OD pulp. Since the formation of the hydroxyl radicals is regulated due to the concerted reaction mechanism during the catalyzed hydrogen peroxide delignification, the chelant used to control the metal profile in the base case can be eliminated in the alternative case, see Table 4.2. The operating parameters for the P stage and the P^{Mn} stage are shown in Table 4.3.

Table 4.2. Operation parameters of A stage before P and P^{Mn} stage.

	A Stage before P	A Stage before P ^{Mn}
Temperature	80°C	80°C
H ₂ SO ₄ Charge	2%	2%
Consistency	11.1%	11.1%
EDTA Charge	0.14% on OD pulp	----

Table 4.3. Operation parameters of P stage and P^{Mn} stage.

	P Stage	P ^{Mn} Stage
Temperature	90°C	77°C
pH	12	12
Consistency	13.6%	13.6%
Delignification	40%	40%
H ₂ O ₂ Charge	4% on OD Pulp	2.5% on OD Pulp
Catalyst Charge	----	60ppm on OD Pulp

Considering the difference between the base case and the alternative case, the alternative case is expected to have much lower steam consumption than the base case. Indeed, the steam demand decreases significantly when P^{Mn} is used, see Table 4.4. The base case needs 57.01mt/hr steam while the alternative case needs 57.82mt/hr steam in the pulping section (a 1.3% increase). The base case consumes 46.17mt/hr steam vs. 26.45mt/hr consumed in alternative case by the bleaching section. This 42.7% decrease is due to the significantly lower temperature at which the catalyzed hydrogen peroxide delignification is operated. The steam usage in the evaporator sees a slight decrease from 51.07mt/hr to 50.61mt/hr when the traditional P stage is substituted by P^{Mn}, a 1% decrease. The steam consumption of the alternative case totals 135.14mt/hr vs. 154.52mt/hr in the base case (a 14.3% decrease).

The steam is generated at almost the same amount, 271.11mt/hr in the base case vs. 271.01mt/hr in the alternative case.

Chemical make-up is only slightly affected by substitution of P^{Mn} for the traditional P stage. The make-up of NaOH, Na₂SO₄, and CaO are 37.3, 13.9, and 7.2kg/ODT respectively in the base case, and the make-up of NaOH, Na₂SO₄, and CaO are 37.5, 14.2, and 7.2kg/ODT respectively in the alternative case. The fresh water consumption for both cases is 3256gal/min. The bleaching chemicals of O, E, and A stages were consumed at about the same amount in both cases. EDTA was charged at 2.2kg/ODT for the base case, and no EDTA was used in the alternative case. The alternative needs to have a 0.066kg/ODT charge of the catalyst, which is not used in the base case. In return, hydrogen peroxide was charged at 44.0kg/ODT for the base case, and at 33.0kg/ODT for the alternative case (a 25% decrease).

Table 4.4. Steam and Chemical Consumption

Steam Consumption (mt/hr)	Base Case	P ^{Mn} Case
Pulping Section	57.01	57.82
Bleaching Section	46.17	26.45
Evaporation Section	51.07	50.61
Green Liquor Heating	0.27	0.26
Total	154.52	135.14
Steam Generated (mt/hr)	271.11	271.01
Chemical Makeup (kg/ODT)		
NaOH	37.3	37.5
Na ₂ SO ₄	13.9	14.2
CaO	7.2	7.2
Fuel	31.3	30.1
Fresh Water Consumption (gal/min)	3256	3256
Bleaching Chemicals		
O ₂ (kg/ODT)	26.7	26.7
H ₂ SO ₄ (mt/hr)	0.72	0.72
EDTA (kg/ODT)	3.1	----
H ₂ O ₂ (kg/ODT)	44.0	33.0
Catalyst(kg/ODT)	----	0.066

In both cases, a significant portion of washing filtrate is recycled to be used as the shower of the previous washing stage. Due to its acidic nature, the washing filtrate of the AQ stage in the base case or the A stage in the alternative case must be discharged. The washer performances of the base and alternative cases are very similar to each other. In order to maintain the saltcake carryover in the bleached pulp stream at approximately 11.8kg/ODT, the washer in the P stage needs to run at a D factor of 2.36 using fresh water at 1764gal/min in both cases. The shower flows, D factors, and carry-overs of the washers at different stages in both cases are listed in Table 4.5.

Table 4.5. Washer Performance

	Base Case	Alternative Case
Brown Stock Washing		
Shower Flow (gal/min)	1687	1676
D Factor	2.89	2.83
Carryover (kg/T as Na ₂ SO ₄)	144.8	147.0
O Stage Washing		
Shower Flow (gal/min)	1922	1911
D Factor	2.82	2.76
Carryover (kg/T as Na ₂ SO ₄)	139.7	141.4

To be continued.

Table 4.5. Washer Performance(continued).

E Stage Washing	Base Case	Alternative Case
Shower Flow (gal/min)	1859	1849
D Factor	2.67	2.61
Carryover (kg/T as Na ₂ SO ₄)	64.2	65.4
Q (A) Stage Washing		
Shower Flow (gal/min)	1587	1587
D Factor	1.07	1.07
Carryover (kg/T as Na ₂ SO ₄)	15.6	15.9
P(P ^{Mn}) Stage Washing		
Shower Flow (gal/min)	1764	1764
D Factor	2.36	2.36
Carryover (kg/T as Na ₂ SO ₄)	11.8	11.8

As expected, the base case and the alternative case will have similar environmental impact as far as effluents and emissions are concerned, since the substitution of P^{Mn} stage for the traditional P stage does not seem to significantly alter the properties pulp and liquor streams. The bleaching effluents and the air emissions as well as grits and dregs discharged in the recovery process in both cases are listed in Table 4.6.

Table 4.6. The bleaching effluents and air emissions of both cases.

	Base Case	Alternative Case
Pulping Effluents		
Flow (gal/min)	6.7	6.7
Dissolved Solid (kg/hr)	40	41
Recovery (Soap Skim)		
Flow (gal/min)	16.7	16.7
Dissolved Solid (mt/hr)	2.2	2.2
Bleaching Effluents		
Flow (gal/min)	1616	1616
Dissolved Solid (mt/hr)	2.79	2.78
Flue Gas		
Flow (mt/hr)	338.32	338.23
CO ₂ (mt/hr)	71.7	71.7
Na ₂ SO ₄ (kg/hr)	20	20
Na ₂ CO ₃ (kg/hr)	5.5	5.5
Slaker Grits (kg/hr)	84	84
Dissolved Solid (kg/hr)	24	24
Total Dregs (kg/hr)	614.5	614.5

3. Economic evaluation of P^{Mn} delignification

The economic impact of substitution of a P^{Mn} stage for the traditional P stage is summarized in the Table 4.7. The P stage reinforced by Mn(IV)₂-Me₄DTNE does not require any additional equipment purchase. Although the cost of the catalyst is rather high, the saving should be quite significant due to the lower steam usage, and lower hydrogen peroxide charge, and the savings of not using EDTA, or other chelants. All of these chemicals are rather expensive. Shown in Figure 4.1. is the profitability of substitution of traditional P^{Mn} stage for P as a function of the cost of Mn(IV)₂-Me₄DTNE, assuming that the indicated chemicals are available at the indicated prices ^[73]. Overall, the economic outcome of the catalyzed delignification is positive, if the cost of the catalyst is less than \$330/kg. Currently, there is no official quote for the cost of Mn(IV)₂-Me₄DTNE available yet, however, it is estimated that the cost of Mn(IV)₂-Me₄DTNE will not exceed \$50/kg. There will be a significant amount of savings generated by application of the catalyst. By all means, efforts should be made to simplify the synthesis of the catalyst and increase the yields of the reactions. Alternatively, a more easily available catalyst should be identified, or deactivated catalyst can be easily recovered.

Table 4.7. Economic evaluation of P^{Mn} system

Chemical/Steam (mt/hr)	Base Case	P ^{Mn} Case	Annual Saving (mil \$)
¹ Steam Consumed	154.52	135.14	0.98
Steam Generated	217.11	271.01	-----
NaOH	1.55	1.56	-----
Na ₂ SO ₄	0.58	0.59	-----
CaO	0.30	0.30	-----
Fuel	1.30	1.24	-----
H ₂ SO ₄ (mt/hr)	0.72	0.72	-----
O ₂ (mt/hr)	0.90	0.90	-----
² EDTA (kg/hr)	50	----	0.39
² H ₂ O ₂ (mt/hr)	1.43	1.07	4.44
³ Mn(IV) ₂ -Me ₄ DTNE (kg/hr)	----	2.1	-0.88
Total Annual Saving (mil \$)	----	----	4.93

¹ Price of steam is considered to be \$6/mt.

² Prices of EDTA and hydrogen peroxide are obtain from Chemical Market Report ^[75].

³ Price of Mn(IV)₂-Me₄DTNE is assumed to be \$50/kg.

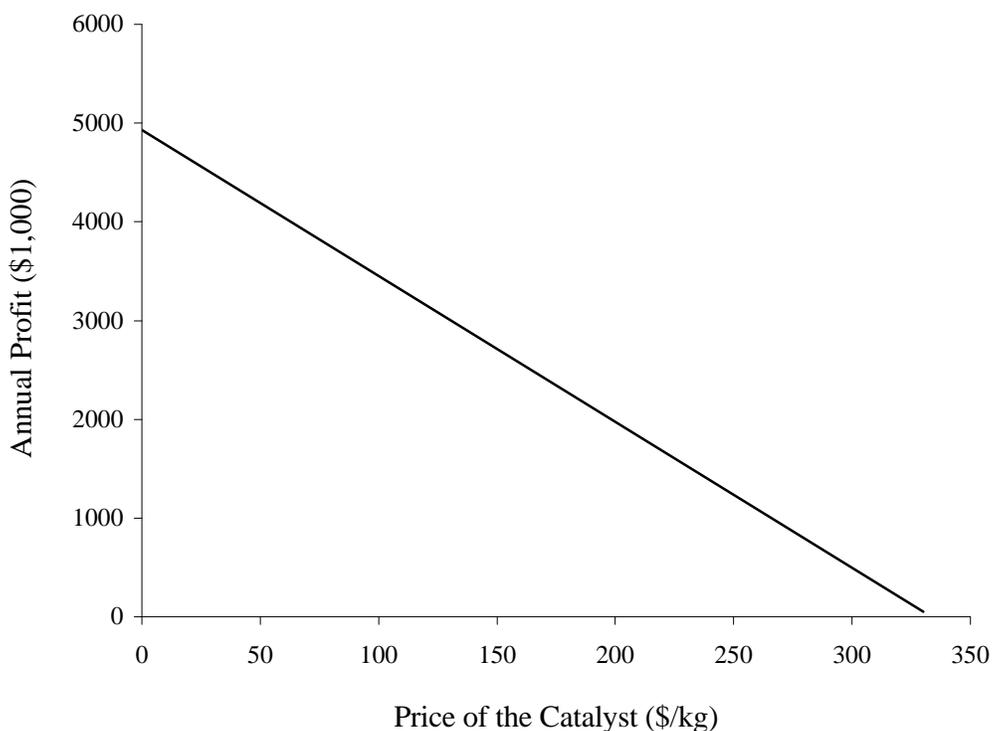


Figure 4.1. The estimated annual profit of catalyzed hydrogen peroxide delignification¹.

¹ Assume that the price of steam, hydrogen peroxide, and EDTA is \$6/ton, \$0.37/kg, and \$0.93/kg respectively, and the bleached pulp production is 940 ODT/day.

III. Conclusions

According to the simulation performed by using WinGEMS4.0, hydrogen peroxide delignification catalyzed by $Mn(IV)_2-Me_4DTNE$ is profitable if the price of the catalyst is kept below \$330/kg. Compared to traditional P stage, the P^{Mn} stage consumes less hydrogen peroxide and runs well at much lower temperature, which in turn consumes less steam. In addition, the addition of chelants such as EDTA is avoided. As a result, a significant amount of savings is

generated to achieve same degree of delignification with hydrogen peroxide catalyzed by Mn(IV)₂-Me₄DTNE.

CHAPTER FIVE
EXPERIMENTAL

I. Reagents and Equipment

Reagents

1-(3,4-dimethoxyphenyl)acetophenone, *E*-diphenylethene, and 1-(3,4-dimethoxyphenyl)-1-propene were purchased from Aldrich. 1-(3,4-dimethoxyphenyl)ethanol was synthesized by reducing 1-(3,4-dimethoxyphenyl)acetophenone with NaBH₄ [30] which was purchased from Aldrich and Fisher.

Hydrogen peroxide was purchased from Fisher in the form of 30% aqueous solution then diluted for experiments. Sodium hydroxide was purchased from Fisher in form of tablets. Sulfuric acid acid was purchased from Fisher in form of 98% aqueous solution. Hydrochloric acid was purchased from Fisher in form of 37% aqueous solution. The kraft-AQ southern pine pulp was a courtesy from Westvaco Corporation. The precatalyst was a courtesy from Deguasse AG.

3,4-dichlorotoluene was purchased from Lancaster and was used as the internal standard in GC and GCMS experiments. Lithium chloride was purchased from Aldrich and used as elution solution for GPC. Cellulase (EC 3.2.1.4) from *Trichodema viride* was purchased from Sigma. DMSO-d₆ was purchased from Cambridge Isotope Laboratories, Inc. as NMR solvent.

Potassium permanganate standard solution, and sodium thiosulfate standard solution used for kappa number determination were purchased from Aldrich. Cupriethylenediamine 1.0M solution used for viscosity determination was purchased from Reagent Inc. The elemental analysis was performed by E & R Microanalytical Laboratory, Inc.

Equipment

Hewlett Packard Gas Chromatograph 5890 Serial II

Hewlett Packard Gas Chromatograph Electron Ionization Detector

Pharmacia Gel Permeation Chromatograph FPLC System

Perkin Elmer FTIR 16PC

Bruker AVANCE 500 MHz Spectrometer

Brightness Meter

Precision Reciprocal Shaking Bath

II. Synthesis of 1-(3,4-Dimethoxyphenyl)ethanol^[30]

4.32g (22.2mmol) of (3,4-Dimethoxyphenyl)acetophenone was dissolved in 100ml absolute ethanol, then was added 0.45g (11.9mmol) NaBH₄. Raise temperature to 60°C. After 8 hours, evaporate the solvent and dissolve the concentrate in 100ml methylenechloride. Wash the solution with deionized water

several times, and dry the solution over MgSO_4 overnight. TLC experiment should show one spot under UV light. If not, separate the desired product with a column loaded with silica gel using a mixture of ethyl acetate and hexane (volume ratio 1:6).

III. General Procedures of Oxidation of Lignin Model Compounds

1. General Procedure of Uncatalyzed Oxidation

To a solution of 0.05mmole substrate in 5 mL $(\text{CH}_3)_2\text{CO}$ were added 0.57g 30% aqueous solution of H_2O_2 (approximately 5mmole) and 0.05mmole 3,4-dichlorotoluene as the internal standard. $(\text{CH}_3)_2\text{CO}$ was then added to the resulting solution until the total volume is 10mL. The uncatalyzed oxidation was carried out at 50 and 60°C. Samples of the reaction mixture were then taken at the certain time intervals by pipette followed by extraction with CH_2Cl_2 . The sample solutions were dried over Na_2SO_4 , then analyzed by GC and GCMS.

2. General Procedure of Catalyzed Delignification

To a solution of 0.05mmole substrate in 5 mL $(\text{CH}_3)_2\text{CO}$ were added 0.57g 30% aqueous solution of H_2O_2 (approximately 5mmole) and 0.05mmole 3,4-dichlorotoluene as the internal standard. $(\text{CH}_3)_2\text{CO}$ was then added to the resulting solution until the total volume is 10mL. The catalyzed oxidation was initiated by addition of 0.9mg (0.0012mmole) precatalyst $[\text{LMn(III)}(\mu\text{-O})_2(\mu\text{-O})_2]$.

OAC)Mn(IV)](ClO₄)₂ that was oxidized by H₂O₂ *in situ* into the catalyst [LMn(IV)₂(μ-O)₃Mn(IV)](ClO₄)₂. The catalyzed oxidations were carried out at 30, 40, 50, and 60°C. Samples of the reaction mixture were taken at the certain time intervals by pipette followed by extraction with CH₂Cl₂. The sample solutions were dried over Na₂SO₄, then analyzed by GC and GCMS.

IV. General Conditions of Gas Chromatography and GCMS

1. General Conditions of Gas Chromatography

GC analysis was carried out with HP 5890 Series II gas chromatograph instrument fitted with a HP 5 column (crosslinked 5% diphenyl and 95% dimethyl polysiloxane; 30m x 0.25mm i.d., film thickness 0.25μm). Samples were injected by the HP automatic injector into the injection port at 200°C. The initial oven temperature was 80°C and was held for 1 min, then raised at a rate of 20°C/min to 200°C and held for another 1 min. The oven temperature was again raised at the rate of 20°C/min to 280°C and held for 1 min. Signals were detected by a FID at temperature of 240°C.

2. General Conditions for GCMS

GCMS analysis was carried out with HP GCD Plus gas chromatography instrument fitted with a HP 5 column (crosslinked 5% diphenyl and 95% dimethyl polysiloxane; 30 m x 0.25 mm i.d., film thickness 0.25 μm). Samples were

injected manually into the injection port at 200 °C. The initial oven temperature was 80 °C and was held for 1 min, then raised at a rate of 20 °C/min to 200 °C and held for another 1 min. The oven temperature was again raised at the rate of 20°C/min to 280°C and held for 1 min. Signals were detected by an EID at 240°C.

V. Compounds Identified by GCMS Analysis

1. Internal Standard

3,4-dichlorotoluene: GC-retention time, 4.4 min; eims, m/z (rel. int.), 164 (M+4⁺, 4.3), 162 (M+2⁺, 26.1), 160 (M⁺, 41.3), 127 (32.6), 125 (100).

2. Compounds Identified in the Oxidation Mixture of (3,4-Dimethoxyphenyl) ethanol

(3,4-Dimethoxyphenyl)ethylene: GC-retention time, 5.9 min; eims, m/z (rel. int.), 164 (M⁺, 100), 149 (36.2), 133 (0.9), 121 (14.9), 103 (23.4), 91 (38.3), 77 (31.9).

1-(3,4-Dimethoxyphenyl)ethanol **3**: GC-retention time, 7.0 min; eims, m/z (rel. int.), 182 (M⁺, 61.7), 167 (91.5), 164 (9.5), 151 (4.9), 139 (100), 124 (29.8), 108 (18.1), 91 (6.4), 77 (16.0).

3,4-Dimethoxyacetophenone **6**: GC-retention time, 7.3 min; eims, m/z (rel. int.), 180 (M^+ , 45.7), 165 (100), 149 (0.9), 137 (10.6), 122 (7.4), 107 (4.3), 79 (11.7).

3. Compounds Identified in the Oxidation Mixture of 1-(3,4-Dimethoxyphenyl)-1-propene

3,4-Dimethoxybenzaldehyde **12**: GC-retention time, 6.7 min; eims, m/z (rel. int.), 166 (M^+ , 100), 165 (61.7), 151 (10.6), 137 (4.3), 95 (31.9), 77 (27.7), 165 (59.6).

1-(3,4-Dimethoxyphenyl)-1-propene **6**: GC-retention time, 6.8 min; eims, m/z (rel. int.), 178 (M^+ , 100), 163 (36.2), 148 (0.9), 147 (10.6), 135 (8.2), 115 (12.8), 107 (37.2), 91 (31.9), 77 (14.9).

1-(3,4-Dimethoxyphenyl)propane-1,2-epoxide **10**: GC-retention time, 7.3 min; eims, m/z (rel. int.), 194 (M^+ , 16.0), 165 (0.1), 151 (100), 135 (3.2), 107 (10.6).

1-(3,4-Dimethoxyphenyl)propane-1,2-diol **11**: GC-retention time, 8.7 min; eims, m/z (rel. int.) 212 (M^+ , 7.4), 194 (1.1), 178 (2.1), 168 (12.6), 167 (100), 152 (0.9), 151 (6.4), 139 (63.8), 124 (21.3), 108 (14.9), 95, 77.

4. Compounds Identified in the Oxidation Mixture of **E**-Diphenylethene

E-Diphenylethene 7: GC-retention time, 8.3 min; eims, m/z (rel. int.) 180 (M^+ , 100), 179 (97.9), 178 (61.7), 165 (48.9), 152 (12.8), 89 (23.4), 76 (14.9).

E-Diphenyletheneoxide 13: GC-retention time, 8.4 min; eims, m/z (rel. int.) 196 (M^+ , 48.7), 195 (50.7) 167 (100), 152 (19.7), 105 (12.3), 90(84.5), 89(95.8), 77 (32.4) 63 (24.6), 51 (21.1).

VI. Acid Treatment and Delignification of Pulp

100g O.D. Pulp (3% consistency) was added in a plastic bag placed in a constant temperature water bath. The pH of the pulp slurry was adjusted to 2.0 by sulfuric acid then the temperature was raised to 70°C. After 30 minutes, the bag was removed from the bath and the resulting pulp was dewatered to about 33% consistency for the subsequent experiments. 3g OD pulp treated with sulfuric acid was placed in an Erlenmeyer flask. 0.06g NaOH (2% on O.D. pulp) and 0.12 g H_2O_2 (4% on dry pulp) were added to the flask in the form of a mixed solution simultaneously with 0.45mL 0.4mg/mL catalyst solution (60 ppm on O.D. pulp). Depend on the starting consistency of the pulp to be delignified, an appropriate amount of DI water was added immediately to bring the final consistency to 10% under vigorous mechanical stirring. The delignification was allowed to proceed for designated periods of time then taken out of the flask to be washed with 50mLx3 deionized water. After being dewatered, the pulp was ready for handsheet making.

VII. Determination of Kappa Number, Viscosity, and GE Brightness

Handsheets were made from the pulp obtained using the procedure described above and conditioned at $23\pm 1^{\circ}\text{C}$ and $50\pm 2\%$ relative humidity overnight ^[76]. Then the GE brightness of the handsheets was measured according to Tappi Standard T 452 ^[77]. The kappa number and the viscosity were measured according to Tappi Standard T236 ^[78] and T230 ^[79], respectively.

VIII. General Procedures of Residual Lignin Isolation from Pulp

30g pulp (O.D.) was beaten in PFI mill to a final Canadian Standard Freeness of 200-300mL. 10g (O.D.) beaten pulp was placed into an Erlenmeyer flask to which was added 5,000 units of cellulase in 10mL pH 4.5 acetate buffer solution. Then the buffer solution was added until the total volume is 200mL. The flask was placed in to a 45°C shaker bath for 48 hr. Remove the hydrolates by centrifugation. The residual was then mixed with 2,500 units of cellulase in 5mL acetate buffer solution. Add buffer solution to a final volume of 100mL. After 48 hr incubation at 45°C , the residual was again collected by centrifugation, and was mixed with 1,250 units of cellulase in 2.5mL acetate buffer solution. Add buffer solution to a final volume of 50mL, and incubate the mixture for 48hr at 45°C . After collecting the residual, repeat the last enzymatic treatment. Collect the residual, and dissolve it in 1M NaOH solution at a lignin concentration about 1%. The solution was stirred vigorously at room temperature under

nitrogen atmosphere for 2 hr. Remove any precipitate by centrifugation, and acidify the supernatant to pH 2.5. Collect the precipitate by centrifugation and redissolve it in an appropriate amount of 2M NaOH solution to a lignin concentration of 1%. The solution was stirred under the nitrogen atmosphere at 70°C, for 72 hr, then neutralized with acetic acid. The resulting mixture was dialyzed in a dialysis tube having a molecular weight cut off of 1,000 against water for 48 hr, dilute acetic acid (pH 3.0) for 24hr, and water again for 24 hr. The purified lignin is recovered upon freeze-drying, and dried in a drying pistol until constant weight.

IX. General Procedures of Lignin Precipitation from Spent Bleaching Liquor

50mL spent bleaching liquor is acidified to pH 2.5, the precipitate was collected by centrifugation and redissolved in 25mL 0.5 M NaOH solution. The solution was neutralized by hydrochloric acid, and dialyzed against water in a dialysis tube with a molecular weight cut off of 1,000 for 48 hr. Lignin was then recovered upon freeze-drying and dried in a drying pistol until the sample reaches a constant weight.

X. General Condition for Gel Permeation Chromatography

Gel permeation chromatography was performed on Pharmacia FPLC system equipped with a Superdex 75 column. 5mg Lignin sample was dissolved in 5mL mixture solution of 0.1M NaOH and 0.5M lithium chloride. All samples were eluted with 0.1M NaOH and 0.5M lithium chloride mixture solution at a flow rate of 0.3mL/min. The signals were detected by an UV detector at 900nm.

XI. General Conditions for FTIR

FTIR experiments were performed using Perkin-Elmer FTIR 16-PC system. A standard 12-mm diameter pellet was prepared by pressing 1mg lignin sample into 150mg potassium bromide anhydrate in an evacuated die. The data were acquired by 64 scans from 4400 to 400cm⁻¹.

XII. General Conditions for ¹H-¹³C Correlation 2D NMR

Approximately 30mg of lignin sample was dissolved in 0.75ml DMSO-d₆, sometimes under carefully controlled heating. Then NMR spectra were recorded at 25°C by a Bruker AVANCE 500 MHz spectrometer (1996 model) with the Oxford narrow bore magnet (1989 model). The system was controlled by the SGI INDY host workstation and the data was processed using the XWINNMR. The spectrometer was equipped with three frequency channels with waveform

memory and amplitude shaping, three channel gradient control units (GRASP II) and one variable temperature unit, as well as one unit for pre-cooling and temperature stabilization. All measurements have been carried out with a 5mm ID 1H/BB (109Ag-31P) triple-axis gradient probe (ID500-5EB, Nalorac Cryogenic Corp.). The operational frequency for ^1H nucleus was 500.128MHz, and conditions for analysis included a pulse width of 10msec, PL of 0.00dB and a 1.5sec pulse delay (d1).

CONCLUSIONS

I. The reactivity of hydrogen peroxide as an oxidant to residual lignin in chemical pulp was significantly improved upon the catalysis of $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$. The selectivity of hydrogen peroxide delignification was also considerably improved, indicated by the viscosity data. The catalyzed delignification followed the first order kinetics and was mostly complete within 20 minutes, which offers an attractive feature of this process. Because of the decreased activation energy of delignification due to the application of catalyst, the rate of delignification was not very sensitive towards changes of temperature. Consequently, the degree of delignification was satisfactory at relatively low temperatures. In the meantime, hydrogen peroxide remained an excellent nucleophile as far as the brightness improvement is concerned.

II. Hydrogen peroxide catalyzed by $\text{Mn(IV)-Me}_4\text{DTNE}$ is believed to degrade the low molecular mass portion of the residual lignin to soluble fragments very quickly. From the reaction mechanism point of view, hydrogen peroxide catalyzed by $\text{Mn(IV)}_2\text{-Me}_4\text{DTNE}$ is able to oxidize the α -hydroxyl group, and the conjugated C-C double bond in non-phenolic lignin moieties to the corresponding carbonyls and epoxides, respectively. The resulting carbonyls and epoxides undergo further degradation to form soluble fragments. The FTIR spectra agreed with this finding. It is also evident that in addition to the side chain oxidation, a significant amount of aromatic ring cleavage also takes place. This has been

confirmed by ^1H - ^{13}C correlation 2D NMR data. In addition, due to the formation of hydroxyl radicals by the concerted reaction mechanism, the fibers are better preserved compared to the traditional hydrogen peroxide delignification.

III. According to simulation using WinGEMS4.0, this catalyzed hydrogen peroxide delignification process is profitable if the cost of the catalyst is kept below \$330/kg. Even though the cost of catalyst is expected to be high at the present time, catalyzed hydrogen peroxide delignification still offers a great deal of savings due to reduced energy cost and reduced chemical cost. With the potential of lowering the cost of catalyst, the catalyzed hydrogen peroxide delignification is very cost effective.

FUTURE WORKS

I. Simplify the synthesis of the catalyst.

The cost of the catalyst is the major concern of this hydrogen peroxide delignification process. Research is ongoing to develop an easy-to-use method to synthesize the catalyst, and to improve the yield of the reactions.

II. Identify more easily available catalyst.

The mechanism of this catalytic process is centered on the concerned release of hydroxyl radicals with the oxidation of residual lignin. Therefore, similar selectivity is expected when a catalyst that is able to regulate the formation of hydroxyl radicals through concerted reaction mechanism is applied.

III. Regenerate deactivated catalyst.

The kinetics of the model compound study and the pulp delignification share a common behavior, that is, the rate of the reaction increases sharply at the beginning then levels off after approximately 20 minutes. Most likely, the deactivation of the catalyst is the reason of the leveling off of the reaction. If the deactivated catalyst can be regenerated easily, significant profit is expected even if the cost of the catalyst is high.

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