

**CHARACTERIZATION AND ENHANCEMENT OF CARBOXYL GROUPS IN
SOFTWOOD KRAFT PULPS DURING OXYGEN DELIGNIFICATION**

A Dissertation
Presented to
The Academic Faculty

By

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In Partial Fulfillment
Of the Requirements for the Degree
Doctor of Philosophy in the
School of Chemical & Biomolecular Engineering

Georgia Institute of Technology

December 2006

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ACKNOWLEDGEMENTS

First I would like to express my sincere gratitude to my thesis advisor, Dr. Arthur J. Ragauskas for his encouragement, guidance, advice, and support throughout this study. Meanwhile I appreciate Dr. Jeffery Hsieh, my co-advisor whose constant enthusiasm is a source of inspiration and his insight was always very helpful. Sincere appreciation is extended to my thesis committee, Dr. Yulin Deng, Dr. John Muzzy, and Dr. Preet Singh for their support throughout this project.

In addition, many thanks go out to the following colleagues, faculty, and staff:

Dr. Yunqiao Pu for his kind help to run NMR and support to prepare for double-stage oxygen delignified samples; Mrs. Lenong Allison for her strong support through my experimental study; Mr. Cameron Thomson and Rob Lowe for their thoughtful discussion with me about my research; Dr. Kristina Knudsen for her reviewing my paper and thesis manuscript; Dr. Xinsheng Chai in recovery group for his great help and support for fiber carboxyl group analysis using Headspace Gas Chromatography; Mr. Charles Courchene for equipment operation training and running ozone bleaching; Ms. Tuwanda Strowbridge for her training in paper physical strength testing; Mr. Shaobo Pan for his help to take SEM pictures; Dr. Paul Gateholm and Ms. Anne Wenolel at Chalmers Institute of Technology in Sweden for their help and support with ESCA; Dr. Dehai Zhao in University of Georgia for his support and analysis for the nonlinear model variable estimation using SAS program.

I would like to thank Dr. Jian Jiang at International Paper for his kind help to obtain mill produced unbleached SW kraft pulp for this research and financial support from IPST member companies and IPST endowment.

Most of all, the most recognized people throughout my Ph.D. study are my wife Cuihua Zhu and my son Han Zhang who gave me their endless love, support, patience, and sacrifices.

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NOMENCLATURE

AA	Active alkali
AQ	Anthraquinone
CMC	Carboxymethylcellulose
D	Chlorine dioxide
D+C	Chloration stage with 50% chlorine dioxide substitution
DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
DTPA	Pentasodium salt of diethylenepentaacetic acid
E	Alkaline extraction
EO	Alkaline extraction reinforced with oxygen
EP	Alkaline extraction reinforced with peroxide
EPO	Alkaline extraction reinforced with peroxide and oxygen
ECF	Elemental chlorine free
EDTA	Disodium salt of ethylenediaminetetraacetic acid
ESCA	Electron spectroscopy for chemical analysis
GC	Gas chromatography
HW	Hardwood
HSGC	Headspace gas chromatography
HexA	Hexenuronic acid
k.f.	Kappa factor
ICP	Inductively coupled plasma-atomic emission spectroscopy
KN	Kappa number
LCC	Lignin-carbohydrate complex
MC	Medium consistency
NMR	Nuclear magnetic resonance
O	Oxygen stage
OwO	Double oxygen stage with an inter-stage washing
P	Hydrogen peroxide stage
Q	Chelation stage
RL	Residual lignin

SEM	Scanning electron microscopy
SW	Softwood
TCF	Totally chlorine free
TEA	Tensile energy adsorption
TMP	Thermomechanical pulp
UV	Ultraviolet
WRV	Water retention value
Z	Ozone stage

SUMMARY

This study first examined the kinetic changes of fiber carboxyl group content in bulk fiber, polysaccharide, and residual lignin of oxygen delignified pulps during one-stage oxygen delignification of a low kappa (32.5) kraft pulp. The carboxyl group contents determined in different chemical components of oxygen delignified pulps were used to establish the distribution of carboxyl groups in lignin and pulp polysaccharide and decouple the responses from residual lignin and polysaccharide. Following this study, two high kappa (~ 49.0) SW kraft pulps prepared were delignified through two-stage oxygen delignification. Fiber carboxyl group profiles of these pulps were elucidated to investigate the effect of lignin content of incoming unbleached kraft pulps on fiber carboxyl group formation. Due to a limitation to enhance fiber carboxyl groups only by parameter optimization during one- and two- stage oxygen delignification, a catalytic oxidation program was developed to enhance fiber carboxyl group content by 52.2 – 116.0 % employing 0.10 - 0.18% of a bismuth ruthenium pyrochlore oxide catalyst during oxygen delignification. The mechanism of fiber carboxyl group formation through the catalytic oxidation was proposed. The main factor on carboxyl group formation in pulp carbohydrate was identified to follow the order: NaOH > oxygen pressure > reaction temperature through a 3-factor at 3-level (L_93^3) orthogonal experimental design and the optimal conditions were found at 2.5% NaOH, 85-100 °C, and 800-960 kPa O₂ during the catalytic oxidation.

ECF bleaching study was also conducted on these pulps with higher amount of fiber carboxyl group enhanced at early pulping and oxygen delignification processes. The bleaching results demonstrated that the early-stage enhanced fiber carboxyl groups were

partially retained through ECF bleaching. Additionally, fiber carboxyl groups of fully bleached kraft pulps were ~ 20% different from typical bleaching protocols, depending on bleaching chemicals used and the bleaching sequences such as DEDED, (D+C)EDED, ODEDD, and OQPZP.

This study finally demonstrated that an increase of fiber carboxyl groups by 17.4-62.1% through chemical oxidation resulted in reduced fiber curl, increased fiber WRVs, 4.3-25.5 % increase in paper tensile index at comparable pulp viscosity; and 4.4 -30.1% increase in paper dry tensile stiffness.

CHAPTER 1 INTRODUCTION

Paper is made from pulp fiber with some parameters such as length, width, wall thickness, mainly established in trees, and a variety of properties formed during pulping and bleaching process. Today's pulp and paper industry shows increasing interest in producing better fibers to make new products with improved properties, reduced costs, and acceptable environmental performance, while utilizing the existing manufacturing infrastructure.

As highlighted in the recent TAPPI technology summit [1], fiber engineering has been acknowledged to have great potential to improve almost all grades of paper and papermaking process. An important component of fiber modification is the control of fiber charge.

Early studies by Lindstrom *et al* [2] and Scallan *et al* [3] established that pulp fibers in water behaved as a swollen polyelectrolytic gel when provided sufficient charge. A primary characteristic of a polyelectrolytic gel is its ability to swell due to electrostatic repulsions between existing like charges. The maximum swelling effect occurs when charged groups are ionized in low ionic strength solutions. The ionizable groups in cellulosic fiber may be carboxylic acids, sulfonic acids, phenols or hydroxyl groups, depending on different pulping process and pH involved. Under typical papermaking process conditions, the main groups that are ionized and contribute to fiber charge are carboxyl groups and sulfuric groups. The effect caused by anionically charged groups in a fiber and resulting counter cation groups cause additional water to enter fiber wall by osmotic pressure. The accompanying swelling increases fiber conformability and inter-fiber bonding. Therefore, fiber charge/acidic groups of pulps are of great importance for

both the behavior of fibers in pulping and papermaking process and the properties of the final paper products.

In terms of these effects, a series of fiber modifications have been conducted for mechanical and chemical pulps mainly by introducing acidic groups into fibers through carboxymethylation, grafted polymerization, chemical adsorption/precipitation, and enzymatic modification [4-10]. However, these treatments require additional operation units and rarely put into practice.

In 2003, Ragauskas *et al* [11] developed a fiber charge database for USA mill produced fully bleached kraft pulps. The main chemicals used from these pulp bleaching processes were molecular oxygen, chlorine dioxide, hydrogen, and/or ozone. The fiber charge of these pulps was found in the range of 16 -70 $\mu\text{mol/g}$ and fiber sources as well as process parameters were the only fiber charge control mechanism. Evidently, acidic groups can be introduced into fibers during pulp bleaching by chemical oxidation of fiber chemical components. The amount of the acidic groups varies depending on process conditions and chemicals used. Therefore, a practical interest is to understand how different chemical treatments affect fiber charge differently and the possibility to enhance fiber charge/acidic groups from existing bleaching processes. The present study was motivated by fiber charge development/carboxyl group formation during oxygen delignification and bleaching processes.

A benchmark study was first conducted on fiber carboxyl group formation during typical one-stage oxygen delignification of a SW kraft pulp. Then the subsequent studies focused on the following aspects: elucidation of fiber carboxylic acid content profiles during double-stage oxygen delignification when the incoming unbleached SW kraft

pulps contained more residual lignin (*i.e.* higher pulp kappa number); fiber carboxyl group enhancement by catalytic oxidation during typical one-stage oxygen delignification; and the retention of fiber carboxyl groups introduced during pulping and oxygen delignification through a ECF bleaching sequence and the effect of different bleaching protocols on fiber carboxyl group content. Finally, the effect of fiber carboxyl groups enhanced by chemical oxidation on fiber and paper sheet properties was evaluated. The research results were presented in the format of publications. Because of this format, there are some duplication of the introduction and experimental sections. The detailed experimental procedures were generally described in APPENDICES. In addition, these papers have been changed only slightly from the published or submitted version.

An outline of the subsequent chapters for this thesis is as follows:

CHAPTER 2 summarized the background and fundamentals for this work. It included chemical composition of pulp fiber, the origin of fiber charge and the effects of fiber charge/acidic groups on fiber and paper physical properties, oxygen delignification chemistry and its effect on fiber charge/acidic groups, and the effect of bleaching chemicals on fiber charge/acidic group formation.

CHAPTER 3 outlined the objectives of the dissertation research.

CHAPTER 4 described the dynamic change of carboxylic acid formation in bulk fiber, polysaccharide fraction, and residual lignin during typical one-stage oxygen delignification of a SW kraft pulp with a low kappa number of 32.5 as well as the relative contributions of each chemical component to total fiber carboxylic acid content.

CHAPTER 5 elucidated fiber carboxyl group content profiles from the integration of high kappa (~49) cooking and extended oxygen delignification. The carboxylic acid

content in bulk fiber as well as both residual lignin and holocellulose isolated from unbleached kraft pulps and the corresponding oxygen delignified pulps were comparatively studied.

CHAPTER 6 reported the results of employing a catalyst into one-stage oxygen delignification to increase carboxyl groups in polysaccharide of oxygen delignified pulps. The optimal conditions were investigated using a 3-factor at 3-level orthogonal experimental design.

CHAPTER 7 first examined the retention of fiber carboxyl groups enhanced during pulping and oxygen delignification after fully ECF bleaching. Then a comparative study was conducted to examine how different bleaching protocols affect fiber carboxyl group content when bleaching a pulp to a common pulp brightness of ~88% (TAPPI brightness). The effects of second alkaline extraction stage and hydrogen peroxide on pulp fiber carboxyl group content were also studied.

CHAPTER 8 examined the effect of fiber carboxyl groups enhanced by oxidation of bleaching chemicals on fiber properties as well as dry tensile strength and tensile stiffness of paper sheet dried at room and an elevated temperature (105 °C).

CHAPTER 9 summarized the overall conclusions from this study.

CHAPTER 10 listed some recommendations for future research work.

In addition, APPENDIX M described carbonate formation in the effluent during one-stage oxygen delignification of a SW kraft pulp (kappa number of 32.5). An empirical model for carbonate formation was developed and validated by the lab experimental data. The applications of the model for prediction of pulp kappa number in solid phase and process control strategy were also discussed.

CHAPTER 2 LITERATURE REVIEW

2.1. Chemical composition of wood fiber

Wood is essentially composed of cellulose, hemicelluloses, lignin, and extractives. Table 2.1 presents major chemical compositions of some wood species. Each of these components contributes to fiber properties, which ultimately impact product properties.

Table 2-1. Chemical Composition of Some Wood Species [12]

Constituent	Scots Pine (<i>Pinus sylvestris</i>)	Spruce (<i>Picea glauca</i>)	Eucalyptus (<i>Eucalyptus camaldulensis</i>)	Silver Birch (<i>Betula verrucosa</i>)
Cellulose (%)	40	39.5	45.0	41.0
Hemicellulose				
-Glucomannan (%)	16.0	17.2	3.1	2.3
-Glucuronoxylan (%)	8.9	10.4	14.1	27.5
-Other polysaccharides (%)	3.6	3.0	2.0	2.6
Lignin (%)	27.7	27.5	31.3	22.0
Total extractives (%)	3.5	2.1	2.8	3.0

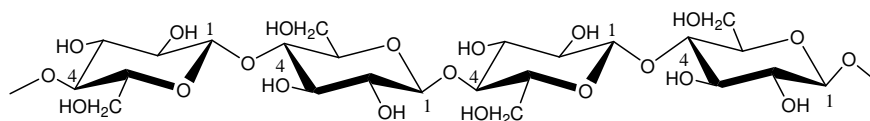


Figure 2.1. The Structure of Cellulose [12]

2.1.1. Cellulose

Cellulose, the major chemical component of fiber wall and contributing 40-45% of the wood's dry weight, is composed of linear chains of D-glucose linked by β -1,4-glycosidic bonds (Figure 2.1) with the degree of polymerization from 10,000 in native wood to 1,000 in bleached kraft pulps [12]. Each D-anhydroglucopyranose unit possesses hydroxyl groups at

C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols [13]. The molecular structure imparts cellulose with its characteristic properties: hydrophylicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of hydroxyl groups [14].

Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure [12] and give cellulose a multitude of partially crystalline fiber structures and morphologies [14]. The degree of crystallinity of different cellulose samples are presented in Table 2-2 [13].

Table 2-2. X-Ray Crystallinity of Some Cellulose Materials [13]

Sample	X-ray crystallinity (%)
Cotton linters	56-63
Sulfite dissolving pulp	50-56
Prehydrolyzed sulfate pulp	46
Viscose rayon	27-40
Regenerated cellulose film	40-45

The ultrastructure of native cellulose (cellulose I) has been discovered to possess unexpected complexity in the form of two crystal phases: I_{α} and I_{β} [15]. The relative amounts of I_{α} and I_{β} have been found to vary between samples from different origins. The I_{α} -rich specimens have been found in the cell wall of some algae and in bacterial cellulose, whereas I_{β} -rich specimens have been found in cotton, wood, and ramie fibers [16, 17]. The crystal and molecular structure, together with hydrogen-bonding system in cellulose I_{α} and I_{β} has been determined recently by Nishiyama *et al* using atomic-resolution synchrotron and neutron diffraction data recorded from oriented fibrous

samples prepared by aligning cellulose microcrystals from the cell wall of the freshwater alga [18] and tunicin [19].

Mechanical damages to wood fiber usually produce dislocations in cellulose lattice (called “disturbed zones”), which decreases the order and makes cellulose more available for chemical attack [20].

The presence of crystalline cellulose, with regions of less order, and the size of the elementary fibrils work together to produce interesting combination of contrary properties such as stiffness and rigidity on one hand and flexibility on the other hand [20]. Crystalline cellulose has a very limited accessibility to water and chemicals. Chemical attack can therefore be expected to occur primarily on amorphous cellulose and crystalline surface.

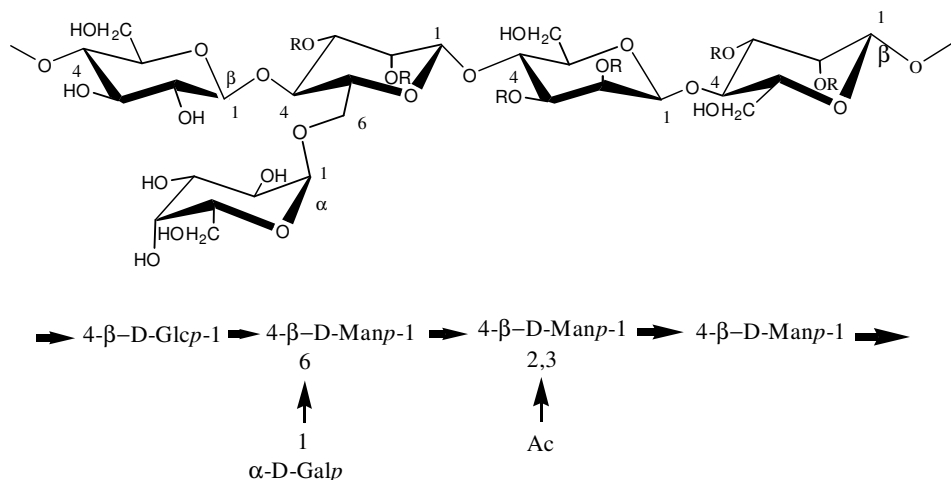


Figure 2.2. Principal Structure of Galactoglucomannans in Softwood [12]

Sugar units: β -D-glucopyranose (GlcP); β -D-mannopyranose (Manp); β -D-galactopyranose (Galp). R = CH₃CO or H. The lower representation is the abbreviated formula showing the proportions of the units (galactose-rich fraction)

2.1.2. Hemicellulose

Unlike cellulose, hemicelluloses have lower DP (only 50-300) with side groups on the chain molecule and are essentially amorphous. The main hemicelluloses of softwood are galactoglucomannans (Figure 2.2) and arabinoglucuronoxylan (Figure 2.3), while in hardwood is glucuronoxylan (Figure 2.4) [12]. Table 2-3 summarizes the main structural features of hemicelluloses appearing in both softwood and hardwood [12].

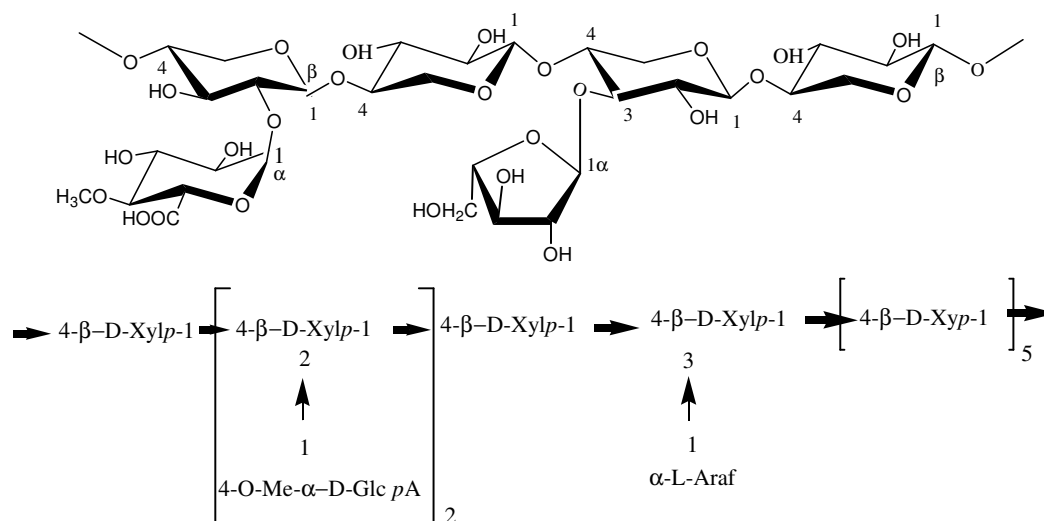


Figure 2.3. Principal Structure of Arabinoglucuronoxylan in Softwood [12]

Sugar units: β -D-xylopyranose (XylP); 4-O-methyl- α -D-glucopyranosyluronic acid (Glc pA); α -L-Arobinofuranose (Araf). The lower representation is the abbreviated formula showing the proportions of the units.

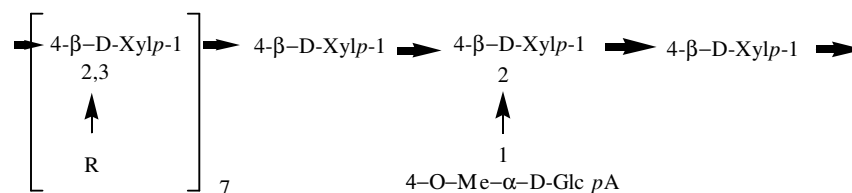


Figure 2.4. Principal Structure of Glucuronoxylan in Hardwood [12]

Sugar units: β -D-xylopyranose (XylP); 4-O-methyl- α -D-glucopyranosyluronic acid (Glc pA); R = Acetyl group (CH_3CO).

Table 2-3. The Major Hemicellulose Components in Softwood and Hardwood [12]

Wood	Hemicellulose type	Amount (% on wood)	Composition			DP
			Units	Molar ratios	Linkage	
SW	Galacto-glucomannan	5-8	β -D-Manp β -D-Glcp α -D-Galp Acetyl	3 1 1 1	1 \rightarrow 4 1 \rightarrow 4 1 \rightarrow 6	100
	(Galacto)-glucomannan	10-15	β -D-Manp β -D-Glcp α -D-Galp Acetyl	4 1 0.1 1	1 \rightarrow 4 1 \rightarrow 4 1 \rightarrow 6	100
	Arabino-glucuronoxylan	7-10	β -D-Xylp 4-O-Me- α -D-GlcpA α -L-Araf	10 2 1.3	1 \rightarrow 4 1 \rightarrow 2 1 \rightarrow 3	100
HW	Glucuronoxylan	15-30	β -D-Xylp 4-O-Me- α -D-GlcpA Acetyl	10 1 7	1 \rightarrow 4 1 \rightarrow 2	200
	Glucomannan	2-5	β -D-Manp β -D-Glcp	1-2 1	1 \rightarrow 4 1 \rightarrow 4	200

Unlike glucomannan, xylan contains acidic groups (glucuronic acid) (Figure 2.3 and Figure 2.4) and has a molecular structure similar to cellulose when their branches are removed from xylan, which may make xylan combine with cellulose in more ordered structure after kraft pulping [21].

Glucomannan is very sensitive to kraft cooking conditions and is already dissolved to a large extent at the beginning of kraft cooking, whereas xylan is more resistant [20]. Therefore, the content of xylan in chemical softwood kraft pulp becomes almost the same

as that of glucomannan in spite of considerably higher content of glucomannan in softwood (Table 2-4). Hemicelluloses in hardwood kraft pulps are dominated by xylan [20]. Furthermore, relocation of xylan in fiber can occur during kraft cooking due to the sorption of xylan from cooking liquor. Consequently, enhanced hemicellulose (xylan) levels on pulp fiber surfaces have been reported for both softwood and hardwood kraft pulps [22, 23].

Table 2-4. The Change of Chemical Composition before and after Kraft Pulping of Birch and Pine [12]

Constituents	Pine (<i>Pinus sylvestris</i>)	Birch (<i>Betula verrucosa</i>)	Pine kraft pulp	Birch kraft pulp
Cellulose (%)	40.0	41.0	35.0	34.0
Hemicellulose				
-Glucomannan (%)	16.0	2.3	4.0	1.0
-Glucuronoxytan (%)	8.9	27.5	5.0	16.0
-Other polysaccharides (%)	3.6	2.6	-	-
Lignin (%)	27.7	22.0	3.0	2.0
Total extractives (%)	3.5	3.0	0.5	0.5

In addition, all sugar components can take part in the formation of lignin carbohydrate complexes by covalent linkages between lignin and carbohydrates in both wood [24, 25] and pulp [26-28]. The most frequently suggested LCC-linkages in native wood are benzyl ester, benzyl ether, and glycosidic linkages [29]. However, the benzyl ester linkage is alkali-labile and may therefore be hydrolyzed during kraft pulping process. The latter two linkages are alkali-stable and would survive from the hydrolysis during kraft pulping process. The existence of xylan-lignin, glucan-lignin, glucomannan-lignin-xylan, and galactan-lignin complexes in unbleached kraft pulp (pine and spruce)

and oxygen delignified pulps has been identified by isolation of LCCs through enzymatic hydrolysis [30, 31].

Table 2-5. The Accessible Xylan Structure in Pine and Birch Kraft Pulps [32]

Wood	Pulp	Kappa number	Xylan (% of d.p.)	Side groups in accessible xylan (mol/100 mol xylan)		
				HexA	MeGlcA	Arabinose
Pine	Conventional batch	25.9	11.1	6.6	0.8	8.8
	MCC + O ₂	13.8	n.d.	7.6	0.8	7.8
	Superbatch	12.5	18.0	1.4	0.2	6.3
Birch	Conventional batch	18.2	29.0	6.0	2.1	-
	Superbatch	10.5	23.8	3.1	0.3	-

n.d. = not determined; MCC: modified continuous cooking; d.p.: oven-dried pulp

Uronic acids present as side groups in xylan chain (Figure 2.3 and Figure 2.4) are modified or removed and xylan polysaccharide is partly depolymerized during pulping process. Table 2-5 compares the chemical structure of accessible xylan in industrial and laboratory made kraft pulps [33]. Softwood pulps cooked with modified continuous cooking and conventional batch methods appeared to be rather similar with respect to the uronic acid profile of the accessible xylan, whereas lower kappa number superbatches contained very low amounts of these acids. Depending on the cooking methods, the uronic acid profile may differ profoundly from that of conventional pulps.

In addition, there is a difference for these uronic acids in softwood and hardwood kraft pulps. As shown in Table 2-6, birch kraft pulp contained much higher uronic acids and HexA than pine kraft pulp due to their different amount of xylan [33].

Table 2-6. MeGlcA and HexA Content in Conventional Unbleached Pine and Birch Kraft Pulps [32]

Pulp	Kappa number	Xylan (% of d.p.)	MeGlcA (% of d.p.)	HexA (% of d.p.)
Birch	25.9	29.0	0.9	1.4
Pine	18.2	11.1	0.3	1.0

d.p.: oven-dried pulp

2.1.3. Lignin

Lignin is an amorphous, cross-linked, and three dimensional phenolic polymer with the highest concentration in middle lamella. However, secondary fiber wall contains 70% of the lignin despite at lower lignin concentration [12]. It is widely accepted that the biosynthesis of lignin stems from the polymerization of three types of phenylpropane units as monolignols: coniferyl, sinapyl, and *p*-coumaryl alcohol [12]. Figure 2.5 depicts the three structures. Softwood lignin is composed mainly of coniferyl alcohol units, while hardwood lignin is composed mainly of coniferyl and sinapyl alcohol units.

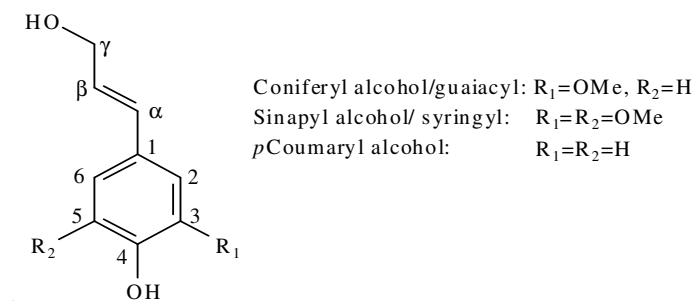


Figure 2.5. The Three Building Blocks of Lignin [12]

The polymerization process is initiated by an enzyme-catalyzed oxidation of the monolignol phenolic hydroxyl groups to yield free radicals [12]. A monolignol free radical can then couple with another monolignol free radical to generate a dilignol.

Subsequent nucleophilic attack by water, alcohols, or phenolic hydroxyl groups on the benzyl carbon of the quinone methide intermediate restores the aromaticity of the benzene ring. The generated dilignols then undergo further polymerization to form protolignin [12].

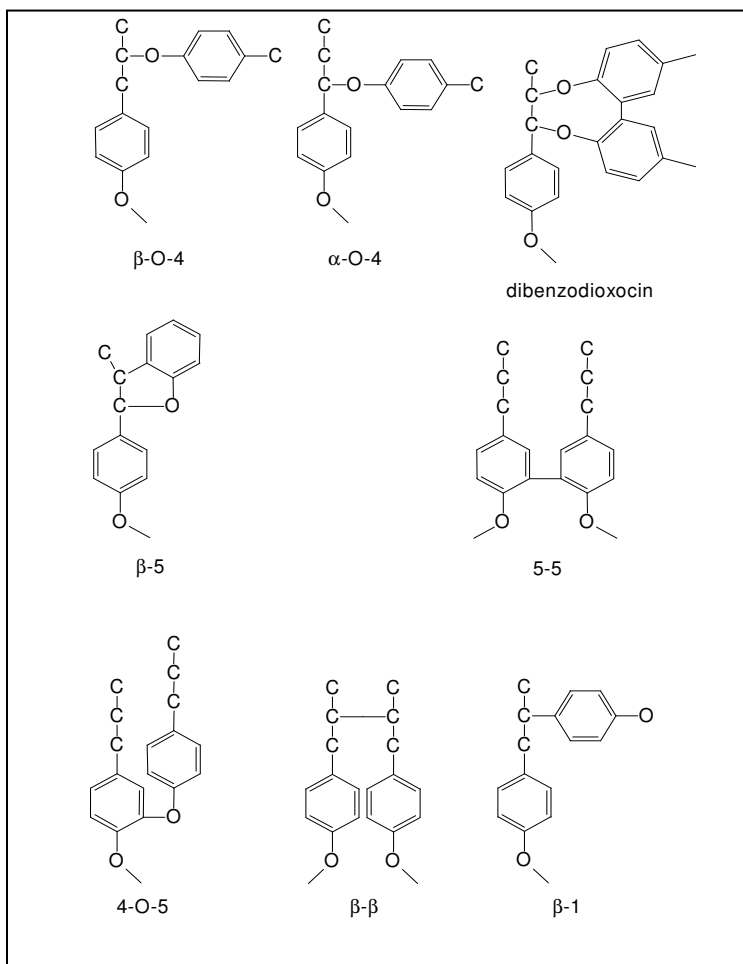


Figure 2.6. Common Linkages between Phenylpropane Units in Lignin [12]

The exact structure of protolignin is virtually unknown. However, improvements in methods for identifying lignin degradation products and advancements in spectroscopic methods have enabled scientists to elucidate some of the structural features of lignin, such as the dominant linkages between phenylpropane units and their abundance, as well

as the frequency of some functional groups [12]. Figure 2.6 depicts some of common linkages found in softwood lignin. The abundance of these types of linkages is shown in Table 2-7 [12, 34]. Table 2-8 illustrates the abundance of some of the functional groups found in softwood lignin [35].

Table 2-7. Proportions of Different Types of Linkages Connecting the Phenylpropane Units in Softwood Lignin [12, 34]

Linkage Type	Dimer Structure	Percentage
β -O-4	Phenylpropane β -aryl ether	50
β -5	Phenylcoumaran	9-12
5-5	Biphenyl	15-25
5-5/ α -O-4	Dibenzodioxicin	10-15
4-O-5	Diaryl ether	4
β -1	1,2-Diaryl propane	7
β - β	β - β -linked structures	2

Table 2-8. Functional Groups in Softwood Lignin (per 100 C9 Units) [35]

Functional Group	Native MWL Spruce Lignin	Pine Kraft Lignin
Carbonyl	0.8	-
Carboxyl	-	2.1
Olefinic + Substituted aromatic	39	54
Aliphatic CH _x -OR	23.6	9.5
Methoxyl	11.2	9.1
Aliphatic CH _x	4.9	10.4

A model for the macromolecular structure of lignin was described by Alder as presented in Figure 2.7a [36]. This model has been modified to consider a new linkage

structure (*i.e.* Dibenzodioxicin) connecting the phenylpropane units of softwood lignin (Figure 2.7b) [37]. It is important to note that the model proposed by Adler does not depict the actual structure of lignin, but serves as a tool to visualize the linkages and functional groups that are believed to occur in lignin.

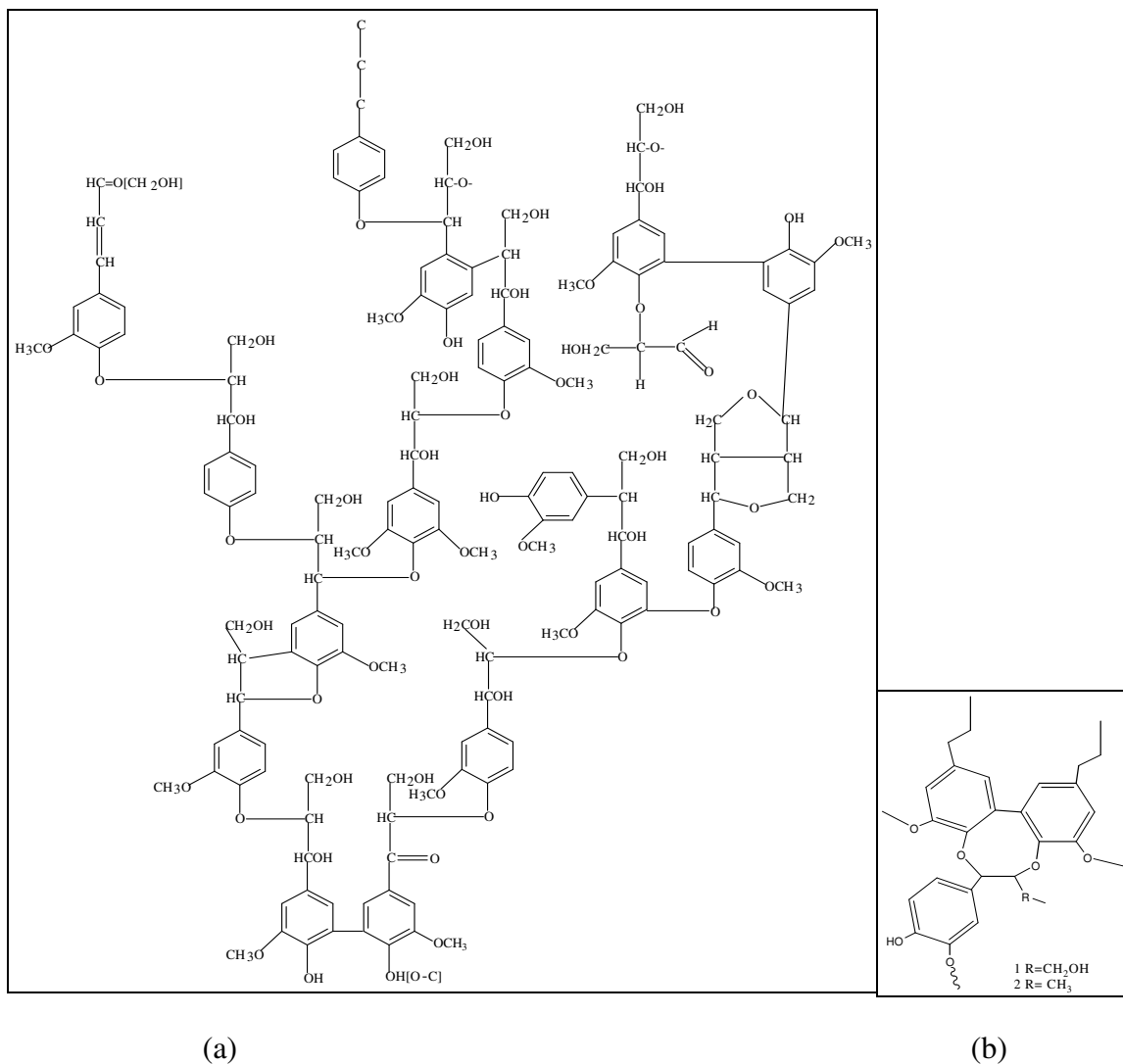


Figure 2.7. Models for the Structure of Spruce Wood Lignin [36, 37]

Lignin is much less hydrophilic than either cellulose or hemicelluloses. Unless hydrophilic groups are introduced into lignin during pulping, it has a general effect of

inhibiting water adsorption and fiber swelling. Unlike mechanical pulping, the main objective of chemical pulping is delignification, in many cases together with a modification of the swelling property of residual lignin. Delignification in kraft process occurs mainly through fragmentation and creation of phenolates into lignin fragments and the residual lignin. The rather low swelling of kraft lignin is due mainly to a low amount of carboxyl acid groups. Bleaching solubilizes lignin primarily through the introduction of carboxyl groups and fragmentation. The very low amount of residual kraft lignin in bleached kraft pulp can be expected to have an increased amount of carboxyl acid groups and hence a considerably stronger swelling power. In fact, a fair amount of acidic groups in fully bleached pulps could be attributed to the very low amount of oxidized residual lignin structures [38].

2.1.4. Extractives

A large diversity of wood components, usually representing a minor fraction (less than 10% in trees), are called extractives. Extractives include terpenoids and steroids, fats (fatty acid and glycerol esters), waxes (fatty acid esters of fatty alcohols, terpene alcohols, and sterols), and phenolic constituents (stilbenes, lignans, tannins, and flavonoids). Most of them are removed during kraft pulping [12, 39]

2.2. Kraft pulping and bleaching

2.2.1. Kraft pulping

The objective of chemical pulping processes is to remove enough lignin to separate cellulosic fibers one from another, producing a pulp suitable for the manufacture of paper and other related products [40]. Krafting pulping process is the most commonly used

chemical process, accounting for 98% of chemical pulp production in the United States and 92% of the chemical pulp production in the world [41].

In a conventional kraft cook, an aqueous solution of sodium hydroxide and sodium sulfide, also known as white liquor, is reacted with wood chips in a large pressure vessel, called a digester. The white liquor and the chips are heated to a temperature of about 170°C and allowed to cook at that temperature for about two hours [40]. During this treatment, the hydroxide and hydrosulfide anions react with the lignin, causing lignin macromolecule to fragment into smaller water/alkali-soluble fragments. The fragmentation of lignin macromolecule proceeds through the cleavage of the linkages holding phenylpropane units together, with a concomitant generation of free phenolic hydroxyl groups [35, 42]. The presence of these hydroxyl groups increases the hydrophilicity of lignin and lignin fragments. As a result, the solubility of lignin in the cooking liquor is increased. The carbon-carbon linkages, being more stable, tend to survive from pulping process.

Delignification in kraft cooking proceeds in three distinct phases: the initial phase, the bulk phase, and the final or residual phase. The initial phase of delignification takes place up to a temperature of about 150°C and is controlled by diffusion [40]. The bulk phase includes a heating period where the temperature goes from about 150 °C to 170°C and then stays at 170°C for approximately 2 hours. The rate of delignification in the bulk phase is controlled by chemical reactions. Most of the lignin is removed in this phase. The residual or final phase, in which the rate of delignification significantly decreases, begins when about 90% of the lignin has been removed and marks the end of the cook. The selectivity in this phase is poor, and further pulping could result in significant

degradation of carbohydrate. The remaining or residual lignin, typically 4-5% (by weight) at the end of a conventional softwood kraft cook, is removed via bleaching [40, 43].

2.2.2. Pulp bleaching

Pulp bleaching is the treatment of lignocellulosic pulps with chemical agents to increase their brightness. Brightness is increased by decolorizing or dissolving the colored components in pulp, primarily lignin [12, 40]. Delignifying bleaching, which results in both high and permanent brightness, is applicable to chemical pulps. Common bleaching chemicals are chlorine (C), oxygen (O), hypochlorite (H), chlorine dioxide (D), hydrogen peroxide (P), and ozone (Z). Because of environmental concerns, chlorine has been partially or completely replaced by chlorine dioxide [12, 40].

Single-stage application of bleaching chemicals has a limited effect on brightness improvement or delignification. Multi-stage application of bleaching chemicals can provide enhanced benefits. It is usually performed in a bleaching sequence comprising several treatment stages with bleaching chemicals and alkali. Interstage washing, which removes dissolved impurities, is partially responsible for improvement in the extent and efficiency of bleaching. In addition, multi-stage sequences take advantage of the different action of each chemical and provide synergy in bleaching or delignification. For example, D(EO)DED and OD(EPO)DED are classical ECF sequences for market kraft pulp and OZ(EO)D is the first sequence using ozone for commercial production of kraft pulp in North America [44, 45].

Process conditions govern the extent and efficiency of bleaching reactions and also strongly influence the selectivity [44, 45]. Chemical consumption during a bleaching

stage is the single most important parameter. The pH has a profound effect on most bleaching reactions and may be controlled by addition of alkali or acid before or with the bleaching chemical. The extent to which the applied chemicals are consumed depends on the kinetics of chemical reaction, reaction temperature, and the reaction time. In addition, chemical reaction rates are often increased by increasing chemical concentration, which is fixed by the original equipment design which fixes pulp consistency. Typical process conditions for bleaching a softwood kraft pulp in OD(EO)DED sequence are presented in Table 2-9.

Table 2-9. Typical Process Conditions for Bleaching Softwood Kraft Pulp in OD(EO)DED Sequence [45]

	O	D	(EO)	D	E	D
Chemical applied (kg/t)						
O ₂	30	-	5	-	-	-
ClO ₂	-	15	-	8	-	5
NaOH	30	-	25	5	5	-
End pH	>11.0	3.0	10.6	3.5	10.6	4.0
Temperature (°C)	95	60	70	70	70	70
Time (min)	30	30	60	180	60	180
Pulp consistency (%)	12	3	12	12	12	12

2.3. Fiber charge/acidic groups

2.3.1. The origin

2.3.1.1. *Native wood*

It was reported that most of the carboxyl groups in native wood were of the uronic acid type found in xylan [12], mainly 4-O- methylglucuronic acid (MeGlcA) [8, 12, 46, 47] (Table 2-10). Additionally, a certain fraction of carboxyl groups is located in

accessible regions of the cell wall, which is restricted for diffusion and no ion exchange can take place there. Furthermore, the acidic function of some of carboxyl groups is blocked because of their existence in the form of rather stable lactones or esters [47] as demonstrated in Table 2-10 for the increase of acid groups after hydrolysis.

Table 2-10. Carboxyl Groups in Some Wood Species [47]

Species	Methylglucuronic acid content (mmol/100g)	Carboxylic acid content (mmol/100g)		
		Total	Accessible to ion exchange	
			Untreated	Hydrolyzed*
<i>Picea abies</i>	7	15-25	7	13
<i>Pinus sylvestris</i>	8	15	5	9
<i>Betula Verrucosa/pubesens</i>	15	25-35	6	17

* The sample has been treated to hydrolyze the carboxylic acid lactones and esters.

Another source of carboxyl acid groups in wood is the fraction of free fatty acids and resin acids present in extractives, which is markedly decreased during alkaline pulping [47].

2.3.1.2. Unbleached kraft pulps

The constituents of fiber wall can undergo chemical changes during cooking and bleaching processes, which naturally change overall fiber carboxyl group content. As shown in Figure 2.8 [48], the total amount of charged acidic groups decreases as pulp lignin removal proceeds during kraft pulping.

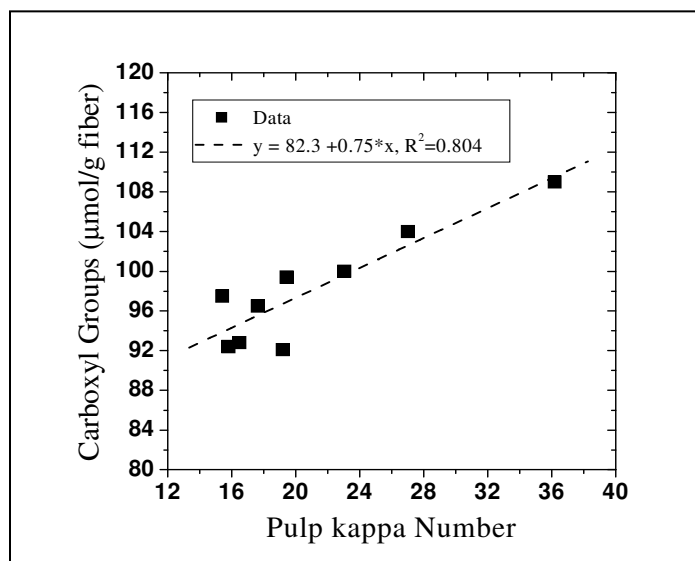
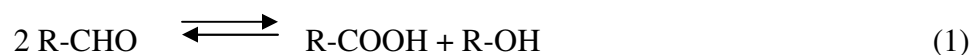


Figure 2.8. The Relationship between Fiber Carboxyl Group Content and Kappa Number of Kraft SW pulps [48]

During alkaline pulping process, lactones and esters present in wood are hydrolyzed and acid groups are formed [12]. Residual lignin in kraft pulps contains some aliphatic carboxyl groups, which are formed by oxidation or in disproportionation reactions of the Cannizzaro type (Equation 1) [8]. Up to 20 % of the phenylpropane units can be transformed to carboxylic acids in this way [47].



Although some new carboxyl groups are formed in residual lignin fraction during alkaline pulping [49, 50], most of them are removed from fiber in the subsequent bleaching process, and will not contribute to the fiber charge of fully bleached pulps.

During kraft pulping, carboxyl acid content of pulp polysaccharide is likely to decrease because of the dissolution of some acidic polysaccharides, particularly xylan [51-53], to which the majority of the carboxylic acid groups in kraft pulps are attached

[47]. Investigations of the xylan structure have shown that the amount of MeGlcA side groups in xylan decreases at the beginning of the cook. In the meanwhile, the amount of another acidic group, HexA increases [32, 54] (Figure 2.9), *i.e.*, the initial MeGlcA present in xylan is to a large extent converted to HexA. HexA is an β -elimination product of MeGlcA, as shown in Figure 2.10. HexA accounts for most of the carboxyl groups present in the xylan after the cook, although some degradation occurs during delignification.

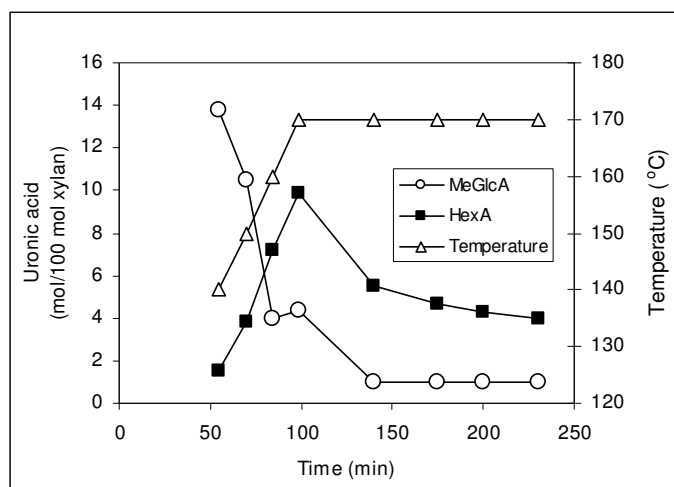


Figure 2.9. Structure of Accessible Xylan as a Function of Kraft Cook Time [32]

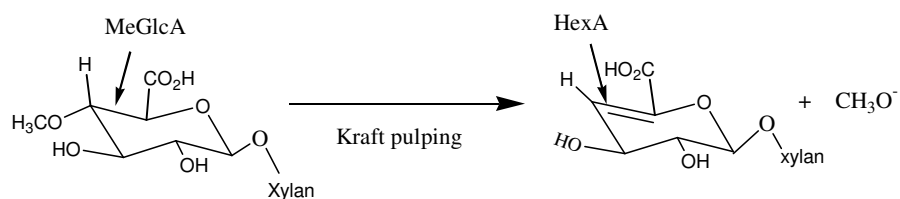


Figure 2.10. Chemical Conversion of MeGlcA to HexA during Kraft Pulping [32, 54]

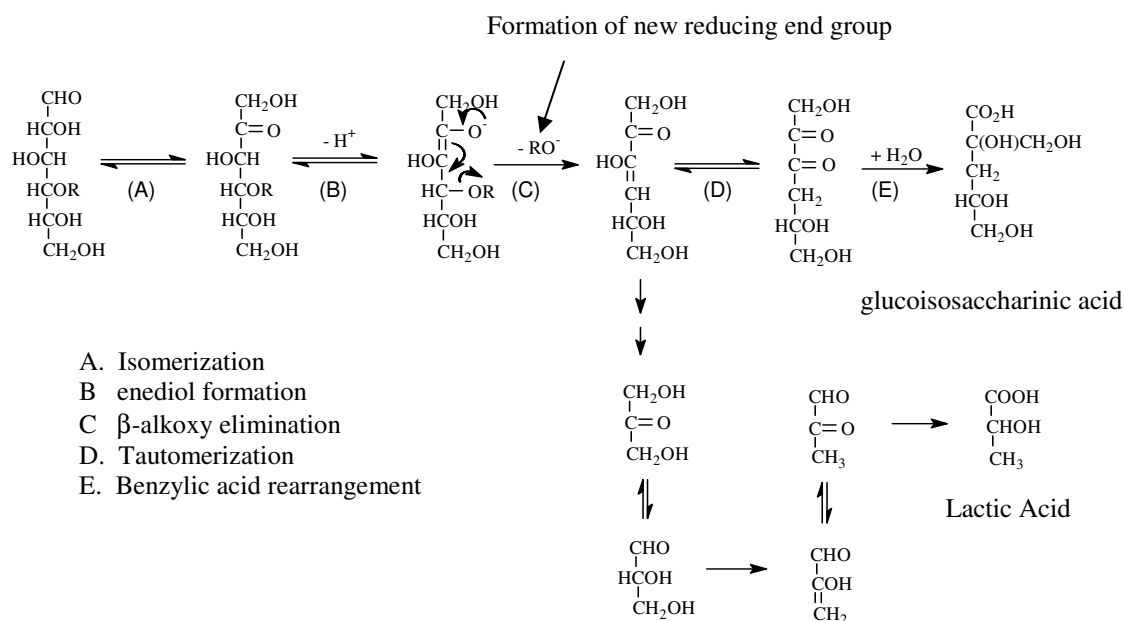


Figure 2.11. Alkaline Peeling of 1,4-Linked Polysaccharides (Cellulose, Glucomannan, and Xylan) [43]

During kraft pulping, some new carboxyl groups are created in the carbohydrate due to peeling reaction, a stepwise depolymerization of carbohydrate occurs at the reducing end sites of the polymer chain, as shown in Figure 2.11 [55]. The reaction generates a monosaccharide that undergoes a benzylic acid rearrangement to form an isosaccharinic acid. Meanwhile the reaction forms a new reducing end on the remainder of the polymer, which can further undergo peeling reactions until the introduction of a carboxyl group at the reducing end, by so-called stopping reaction as shown in Figure 2.12. The stopping reaction stabilizes the carbohydrate against further peeling via generating a carboxylic acid group at the terminal end of the polymer chain. But the amount of these reactions is naturally dependent on the processing conditions and the size of fragmented molecule chains.

Therefore, the main chemical components to contribute fiber charge of unbleached kraft pulps are residual lignin and polysaccharide that consist of uronic acids, oxidized reducing ends, and HexA.

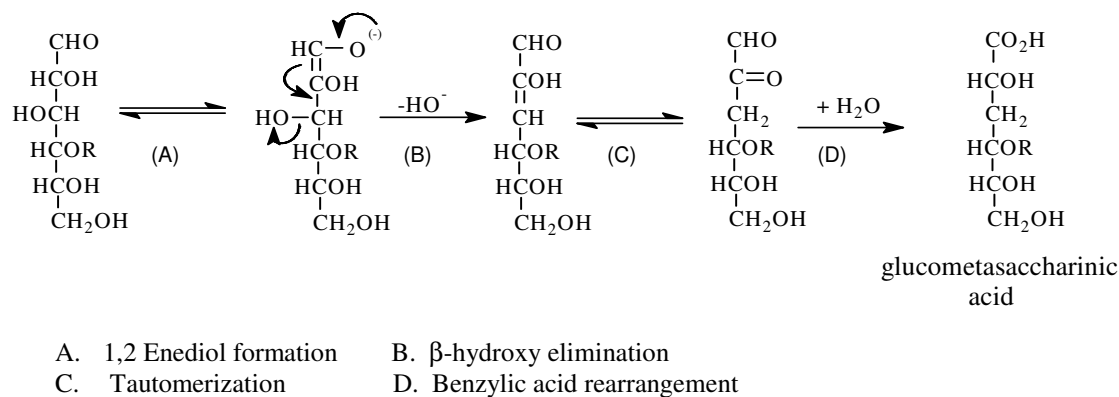


Figure 2.12. The Formation of Metasaccharinic Acid during Stopping Reaction of Carbohydrate [43]

2.3.1.3. Bleached kraft pulps

Generally, bleaching process decreases total fiber charge of chemical pulps due to the dissolution of lignin and hemicelluloses [56] as shown in Table 2-11 [8, 46, 57]. Evidently, pulp fiber charge decreases more from ECF bleaching than from TCF bleaching.

Bleaching of pulp with ECF and TCF agents such as oxygen, ozone, peroxide, and chlorine dioxide can result in the formation of carboxyl groups bound to residual lignin by oxidation [49, 58, 59]. On the other hand, the presence of negative groups increases the solubility of lignin, and consequently the modified lignin molecules are effectively dissolved during bleaching [58].

Table 2-11. Carboxylic Acid Content in Different Pulps [8, 46, 57]

Pulp	Total acidic content ($\mu\text{eq/g}$)
Unbleached SW kraft pulp (KN= 25.9)	85
ECF (O D E D E D) SW kraft pulp	32
TCF (OO QQ PO) SW kraft pulp	70
Unbleached HW kraft pulp (KN= 18.2)	125
ECF (D EO P D D) HW kraft pulp	55
TCF (OO Q PO) HW kraft pulp	120

KN = kappa number.

According to Buchert *et al* [32], HexA is unreactive towards peroxide and oxygen, whereas HexA reacts with electrophilic bleaching chemicals such as chlorine, chlorine dioxide, and ozone. Accordingly, HexA will not contribute significantly to the fiber charge of TCF and ECF fully bleached pulps.

Carboxyl groups can be also introduced into polysaccharides during oxidative bleaching. Bleaching agents such as ozone, oxygen, and peroxide can introduce carboxyl groups into cellulose and hemicelluloses through direct oxidation [12]. In addition, the presence of carbonyl groups in polysaccharide gives rise to alkali-labile glycosidic bond breakdown to form aldonic acid products either by peeling reaction or stopping reactions. Therefore, aldonic acids in polysaccharides are considered the main contributors to fiber charge in fully bleached pulps [32].

In addition, a fair amount of carboxyl groups in fully bleached pulps could be attributed to a very small amount of oxidized lignin structures [60].

2.3.2. Topochemical distribution of fiber charge

It has been found that charged groups on fiber surface can increase fiber specific bonding strength [4, 5, 61]. It is therefore appropriate to consider the topochemical distribution of fiber charge resulting from pulping and bleaching procedures. Studies of mechanical pulping and bleaching procedures on fiber charge topochemical distribution demonstrated that mechanical pulping and bleaching procedures did not greatly affect the charge ratio (surface charge/total charge) [62, 63]. Several investigators have also studied the effects of chemical pulping and bleaching procedures on distribution of acidic groups [64, 65]. Table 2-12 summarizes charge ratios of bleached kraft pulps at different pulping and bleaching processes without intended fiber surface modification [8]. The charge ratios in Table 2-12 demonstrate that ordinary pulping and bleaching processes do not change the charge distribution between surface and bulk in fiber to any great extent.

Table 2-12. Fiber Charge Affected by Different Bleaching Sequences [8]

Pulp sample	Total charge ($\mu\text{eq/g}$)	Surface charge ($\mu\text{eq/g}$)	Charge ratio* (%)
ECF HW(DEPPDD)	55	7	12.7
TCF HW(OOQPO)	119	16	13.4
TCF HW(OOQQPO)	152	17	11.2
TCF SW(OOQQPO)	68	11	16.2

*Charge ratio=surface charge/ total charge

2.3.3. Effect of fiber charge on fiber and paper properties

2.3.3.1. *Fiber-fiber bonding*

It is well known [66-68] that paper sheet strength is significantly affected by pulp fiber properties, either direct (fiber intrinsic strength) or through bonding ability (conformability, fiber strength).

Despite massive efforts over the years, our understanding of the molecular mechanisms of fiber bonding is still in its infancy. There is still argument as to the relative contribution of hydrogen bonds, ionic bonds, dipolar interactions, induced polar interactions, long-range van der Waals forces, and covalent forces in various situations [69]. There are several theories used for explaining adhesion include adsorption, chemical bonding, electrostatic, mechanical interlock, diffusion, and weak boundary layer theories [70, 71]. Most of these theories have been used to explain adhesion phenomenon in paper products.

Adopting a simple approach to paper strength, strength is seen to depend on at least the following factors: fiber strength and length; fiber bonding strength (specific bond strength and relative bond area); sheet formation; and stress distribution-residual stresses. The relative bonded area (RAB) can be estimated from either the scattering coefficient of the sheet or, perhaps better, through the BET surface area of dry paper [72]. The Page equation [67], Equation 2, describes the tensile strength of paper made from chemical pulps, considering the importance of both fiber strength ($\frac{9}{8Z}$) and bonding ($\frac{12Cg}{(RBA)bPL}$) to the strength of paper.

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12Cg}{(RBA)bPL} = \frac{1}{F} + \frac{1}{B} \quad (2)$$

where

T = finite span tensile strength (sheet strength), km

Z = zero span tensile strength (fiber strength), km

C = fiber coarseness, mg/100m

g = acceleration due to gravity, 980 cm/s²

RBA = relative bonded area

B = shear bond strength per unit bonded area, dyne/cm²

P = average fiber perimeter, mm

L = average fiber length, mm

F = resistance of individual fibers to breakage

B = resistance of interfiber bonds to breakage

Fiber strength is an important factor for the tear strength of paper [68]. It also affects on the tensile index. The correlation between the tensile index of industrially bleached kraft fibers with the rewetted zero-span tensile index was found [73], where the rewetted zero-span index was considered as a measure of both the strength of single fibers and the extent of deformation in the fibers (amount of kinks and curls). When the bonding level is low, fibers pull out from the sheet and fiber length plays a significant role with regard to tear strength, whereas at higher levels of bonding the importance of intrinsic fiber strength may increase considerably [74]. It has been reported that degree of crystallinity, degree of polymerization of cellulose, and the number of weaker affect the intrinsic fiber strength [75, 76]. Therefore, both physical and chemical properties of fibers will influence fiber strengths.

To give an exact definition of a fiber bond is not an easy thing. The conventional parameters to characterize fiber bonds are strength of bond, area of bond, and specific bond strength. A simple definition could be the fiber bond is a joint between two fibers and the area of the bond is the part of the geometrical overlapping area where the two fibers are in contact [77]. Since a good correlation between fiber optical contact area and molecular contact area, for practical applications, the relative bond area, denoting the portion of fiber surface engaged in interfiber bonding, is a very useful concept for describing the bonding of fibers in networks. There are several factors known to affect

fiber specific bond strength. The most efficient one is the use of dry strength additives. Others are the hemicellulose content of the pulp and fiber coarseness [77].

Although sheet breakage starts from the weak points in the fibers or the networks, the bonding ability of fibers can be considered to be the most important properties of softwood sulphate pulp fibers [78]. The bonding ability of fibers consists of bonding strength and the ability of fiber to form interfiber bonds (bonded area). According to Retulainen, *et al.* [79], fiber-to-fiber bonding occurs when fibers are close enough for hydrogen bonding, Van der Waals interactions, chemical bonding, and/or intermolecular entanglement to take place. The specific bond strength of any pulps is related to the hydrogen bonding that holds the pulp particles together, which is referred to as the primary theoretical fiber-to-fiber bonding mechanism. Therefore, factors that affect hydrogen bonding in papermaking will influence the specific bond strength. Hydrogen bonding between fibers can occur when the fibers become closer to 2.5 Å [80]. And bonded area is affected by fiber conformability (especially wet fiber flexibility), total surface area (fines, external fibrillation and the number of fibers in the sheet) and the factors affecting surface tension forces (external fibrillation and fines formation). Cell wall thickness of softwood fibers is the dominant morphological factor with regard to flexibility of wet fibers as well as bonding properties of the fiber network [66]. But bonding ability can developed during chemical and mechanical treatments and is a combined effect of the chemical and physical stages of fibers and fiber surfaces. Increased contacts and increased numbers of bonding sites result in greater fiber-to-fiber bonding. The bonding ability of softwood sulphate fibers can be improved by changing either bonding strength or bonded areas. Beating can cause fiber external fibrillation that

changes the physical properties of the fiber surface and creates new surfaces with different capacities to form hydrogen bonding. However, the bonding potential development of wood fibers during beating is also influenced by the process parameters of cooking, bleaching and beating. It is also suggested to improve interfiber bonding through wet pressing and addition of wet/dry strength chemicals, which indicates that fiber chemistry has a great influence on the bonding properties of paper [81].

It has been observed and suggested that certain dry strength resins, such as starches, enhance both specific bond strength and bonded area [82], where polyacrylamides and carboxyl methylcellulose (CMC) grafting primarily tend to improve the specific bond strength [83]. The difference is that those bonding agents that improve the specific bond strength but not the relative bonded area tend to maintain bulk, whereas those that enhance the relative bonded area tend to increase sheet density.

It has been recognized for a long time that the extent of swelling, generated either through mechanical stress or by dissociation of ions, is related to the bonding properties of paper [3]. It has often been assumed that variations in the swelling and flexibility of cellulose fibers are due to variations in the hemicelluloses content [75, 84]. Low lignin, high hemicelluloses contents, and a high proportion of short-chain hemicelluloses on the fiber surface all improve bonding strength [74]. Xylan has been shown to adsorb strongly onto fiber surfaces and high xylan content is favorable for interfiber bonding.

The penetration of water (swelling) affects the conformability of wet fibers by loosening the cell wall structure through debonding and separation of solid elements (microfibrils, lamellae). The increase in conformability facilitates bonding due to the fact a higher fraction of fiber surfaces can get close enough to form fiber-fiber bonds [85].

Therefore, the factors increasing fiber swelling through different chemical and mechanical treatments will improve fiber-fiber bonding.

2.3.3.2. Effect of acidic groups on fiber bonding and paper properties

It is acknowledged that pulp fiber charge is one of the primary factors influencing final paper physical sheet properties. The total charge, surface charge, and surface composition are parameters that determine certain chemical aspects of sheet consolidation and bonding between fibers. The main sources of fiber charge for wood kraft pulps are fiber carboxyl groups. The accepted explanation of the impact of fiber carboxyl groups on paper properties is based on Donnan equilibrium and has been discussed by Scallan [81, 86, 87]. If a pulp's pH is such that its carboxyl groups are deprotonated then they will be fixed anionic sites. According to Donnan theory, fixed anionic sites in a gel surrounded by a semi-permeable membrane can cause swelling because of generation of an osmotic pressure across the membrane. The osmotic pressure is due to the condition of electric neutrality. Fixed anionic sites must have cationic counter ions. This can cause the concentration of cations inside the membrane to be greater than that in bulk solution. The concentration gradient across the membrane induces an osmotic pressure which causes the gel to swell to equalize the concentration of metal ions on both sides of the membrane. The situation is illustrated in Figure 2.13 and the schematic view of fiber wall swelling is shown in Figure 2.14. Scallan's work has shown that wood pulp fibers behave as swollen gels in water surrounded by semi-permeable membranes. If the amount of charged groups is sufficiently high they behave as polyelectrolytic gels and that fiber swelling can be explained by Donnan equilibrium theory [81]. Scallan's explanation is confirmed by Talwar [88] who found that the strength

increase with carboxymethylation was realized only when the acidic groups were deprotonated.

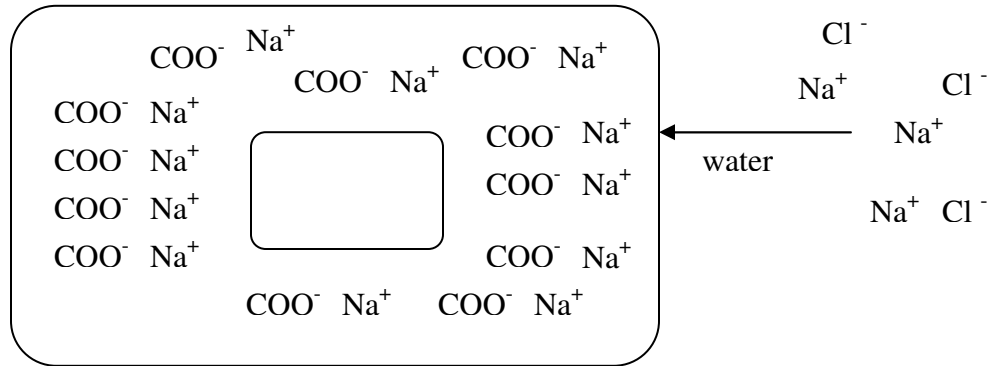


Figure 2.13. An Illustration of How Bound Acidic Groups in Pulp Fiber Can Induce Metal Ion Concentration Gradient Across the Cell Outer Wall Which Acts to Swell the Fiber

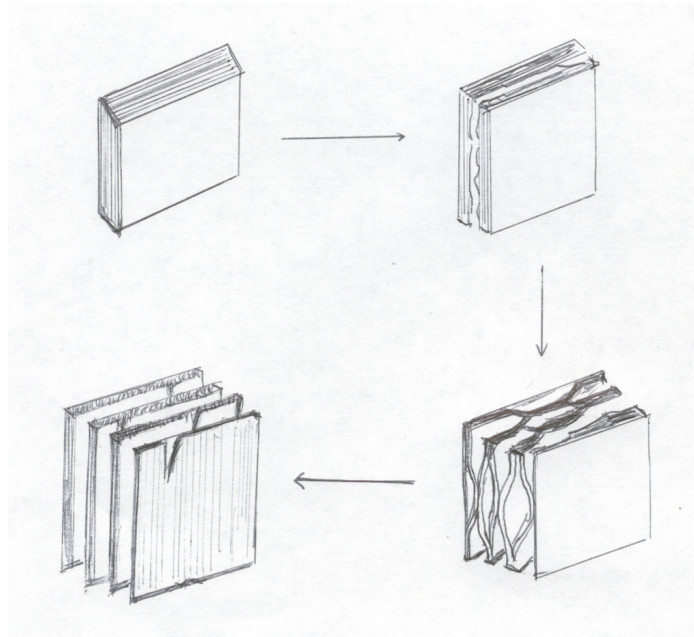


Figure 2.14. Schematic View of How the Fibrillation of the Fiber Wall Takes Place When the Swelling is Increased [89]

The basic factors controlling swelling have been reported to be the type of cation attached to acidic groups, the degree of dissociation, and the ion strength of the solution surrounding the gel [81, 87, 90]. However fiber swelling is also largely controlled by the amount of anionic groups that are bound to fiber. It has been reported that there is a linear correlation between the tensile strength of handsheets made from chemical pulp fibers and the degree of fiber swelling with the charged groups in different ionic forms [86]. If fiber carboxyl groups increase and all other factors are equal, fiber swelling increases as well. A more swollen fiber is more conformable in the wet state and results in a denser sheet with greater bonded area. Therefore, enhanced fiber carboxyl groups can influence fiber bonding by improving fiber swelling ability, which increases fiber flexibility and promotes conformability, allowing fibers to form more fiber-fiber contacts (*i.e.* increased RBA) [64].

A series of studies by Scallan *et al* [3, 81, 87] demonstrated that the strength increase of mechanical pulps after treatment with caustic soda were caused by an increase in the amount of acidic groups within the pulps. A subsequent investigation by Engstrand *et al* [62] showed that charged groups were increased in mechanical pulps from 90 $\mu\text{mol/g}$ to 250 $\mu\text{mol/g}$ using 4% hydrogen peroxide treatment at pH of 9 - 13 and 60 °C for 120 min. As a result, paper tensile index and specific elastic modulus were found to increase up to 177.7% and 117.6%, respectively [62]. Fiber swelling ability was enhanced as indicated by fiber WRV increase from 0.49 g water/g fiber to 0.65 g water/g fiber with fiber total carboxyl groups increase from 90 $\mu\text{mol/g}$ to 180 $\mu\text{mol/g}$. It was found in a study by Barzyk *et al* [6] that paper sheet tensile strength increase was achieved by fiber carboxyl enhancement through carboxymethylation on recycled cotton

fibers. The maximum effect appeared to be at an acid content of 200 meq/kg and the increase in relative bond area alone represented 71% of the increase in tensile strength.

Kitaoka *et al* [91] explored a method to increase fiber carboxyl groups by chemical oxidation of bleached kraft hardwood pulps. When a bleached hardwood kraft pulp was oxidized with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical), NaBr, and NaClO in pulp suspensions at pH 10.5 and 20 °C for 2 hours, total carboxyl group content of the oxidized pulp increased up to 0.47 mmol/g from 0.06 mmol/g in the original pulp. As a result, the tensile strength and Young's modulus for papersheets made from these pulps increased by 18.5% and 10.2%, respectively.

In a study by Zhang *et al* [57], they concluded that fiber surface charge served as one of the basic chemical parameters to characterize fiber surface properties, and both total and surface charged groups were important for physical properties of mechanical pulps.

Another potential effect of fixed acidic groups involves fiber-to-fiber specific bond strength. This effect has been explored with mechanical and bleached mechanical pulps [62, 63, 92]. To further understand how fiber surface charge affects fiber and paper properties, Barzyk *et al* [4] prepared pulp samples with uniform distribution of carboxyl groups across the fiber cell wall and with carboxyl groups located primarily on the fiber surface. It was found that acid groups introduced onto fiber surface, in a chemical way, played a key role in determining the strength of specific fiber-fiber bonding. The tensile strength was improved by 44% for fiber acid content increase from 12 meq/kg to 400 meq/kg. Specific bond strength could be enhanced by approximately 50% by surface enrichment of acid groups. The bonding increase mechanism was not fully understood

but it might be due to an ionic effect or possibly enhanced molecular flexibility of surface cellulose chains to facilitate inter-microfibril diffusion/bonding.

Lindstrom *et al* [10, 83] explored alternative technologies for increasing the amount of fiber surface charge involving adsorption of carboxyl methylcellulose (CMC) with different molecular weight ($2.8 \times 10^5 - 1.7 \times 10^6$) and degree of substitution (0.39 - 0.80) to the surface of bleached softwood kraft pulp at 80 °C. The total fiber charge was found to increase 59% and 95% with CMC-D and CMC-A attached (Table 2-13). The corresponding surface charge for both CMCs attached was 9 times higher than that in the control sample. Physical strength studies demonstrated that such a CMC topochemical modification of pulps provided substantial strength development (tensile, stiffness, TEA) as shown in Table 2-13 [83]. Neither the sheet density nor the light scattering coefficient was affected by the attachment of CMC onto the fibers. The effects were interpreted in terms of improved specific bond strength

Table 0-13. Effect of Attachment of CMCs on Fiber Swelling and Physical Properties of Paper Made of Unbeaten Bleached SW Kraft Pulps (Na-Form) [83]

CMC-sample	CMC attached (mg/g)	Charge ($\mu\text{mol/g}$) Tot./Sur.	WRV (%)	Tensile index (N.m/g)	Tensile stiffness (kN.m/g)	TEA (J/kg)	Light scattering coefficient (m^2/kg)
Control	0	40/3	136	28	3.5	790	28.5
A	5.6	84/29	154	34	4.1	1190	28.0
B	10.3	-	203	52	5.1	2080	27.3
C	5.6	-	213	51	4.8	2020	28.6
D	7.4	67/29	204	56	4.7	2270	28.3
E	6.8	-	238	64	5.6	2390	25.5

(1) CMC molecular weight: CMC-A: 0.28 million Da , CMC-B: 1.0 million Da , CMC-C: 1.1 million Da , CMC-D: 1.0 million Da, CMC-D: 1.7 million Da. (2) CMC degree of substitution: CMC-A: 0.71, CMC-B: 0.39, CMC- C: 0.80, CMC-D: 0.52, and CMC-E: 0.64. (3) CMC addition: 20 mg/g

Paper tensile strength improvement by 18.2- 36.4% was also obtained by Zhang *et al* [93] through absorbing 10-35 mg/g of Dextran (MW: 2 million Da; charge density: 0.161-0.484 meq/g) onto the bleached kraft pulps.

2.3.4. Fiber charge/carboxylic acid content determination

Currently, direct conductometric titration of cellulosic fiber is a widely used method to determine the acidic group content of fibers, in which, the pulp, after transformation of the acidic groups to the proton form, is titrated with 0.10 M NaOH or NaHCO_3 [94-97]. A conductometric titration curve (Figure 2.15) shows a rapid decrease that represents the neutralization of strong acid groups. The first equivalence point represents weaker carboxylic acids beginning to dissociate, and the second equivalence point represents the increase in conductivity due to excess NaOH [94-96].

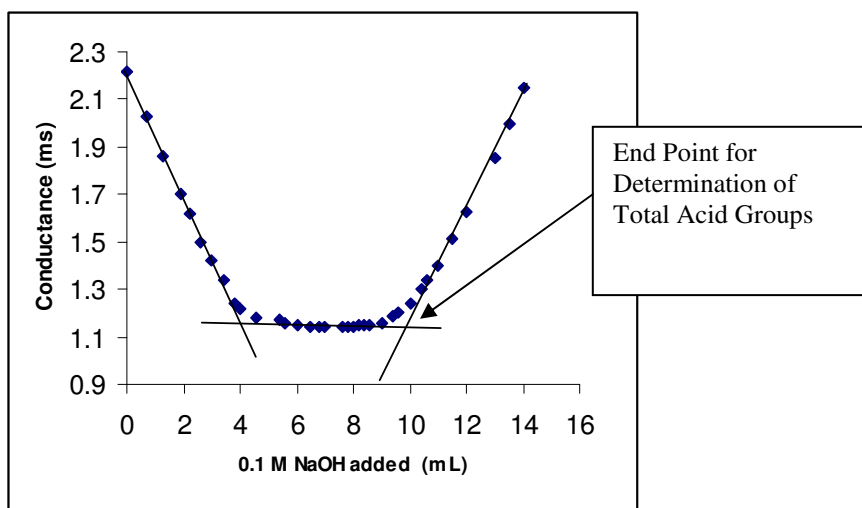


Figure 2.15. A Conductometric Titration Curve for Total Fiber Charge [94-96]

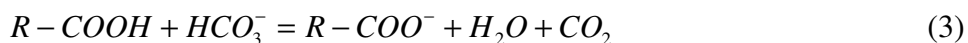
This titration method is an accurate method for determining the concentrations of strong and moderately weak acids in fiber. However, when the acid groups are very weak, the contributions of hydrogen ions to total conductivity may become so small that

accurate titration is not possible [39]. In addition, it also relies on ionization step changes that are plotted in two dimensions, and the neutralization point must be discriminated in the two dimensions, leading to errors approaching 5-10% [98].

Potentiometric titration in combination with ion exchange is also used for determination of total amount of acid groups in fiber. A full analysis of potentiometric titration curves can yield quite detailed information on the amount and dissociation constants of strong, weak, and very weak acids in fiber [39].

These methods for quantifying total carboxyl group content in wood fibers are mainly based on acid-based titration. It is found that these methods are not only complicated and time-consuming, but also demonstrated large variance among them even when they were conducted within the same laboratory.

Headspace gas chromatography (HSGC) has been widely used for analysis of volatile species in complex matrix samples. A novel method for determination of carboxylic acid content in fiber using HSGC technique has been recently developed by Chai *et al* [98]. The method is based on the conversion of carboxylic acids into carbon dioxide through the following reaction with bicarbonate after wood fiber treatment with hydrochloric acid solution.



The conversion reaction is conducted at 60 °C in a 20-mL headspace testing vial. A constant conversion reaction is achieved in 10 minutes. The carbon dioxide generated from the reaction of carboxyl groups with bicarbonate is released into the headspace of a testing vial and can be quantified by headspace gas chromatography with a thermal conductivity detector. The effect of carbon dioxide in the air of headspace of the testing

vial can be quantified through headspace measurements or eliminated by purging the testing vial using nitrogen before experiment. This method is accurate, rapid, and automated with the error less than 5% and was used in this study for total fiber carboxylic acid content determination.

Polyelectrolyte titrations were used to determine fiber surface charge as published by Wågberg *et al* [99]. A polymer with high molecular weight and high charge density was used as cationic adsorption polymer for surface charge measurement.

Prior to titration, pulp fibers are washed with deionized water, adjusted to pH 5 with 0.01 M hydrochloric acid, washed with deionized water, and converted to the sodium form at NaCl concentration of 0.01 M.

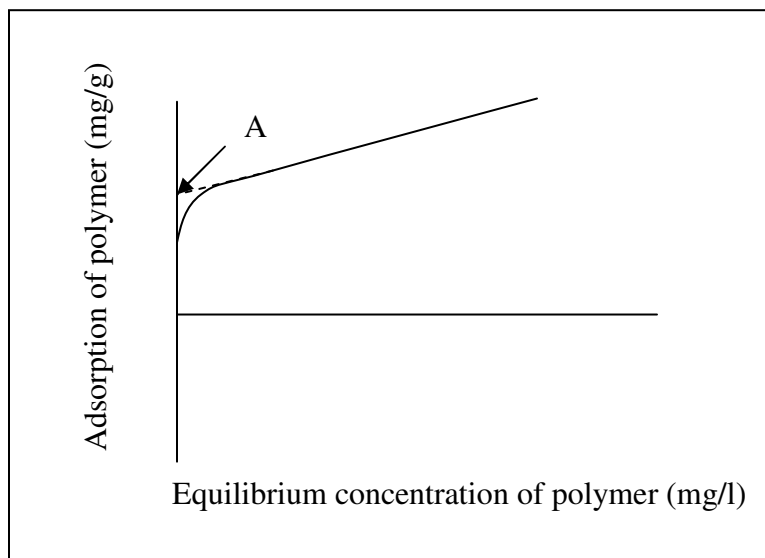


Figure 2.16. Adsorption as a Function of Equilibrium Concentration of Polymer in Solution [99]

The adsorption measurements are performed at a fiber concentration of 5g/l and $22 \pm 1^\circ\text{C}$. Different amounts of polymer are added to series of at least five 100 ml samples

adjusted to the desired pH. The mixtures are stirred for 30 min to reach adsorption equilibrium. The suspension is then filtered on a Buchner funnel and the clear filtrate is collected. The concentration of cationic polymer in solution is determined by polyelectrolyte titration, leading to adsorption isotherms of the type shown in Figure 2.16. The charge on the fibers is estimated from these isotherms by extrapolating the plateau level to zero concentration, A (mg/l) in Figure 2.16.

The amount of polymer charges adsorbed at this point (in $\mu\text{eq/g}$) is then taken to be the charge on the fiber surface [99].

2.3.5. Fiber surface analysis by ESCA

The use of ESCA (or X-ray photoelectron spectroscopy, XPS) to study cellulosic fiber was pioneered by Dorris and Gray [100, 101]. Since then, the ESCA has become one of the most important methods for determining the surface composition of paper and fiber. The only atoms analyzable by ESCA in pure cellulosic fiber are carbon and oxygen. The chemical shifts for carbon (C1s) in pulp fiber can usually be easily classified into four categories: unoxidized carbon (C-C), carbon with one oxygen bond (C-O), carbon with two oxygen bonds (O-C-O or C=O), and carbon with three oxygen bonds (O=C-O) [100, 101].

In ESCA experiment, the sample is irradiated with a source of x-ray (usually Al K alpha or Mg K alpha). The energy of the electrons ejected as a result of this interaction is analyzed. The energies of the detected electrons are used to identify the elements present on the surface of sample and the intensity of each line observed is proportional to the surface concentration. Small energy shifts (so-called chemical shifts) of each line provide

further information regarding chemical bonding. ESCA is inherently a non-destructive technique and has a sensitivity limit of greater than 0.1% [102].

The effect of sampling depth is analyzed by changing the angle of emission, *i.e.* the angle between the paper sheet and analyzer. ESCA analyzes the surface composition to a depth of 5 - 10 nm [39].

Theoretical O/C ratios and relative amounts of draft carbons with different degrees of oxidation can be calculated for carbohydrate, lignin, and extractives from their empirical carbon-oxygen formulae [103]. The amount of alkyl (C-C) carbon in these pulp components decreases in the order: extractives > lignin > carbohydrates. Thus, it should be possible to monitor the amount of surface lignin by measuring oxygen-carbon ratio and the relative amount of alkyl (C-C) carbon compared to carbohydrate-rich surface. When extractives are present in the surface, the amount of C-C carbon will further increase.

Fiber surface chemical composition is evaluated either using C1s and O1s peaks by calculating total O/C atomic ratio or relative amounts of different carbons from the intensities of carbons with different chemical shifts of C1s peak [103].

2.4. Oxygen delignification

Regulatory and economic pressures have driven pulp and paper industry to implement new delignification and bleaching practices. A major transition is the partial replacement of chlorine or chlorine dioxide delignification stages with oxygen delignification. The environmental, technological, and economic benefits of oxygen delignification include lower chemical requirements in subsequent bleaching sequences,

higher brightness with equivalent amount of chemicals, lower rejects and water consumption, as well as lower effluent discharge due to the greater recycling potential of oxygen stage effluents [104]. To date, the pioneered works have intensively addressed the oxygen/lignin/carbohydrate chemistry during oxygen delignification, the protection of carbohydrate degradation, kinetics and parameters optimization [105].

Oxygen delignification is a process by using oxygen and alkali to remove a substantial fraction of residual lignin in unbleached pulps under pressure at elevated temperatures. Therefore, process conditions have important effects on the rate of delignification and pulp properties. Table 2-14 lists some typical process conditions for oxygen delignification of SW kraft pulps [105, 106].

Table 2-14. Typical Process Conditions for Oxygen Delignification of SW Kraft Pulps [105, 106]

	Medium consistency	High consistency
Pulp consistency (%)	10-14	25-34
Retention time (min)	50-60	30-45
Initial temperature (°C)	70-105	100-115
Inlet pressure (kPa)	610-800	415-600
Outlet pressure (kPa)	260-550	415-600
Alkali (kg/t)	18-28	18-23
Oxygen consumption (kg/t)	20-24	15-24
MgSO ₄ (kg/t)	0-2.5	0-1.5

However, the effectiveness of an oxygen delignification stage is limited to 50% delignification. Beyond this level, severe cellulose degradation takes place, resulting in the deterioration of pulp viscosity and strength properties [105, 107]. Therefore, the selectivity issue is a drawback of oxygen delignification. A number of approaches aiming

at extending oxygen delignification have been proposed and implemented in pulp and paper industry [108, 109]. One of them is double stage oxygen delignification that can reach a limit of 70% delignification for a SW kraft pulp. With this advancement, an approach has been developed in the laboratory by halting cook at a high kappa number (*i.e.*, 40-50 for SW kraft pulps) before the selectively of kraft cooking decreases in the terminal phase. The high kappa kraft pulp is then delignified by extended oxygen delignification. Studies on the integration of high kappa cooking and extended oxygen delignification followed by ECF bleaching have been shown to provide 3-4% yield benefits over conventional bleaching technologies [109-115]. These observed yield benefits are then further amplified by reducing organic load in the recovery furnace, resulting in potential productivity benefits for recovery boiler-limited mills [108, 109].

Although a higher delignification limit (*i.e.* 70%) can be reached by double oxygen stages, a significant fraction of residual lignin remains even after four-stage oxygen delignification. One of the themes in oxygen delignification research is to achieve a more fundamental understanding of chemical factors governing delignification and carbohydrate damage during the process.

2.4.1. Oxygen chemistry

Oxygen is an interesting molecule and has two unpaired electrons in its outer shell at ground state. Therefore each of these electrons has an affinity for other electrons of opposite spin. Although less reactive than other free radicals, it shares their tendency to react with appropriate substrates at regions of high electron density.

When oxygen reacts with substrate like lignin, it may be reduced to water by one-electron transfer in four successive stages giving rise to intermediate products, namely,

hydroperoxy radical (HO_2^\bullet), hydrogen peroxide (H_2O_2), and hydroxyl radical (HO^\bullet), as well as their counterparts (Figure 2.17) [12].

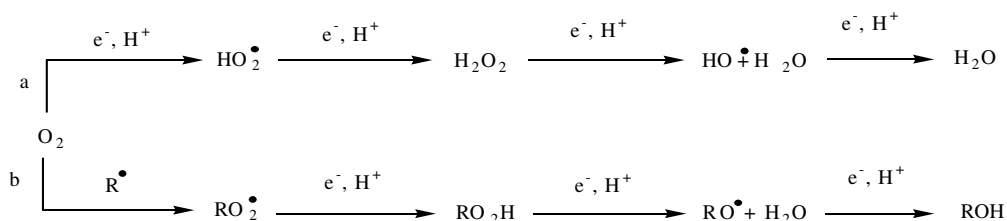
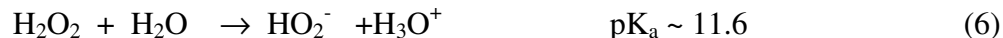


Figure 2.17. Reduction of Oxygen by One-Electron Transfer Mechanism [12]

(a) Each of four reaction steps involves the addition of one electron and one proton, giving rise to hydroperoxy radicals, hydrogen peroxide, and hydroxyl radicals as intermediate products. (b) The corresponding organic intermediates are formed when oxygen reacts with an organic radical R^\bullet .

When the pH of medium is sufficiently high, ionization will take place as follows:



Since bleaching with oxygen is normally performed at rather high pH (> 11.0), reactive species generated from oxygen include hydrogen peroxide anion (HO_2^-), dissociated oxide and superoxide hydroxyl radical ($\bullet\text{O}^-$, $\bullet\text{O}_2^-$), and undissociated and highly reactive hydroxyl radical (HO^\bullet) (Equations 4-6). The formation of superoxide and hydroxyl radicals under the conditions of oxygen delignification and their involvement in oxidative degradation of lignin and carbohydrate structures have been demonstrated by Gierer *et al* [116-122] using a controlled γ -radiolysis and various type of lignin models.

2.4.2. Lignin chemistry

A number of studies in the past addressed lignin oxidation by molecular oxygen under alkaline conditions. The early efforts centered on elucidating reaction mechanism of oxygen delignification using lignin model compounds under homogeneous reaction conditions [123-128]. These studies suggested that the reactivity of phenylpropane units bearing free phenolic hydroxyl groups far surpassed that of non-phenolic structures. The ideal lignin structure for the highest possible reactivity during oxygen delignification should contain a phenolic group with a hydroxyl or a methoxyl group in the ortho position and also α - β unsaturation in the side chain [128]. To this effect, Gierer regarded the role of free phenolic units as the centers of radical formation [121].

Table 2-15. Phenolic Group Content (mmol/g) in Kraft Lignin after Oxygen Delignification as Determined by Quantitative ^{31}P NMR Spectroscopy [129]

Time of O-delignification (min)	Non-condensed guaiacyl units	Total condensed units	5,5' condensed units	p-Hydroxyl-phenyl units	Total free phenolic units
0	0.87	0.96	0.44	0.04	1.87
10	0.63	0.69	0.34	0.10	1.42
20	0.55	0.77	0.38	0.12	1.44
50	0.42	0.70	0.37	0.15	1.27
80	0.44	0.75	0.42	0.15	1.34
160	0.44	0.72	0.49	0.15	1.31

Unbleached kraft pulp: Black spruce with a kappa number of 29.9. Conditions: 10% pulp consistency, 2.5% NaOH, 680 kPa O_2 , and 90 $^{\circ}\text{C}$

However, earlier studies by Chiral *et al* [130] and Johansson *et al* [128] reported that the decrease of the amount of free phenolic hydroxyls was significant but there was still an abundance of such groups within the lignin even after extensive multistage

delignification. Later studies by Argyropoulos *et al* [129] on the oxidation of both kraft pulp and isolated residual kraft lignin found approximately 50-60% of the initial amount of total phenolic hydroxyl groups remained within the lignin structure even under extreme and idealized oxidation conditions (140 °C, 80 min, homogeneous solution with well mixing) (Table 2-15). These results were also supported by Moe and Ragauskas [131] who showed free phenolic hydroxyl content within residual lignin decreased by only 30-40% after oxygen delignification.

The earlier study also demonstrated that the condensed phenolic structures in residual lignin were fairly resistant to oxygen. Among them, 5-5' biphenolic structures showed the highest resistance [128, 132]. The origin of 5-5' biphenolic moieties in kraft lignin are the eight membered dibenzodioxocin ring structures discovered by Brunow and co-workers [37, 133], which constitutes about 10-15% of phenylpropane units in lignin, or about 10-15 such rings are present per 100 phenylpropane units [134, 135]. Dibenzodioxocins, under kraft pulping conditions, open quantitatively to release 5-5' biphenolic moieties in residual lignin [135]. Study by Argyropoulos *et al* [129] demonstrated that during oxygen delignification, 5, 5' biphenolic condensed structures were found to decrease from 0.44 to 0.38 mmol/g at the early phase (20 min) and then started to build up to a value of 0.49 mmol/g level (Table 2-15), suggesting that secondary lignin condensation reactions happened during oxygen delignification.

In addition, diphenylmethane (DPM) structures formed during kraft pulping, and non-phenolic β -aryl ether structure are resistant to oxygen delignification [122, 136, 137]. Charkar and Ragauskas analyzed functional groups of kraft pulps by C^{13} NMR spectroscopy and their results showed that low kappa (26.6) kraft pulp had 3 times more

DPM structures (0.09 units/aromatic ring) than the high-kappa (56.2) kraft pulp (0.03 units/aromatic ring) [137]. The analysis by Lai *et al* [136] estimated that the residual kraft lignin in unbleached kraft pulp contained 20% DPM units and O₂ delignification for 10-180 min resulted in a steady increase to 30-50% in the proportion of DPM units. In addition, as discussed by Chakar and Ragauskas [138], *p*-hydroxylphenyl has been also shown to be resistant toward oxygen species and the amount increases during oxygen delignification (Table 2-15).

Table 2-16. Content of Hydroxyl and Carboxyl Groups in Isolated Lignin before and after Oxygen Delignification

Kraft Lignin	Kappa number	Carboxyl acid (mmol/g)	Phenolic OH (mmol/g)	Aliphatic OH (mmol/g)
Southern pine [139]				
Unbleached	30.0	0.39	1.04	-
O-delignified	16.4	0.68	0.88	-
Spruce [140]				
Unbleached	22.5	0.23	2.20	1.79
O-delignified	10.7	0.51	1.62	1.56
Black spruce [129]				
Unbleached	29.9	0.27	2.20	2.06
O-delignified *	-	0.58-0.76	1.40-0.98	1.40-1.85

O-oxygen; * Oxygen delignification conditions: 80-120 °C, 60 min, 0.68 MPa O₂, and 2.5% NaOH.

As reported [132, 139, 140], the amount of carboxylic acid in isolated lignin from oxygen-delignified pulps increased as shown in Table 2-16. The increase in carboxylic acid was accompanied by a decrease in aromatic hydroxyl groups, reflecting that aromatic rings containing phenolic hydroxyl groups undergo oxidative degradation in the oxygen bleaching stage. The increase in carboxylic acid content compensated for the

reduction in lignin hydrophilicity caused by the reduction in number of phenolic structures.

It has been proposed that the role of reactive intermediates, such as superoxide and hydroxyl radicals, have a decisive influence on both efficiency and selectivity [141, 142]. To understand how these oxygen species react with different lignin structures, superoxide and hydroxyl radicals were generated by Gierer *et al* [116-122] in a controlled way by γ -radiolytic methods and allowed to react with various lignin model compounds. Using this technique, they were able to establish a number of different reaction models by identifying major reaction products and possible pathways of their formation [121]. Based on the accumulated data, Gierer proposed reaction mechanisms which involve the reactions of hydroxyl radicals and superoxide anion radicals with residual lignins as follows [122]:

1. Hydroxyl radicals readily oxidize phenolic structures to phenoxyl radicals. They also react with non-phenolic substrates by electrophilic addition to aromatic rings forming isomeric hydroxycyclohexadienyl radicals (Figure 2.18 and Figure 2.19) or by hydrogen abstraction (Figure 2.20) from aliphatic residues affording carbon-centered radicals. In the presence of oxygen, these radical intermediates are oxidized to hydroxylated- (Figure 2.18 a), dealkolated- (Figure 2.18 b) and $C_\alpha - C_\beta$ cleavage products (Figure 2.18 c and Figure 2.19 c), as well as to carbonyl-containing structures (Figure 2.20), with concomitant formation of superoxide radicals. Hydroxyl radicals alone can not degrade aromatic rings into aliphatic structures.

2. Superoxide readily reacts with phenoxyl and carbon-centered radicals (Figure 21). The reaction with phenoxyl radicals is characteristic of superoxide and is not given by

molecular oxygen to any significant extent. The reaction may lead to ring opening (Figure 21a) or cleavage of a carbon-carbon bond in a ring conjugated side chain (Figure 21b).

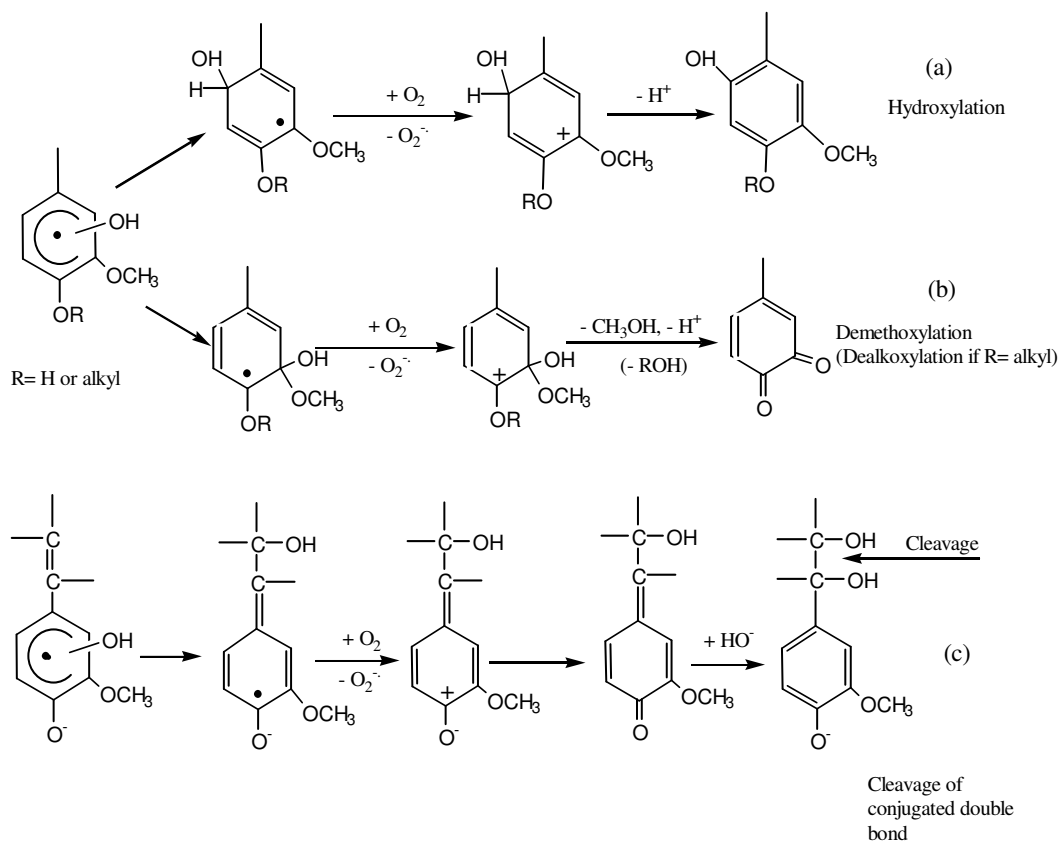
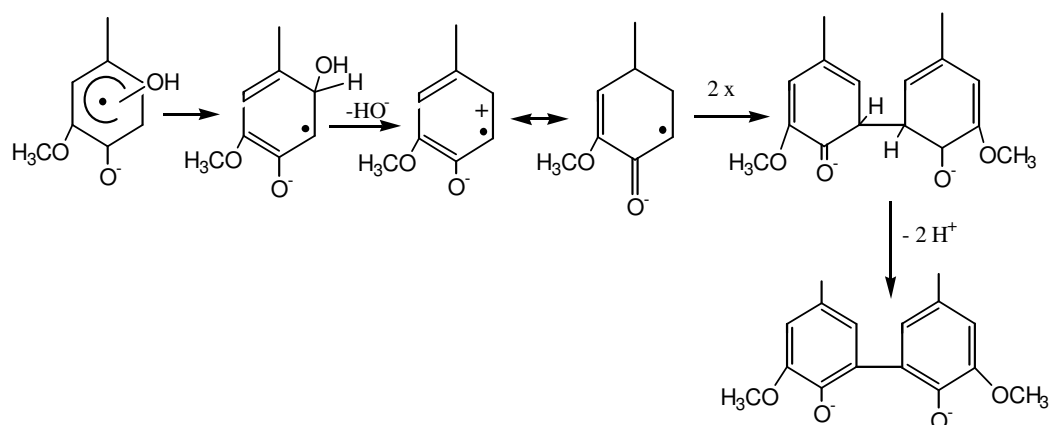
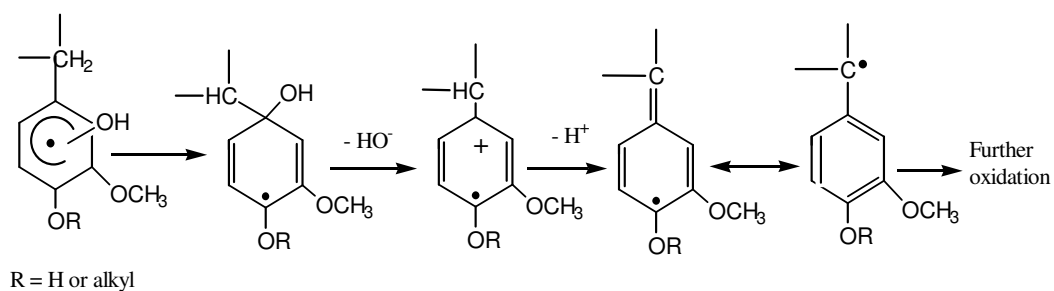


Figure 2.18. Reactions of Aromatic and Ring-Conjugated Structures with Hydroxyl Radicals [121]

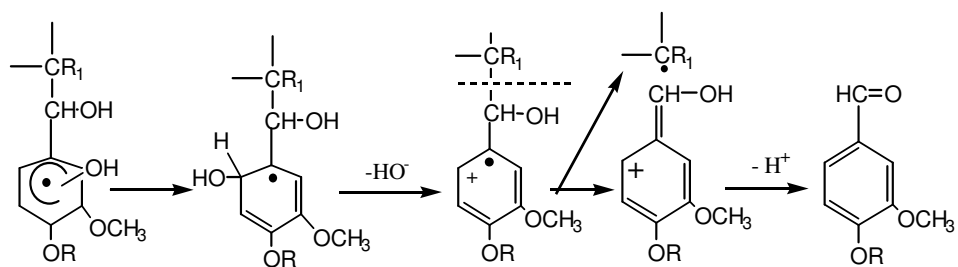
(a) Phenolic coupling



(b) Side chain oxidation



(c) C_α-C_β cleavage



R = alkyl
R₁ = aryl or aroxy

Figure 2.19. Reactions of Aromatic and Side Chain Structures with Hydroxyl Radicals [121]

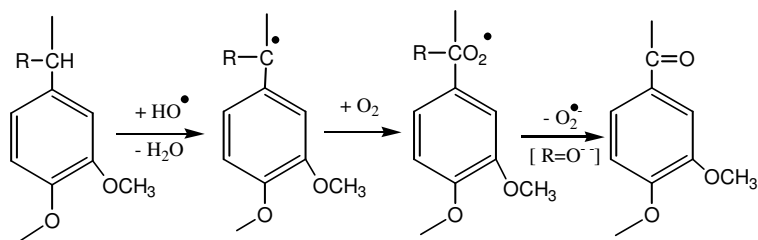


Figure 2.20. Hydrogen Abstraction from Lignin Side Chain [121]

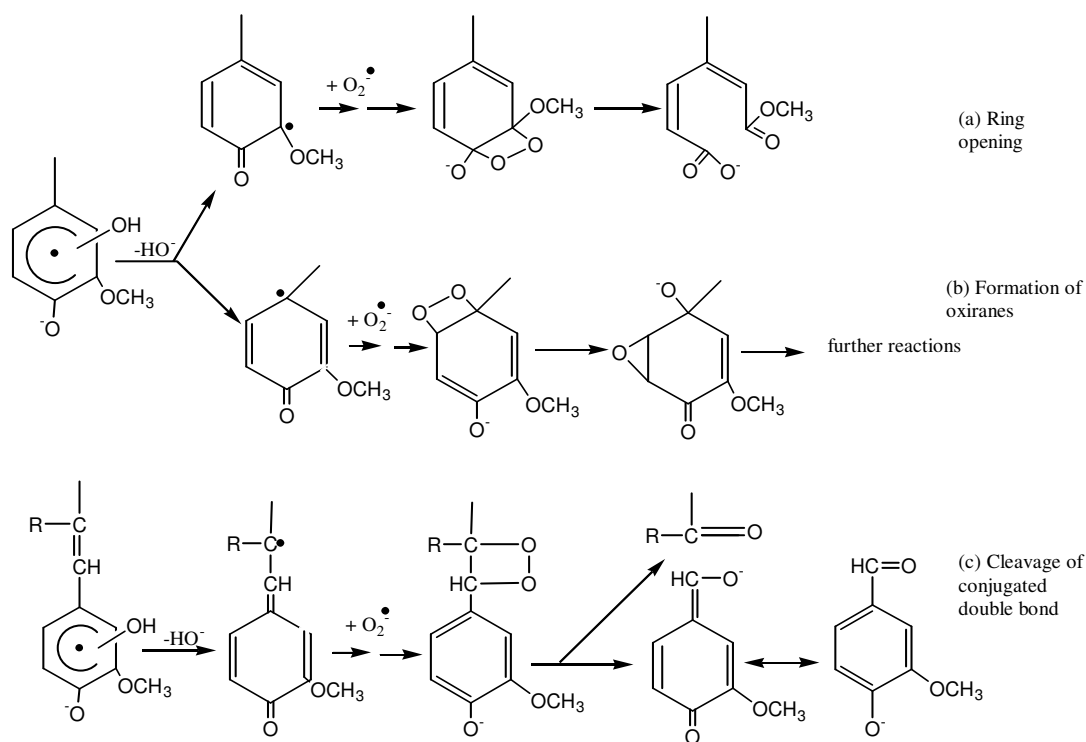


Figure 2.21. Reactions of Superoxide Anion Radical with Phenoxyl and β -Radicals [121]

Figure 21a depicts a mechanism to form muconic acid type conjugated acids. Other conjugated acids can be also generated by the cleavage of $C_{\alpha} - C_{\beta}$ bond of etherified structures containing α - carbonyl group to form benzylic carboxyl acids as shown in

Figure 22 [139]. Both muconic acids and conjugated carboxylic acids are the important functional groups contributing to fiber charge of oxygen-delignified pulps.

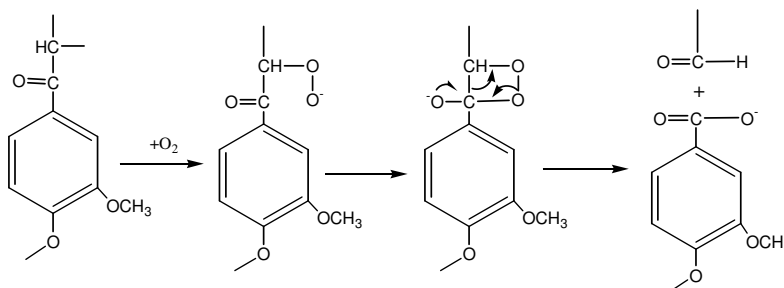


Figure 2.22. Formation of Conjugated Carboxyl Acid through Side Chain Cleavage [139]

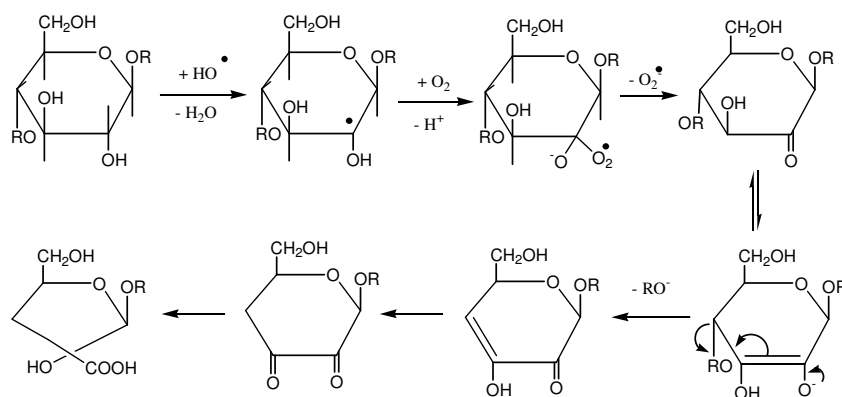


Figure 2.23. Hydrogen Abstraction from Carbohydrate Leading to the Cleavage of the Cellulose Chain [12, 121, 143]

2.4.3. Carbohydrate reactions and protection

2.4.3.1. *Carbohydrate reactions*

As described in section 2.4.1, several oxygen species are present under basic oxygen delignification, including dioxygen, hydroxyl radical, and superoxide anion radical. Literature reviews suggested that hydroxyl radicals were the main species responsible for carbohydrate degradation [12, 121, 143], which was supported by recent studies using

carbohydrate models in the UV/H₂O₂ system [144-146]. The proposed mechanism (Figure 2.23) suggests that hydroxyl radicals degrade carbohydrates by an initial attack at C-2 or C-3 position of the monomeric sugar units in the polysaccharide chains to form carbonyl groups through hydrogen abstraction, oxygenation of the resultant carbon-centered radical, and elimination of superoxide anion radical [121]. The ionized enol form of the resulted carbonyl-containing unit undergoes a, β -alkoxy elimination (“peeling”) at C4, resulting in the cleavage of cellulose chain shown in Figure 2.23. However, the products identified from the studies by Guay *et al* using UV/H₂O₂ system and carbohydrate models (Methyl β -D- Glucoside, Methyl- β -D- Cellobioside, and 1,4-anhydrocellobitol) suggest a different mechanism, *i. e.* hydroxyl radicals initially undergo a substitution reaction with carbohydrate to cleave any randomly encountered glycosidic linkage at the anomeric carbon in carbohydrate. Once reducing end groups form in carbohydrate, they undergo a series of reactions producing aldonic acids and lower order aldoses [144-146]. A mechanism on hydroxyl radical cleavage of 1,4-anhydrocellobitol proposed by Guay *et al* [146] is shown in Figure 2.24.

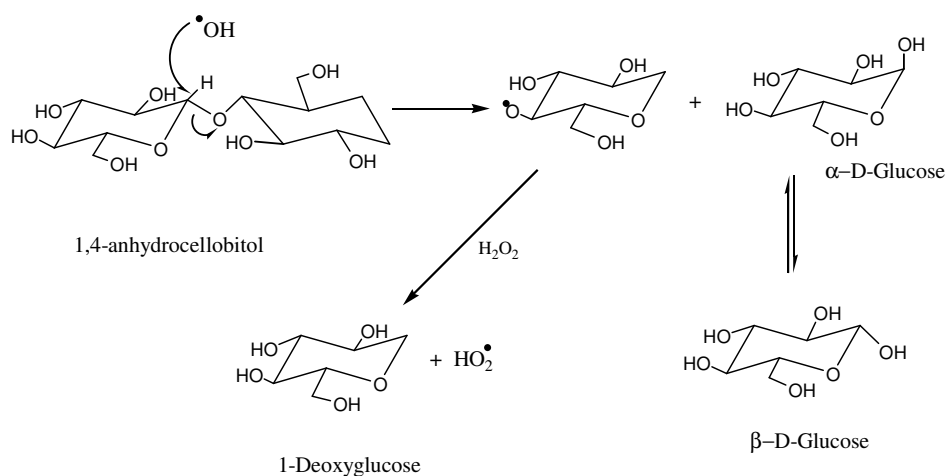


Figure 2.24. Mechanism of Hydroxyl Radical Cleavage of 1,4-Anhydrocellobitol [146]

Therefore, as long as hydroxyl radicals form during oxygen delignification, it is mostly possible to form an aldehyde end group in polysaccharide chains after each cleavage of the glycosidic linkage. Then the aldehydic groups can either be oxidized to carboxyl groups as stopping reactions (Figure 2.25) or a peeling reaction of the polysaccharide chains starts from them.

All the carboxylic acid products from above reactions will be the sources of fiber charge of oxygen delignified kraft pulps if eventually retained in the fibers.

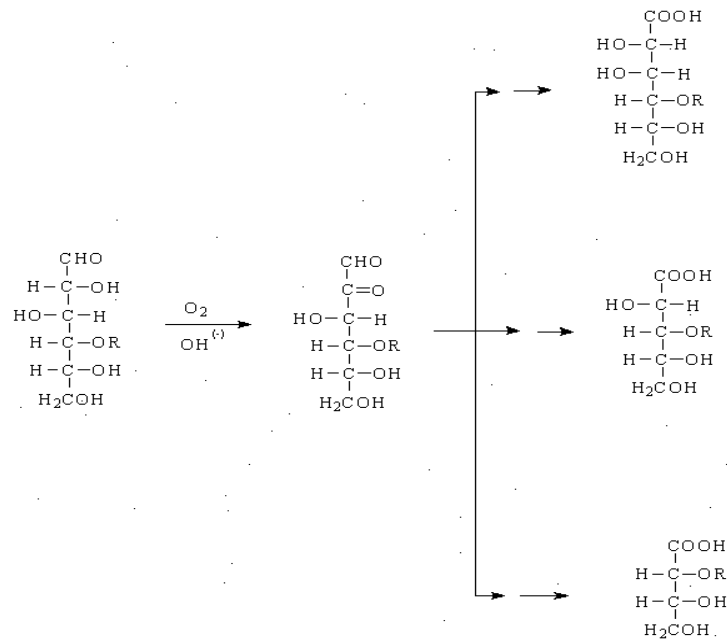
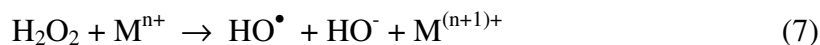


Figure 2.25. Oxidative Stabilization of Cellulose through Formation of Aldonic Acid End Groups [12]

2.4.3.2. Carbohydrate protection

Selectivity of oxygen delignification can be defined as the ratio of attack on lignin to attack on carbohydrate, expressed as $\Delta\kappa_{(\text{initial-final})}/\Delta\text{viscosity}_{(\text{initial-final})}$. It is affected

by process conditions and the presence of pulp contaminants. Of the factors governing selectivity in oxygen bleaching, the transition metal content in the pulp is one of the most important, because these metals catalyze generation of harmful oxygen radical species as shown in equations 7-8 [12]. Most pulps contain appreciable quantities of iron, copper, and manganese, possibly present in the form of finely divided colloidal particles, complexes, or bound to the acidic groups in fiber and all of which have this effect.



Many researchers believe that the highly reactive hydroxyl radical is responsible for cellulose depolymerization [12, 94, 121, 143-146]. Strategies to reduce the degradation during oxygen delignification by radicals include chelating, acid washing pretreatments to remove transition metals, addition of magnesium sulfate to inhibit the catalytic activity of these metals, and the use of radical scavengers.

The use of radical scavengers such as alcohol, sodium gluconate have been shown to increase the selectivity by a factor of two or more in the laboratory study [147]. But the amounts required are too high to give economic benefits without additive recovery.

To date, the magnesium compounds, such as MgSO_4 , are still the best and widely used commercial inhibitors for oxygen delignification. It is normally applied at levels as low as 0.05-0.10 % Mg^{2+} on oven-dried pulp. It is believed to function by precipitating as magnesium hydroxide, which adsorbs metal ions, making them unavailable for catalysis of peroxide decomposition [148] or by forming complexes with them [149].

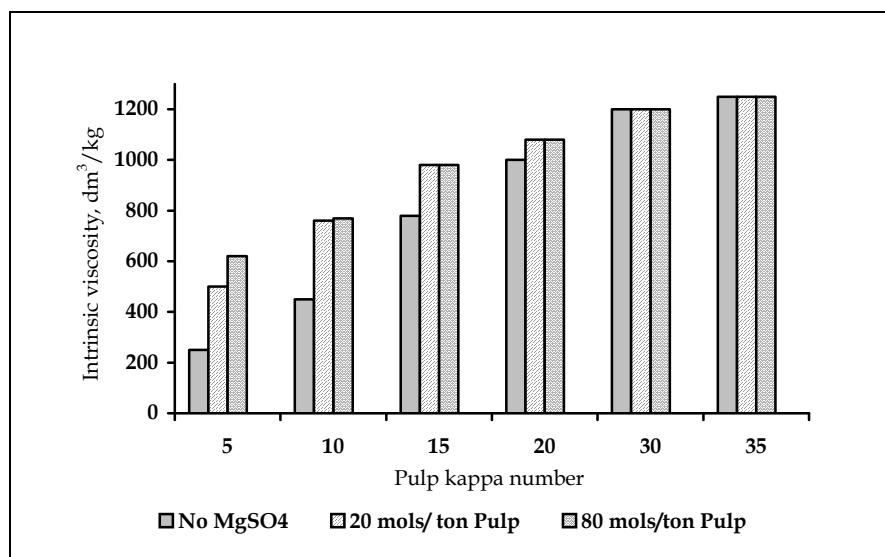


Figure 2.26. The Relationship between Pulp Viscosity and Kappa Number of Oxygen Delignified SW Kraft Pulps [105]

Researchers in the past several years have speculated that Mg^{2+} co-precipitates with Mn^{2+} ion into a “soluble” aggregate that essentially neutralizes the redox activity of Mn^{2+} [150]. It has been determined that the minimum Mg/Mn molar ratio required to offset the redox activity of Mn^{2+} is approximately 30:1 (mol/mol). The study by Lucia *et al* [151] shows that the addition of Mg acts to mitigate the activity of Mn ion at all temperatures (80 and 100°C) and times (60 and 80 min), by reducing the fluctuations of viscosity level. High Mg/Mn molar ratio (33 mol/mol) demonstrates an important increase in viscosity selectivity than in low Mg/Mn molar ratio (22 mol/mol). The highest selectivity at both temperatures for both pulps (with kappa number of 39.8 and 25.3) is obtained with the high Mg/Mn ratio at short time. However, the higher protective metal ratio cannot compensate for the damaging effect of higher temperature, which accelerates cellulose

degradation. Figure 2.26 illustrates the effectiveness of magnesium in preserving pulp viscosity [105].

2.4.4. Kinetics and mass transfer

As shown in Figure 2.27, typical oxygen delignification process indicated by kappa number reduction with time is characterized by two distinct stages: an initial rapid decrease followed by a remaining slower decrease phase [105, 152, 153].

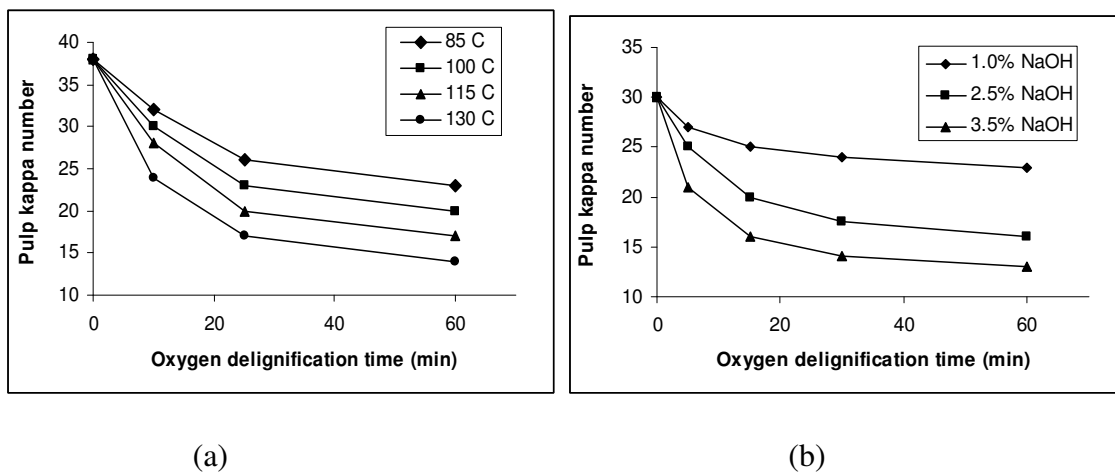


Figure 2.27. Oxygen Delignification Rate of SW Kraft Pulps under (a) Different Temperatures and (b) Alkaline Conditions

This behavior is most likely caused by the presence of two categories of residual lignin that respond differently to oxygen. The first category is removed within about 5-15 minutes, which can be attributed to those very reactive structures toward oxygen species in residual lignin such as catechols, stilbenes, and enol ethers. Additional phenolic hydroxyl groups and unsaturated groups in side chain are structural features that enhance reactivity. A methoxyl constituent in aromatic ring also increases the reaction rate [105].

The second category is the “condensed” phenolic structures (see Section 2.4.2) that are fairly resistant to degradation and a key contributing factor to the slow phase of O₂ delignification process [154].

In addition to lignin chemistry, mass transfer is also an important consideration in oxygen delignification due to the three-phase (solid, liquid, and gas) nature of the reaction system. To react with lignin inside fiber, oxygen must cross the gas-liquid interface, diffuse through the liquid film surrounding fiber, and then through the fiber wall itself. Delivery of oxygen to the inside of fiber can be a limiting factor to the overall rate of process [155]. Rewaltker and Bennington [156] suggested that oxygen mass transfer limitations in retention tower caused the towers to operate on average 20% below their delignification potential. A pseudo steady state analysis by Krothapalli *et al* [157] showed that the fractional oxygen saturation in industrial towers reached 70% after 60-minute reaction time while the laboratory reactors reached full saturation in 1-2 minutes. Therefore, good mixing is critical to improve the efficiency of oxygen delignification.

2.4.5. Effect of oxygen delignification on fiber charge/carboxylic acid content

As previously discussed, acidic groups are formed in residual lignin and carbohydrate of oxygen delignified fiber through oxidation. Acidic groups in residual lignin, either as muconic acids when aromatic rings are opened, or as aliphatic acids when carbonyl groups in side chains are oxidized, increase water solubility of the oxidized lignin fragments. Table 2-17 summarizes literature reported charged groups content before and after oxygen delignification of SW kraft pulps.

Table 2-17. Charged Group Content before and after Oxygen Delignification of SW Kraft Pulps

Kraft pulp	Carboxylic acid in lignin (mmol/g lignin)		HexA ($\mu\text{mol/g}$ pulp)		Fiber charge Total (Surface) ($\mu\text{mol/g}$ pulp)	
	U	UO	U	UO	U	UO
<i>P. radiata</i> [158]	1.0	1.5	-	-	-	-
<i>P. abies</i> + <i>P. sylvestris</i> KN = 24.3 [159, 160]	25**	20**	16.9	17.8	123	113
<i>P. taeda</i> [137] KN = 26.6 KN = 56.2	0.28 0.24	0.70 0.60	- -	- -	- -	- -
<i>P. Sylvestris</i> [161] KN = 25.9	-	-	37.0	44.8	100 (25)	110 (28)
<i>P. taeda</i> [162] KN = 28.2	-	-	-	-	97 (9.5)	72 (6.7)
<i>Spruce</i> (KN = 22.5)[140]	0.23	0.51	-	-	-	-
<i>SW</i> (KN = ~30) [132]	0.27	0.34-0.95				
<i>P. taeda</i> * [115] KN = 30.0 KN = 48.0	0.39 0.31	0.65 0.86	- -	- -	- -	- -
<i>SW</i> * (KN=35.6) [58]	0.74	2.68-3.34				
<i>SW</i> [163] KN = 34.6 KN = 30.0 KN = 21.5	- - -	- - -	- - -	- - -	121 (37) 104 (36) 83 (34)	128 (38) 110 (37) 99 (35)

U and UO: Unbleached kraft pulp and oxygen delignified kraft pulp; KN = pulp kappa number; * Lignin samples were the precipitated lignin in the effluents; ** μmol acid groups in lignin on the basis of oven-dried pulp.

From Table 2-17, oxygen delignification of kraft pulps leads to the introduction of a large amount of carboxyl groups in the lignin, which therefore enhance the hydrophilicity of the lignin. In addition, HexA does not change very much before and after oxygen delignification. However, the reported data for total/surface fiber charge either increases

or decreases after oxygen delignification, which needs further investigation on the possible reasons to cause this discrepancy. One of the factors may be the different process conditions employed.

Although little data was found about the amount of uronic acids in oxygen delignified kraft pulps, the results reported by Toven [159] demonstrated that uronic acids accounted for about 65.8% and 75.0% of total fiber charge before and after oxygen delignification (See data in row 4 of Table 2-17).

2.4.6. Changes in cellulose crystallinity

De Souza *et al* [164] studied the kinetics of crystallinity changes during oxygen delignification for four lignin-free cellulosic substrates at 2.5% NaOH, 95°C, 690 kPa O₂, 10% consistency, and 0-90 min reaction. Three phases of crystallinity change were found in the presence of oxygen: an initial increase in relative degree of crystalline was followed by a small, sharp decrease and then another gradual increase in all cellulose crystallinity. The initial rapid increase of crystallinity was thought to be caused by the removal of easily accessible amorphous cellulose; the sudden decrease of crystallinity involved direct oxidation through oxygen or radicals; and the final slow increase of crystallinity was due to the slow elimination of amorphous cellulose hairs that have formed when direct oxidation opened the crystallite structures [164].

2.4.7. Fiber surface properties

The chemical properties of fiber surfaces are of great importance for the behavior of fiber in bleaching, papermaking processes, as well as for the properties of final paper products.

The studies on fiber surface lignin content and extractives have been done either by mechanical peeling followed by chemical analysis [165] or Electron Spectroscopy for Chemical Analysis (ESCA), a powerful technique recently used for analyzing pulp fiber surfaces [100, 101].

Table 2-18. The Degree of Surface Coverage of Lignin and Extractives for Unbleached and Oxygen Delignified SW Kraft Pulps [74, 161, 163]

SW kraft pulp	Total lignin content (%)	Surface coverage of lignin (%)	Total extractive content (%)	Surface coverage of extractives (%)
Unbleached				
Pulp A	5.4	45 ± 1	0.10	~0
Pulp B	4.5	39 ± 1	0.06	~0
Pulp C	3.5	28 ± 0	0.20	4 ± 1
Pulp D	4.0	16.2	-	8.3
O ₂ -delignified				
Pulp A	2.9	36 ± 0	0.05	~0
Pulp B	2.0	32 ± 4	0.05	~0
Pulp C	1.4	21 ± 1	0.15	3±2
Pulp D	2.0	14.0	-	2.8

Note: Data for Pulp A-C from Hulten *et al* [163] and Data for Pulp-D from Laine *et al* [74].

Fiber surface lignin content analysis by Heijnesson *et al* [165-168] after isolation of surface materials by gentle mechanical peeling procedures revealed that the lignin content of the surface materials (~0.3% on pulp) removed by mild mechanical treatments was 2.5 – 4.5 times higher than that of the bulk fibers. Kleen *et al* [168] also reported that unbleached kraft fiber surface material, as obtained by mechanical peeling, contained lignin-rich (as twice as lignin content in the peeled fibers) surface materials that had a

much higher proportion of high molecular weight lignin (MW > 150,000) and a slightly lower proportion of phenolic lignin units than the bulk fibers. The finding of lignin-rich fiber surfaces was supported by the results from ESCA [74, 103, 169, 170] and ESCA in combination with enzymatic peeling of unbleached kraft pulps [171]. As summarized in Table 2-18, Laine *et al* [74] and Hulten *et al* [163] demonstrated from their studies using O/C technique of ESCA that the surface lignin concentration decreased by only 15-20% while oxygen delignification reduced total lignin content by ~50%. Therefore, oxygen delignification removes significantly less surface lignin in comparison with the lignin content in the bulk of fibers, indicating that surface lignin has a lower reactivity to oxygen. The low reactivity of surface lignin has been suggested to be due to condensed lignin structures and/or to lignin-carbohydrates complexes [74].

However, the amount of surface extractives on fiber surfaces was reported differently by Laine *et al* [74] and Hulten *et al* [163] (Table 2-18). The amounts of surface extractives on both unbleached and oxygen delignified pulps obtained by Hulten *et al* [163] are very low or zero (Pulp A-C in Table 2-18) and oxygen delignification does not reduce significantly fiber surface extractives (Pulp C in Table 2-18). The totally opposite observation on the amount of surface fiber extractives was reported by Laine *et al* [74] (Pulp D in Table 2-18). The difference was probably due to the thorough washing of pulp fibers before extraction by Hulten *et al* [163] and drying papersheet for ESCA analysis at 70 °C by Laine *et al* [74] other than at room temperature by Hultem *et al* [163] . Migration of extractable materials is known to be favored by an increase in temperature and subsequently, leads to a higher amount of extractives on fiber surfaces [172].

By using TOF-SIMS (Time-of-flight secondary ion mass spectrometry) analytical tools, Kleen *et al* [173] concluded that lignin on the outer surface of unbleached pulp fiber structurally resembles bulk lignin. An unexpected dominant extractive, probably a sodium salt of a saturated long-chain fatty acid - $C_{23}H_{47}COONa$, was found on the outmost surface of unbleached pulp fiber and a small amount of Ca-distearate as well as free stearic and oleic acids were also observed. In addition, this study showed that the proportion of metals, such as Mn, Ca, Mg, Na, K, and Si, at fiber surface was higher than the overall metal content of fiber.

By determining the calcium content of the outer surface of ion-exchanged SW kraft pulp fibers by ESCA, Laine *et al* [56] concluded the surface xylan of kraft pulps contained fewer acid substituents than the xylan in other regions of the fibers. Tenkanen *et al* [174] reported that oxygen delignification did not affect HexA content but reduced total acid and the amount of MeGlcA in xylan (Table 2-19).

Table 2-19. The Amount of Different Side Groups in Xylan per 100 Anydrous Xylose Units Analyzed after Enzymatic Hydrolysis [174]

Pulp sample	Kappa number	Arabinose (mol/100 xylose)	MeGlcA (mol/100 xylose)	HexA (mol/100 xylose)	Total acid (mol/100 xylose)
HW kraft pulp	18.7	n.d.	2.6	5.1	7.7
HW O-stage kraft pulp	11.6	n.d.	1.3	4.9	6.2
SW kraft pulp	25.9	9.8	2.9	7.4	10.3
SW O-stage kraft pulp	19.4	8.5	n.d.	6.8	6.8

n.d. = Not detected or under the limit of quantitative determination

Hulten *et al* [163] studied the appearance of oxygen delignified kraft pulp fibers using Scanning Electron Microscopy and found that the fibers had a rectangular shape

even after double oxygen delignification treatment. The surface of the oxygen delignified pulp fibers was more fibrillated in comparison with unbleached fibers. This was probably due to the fact that a higher dissolution of lignin led to a more porous fiber wall, and this further led to fiber surfaces being more easily fibrillated by the process equipment used [163]. Therefore, such a fibrillation from oxygen delignification process should enhance fiber bonding and improve paper tensile strength for oxygen delignified pulps.

2.4.8. Fiber strength and bonding after oxygen delignification

In a study, Allison *et al* [175] treated kraft pulps (kappa number of 30) made from high (443 kg/m³) and low (363 kg/m³) density pine chips in a Quantum high intensity mixer-reactor at room temperature, 10% (medium) consistency (MC), and 2200 rpm for 5 and 12 seconds. The four pulps were then subjected to four different chemical treatments (O₂, ClO₂, O₃, and H₂O₂). It was found that bleaching MC treated pulps resulted in 4-16% decrease in wet zero-span strength index with respect to bleaching untreated pulps. The severity of wet zero-span tensile index loss was in the order: ClO₂ < O₂ < H₂O₂ < O₃. The magnitude of this effect was more apparent for thicker wall pulps from high-density slabwood pulps. However, MC treatment had no effect on pulp DP after bleaching. These results indicated that fiber wall dislocations produced by MC treatment provided sites for localized chemical attack, leading to greater losses of overall fiber strength. The authors also suggested fiber morphology, especially fiber wall thickness, might influence this process. From a practical viewpoint, the direct effect of MC treatment on pulp strength appeared to be equally as important as its subsequent influence on bleaching selectivity.

In a study by Jiang *et al* [176], they found that the wet zero span tensile strength of a northern HW kraft pulp decreased from 11.6 km to 10.5 km after 40% O₂ delignification but fiber specific bond strength measured by Page's method [67] remained the same (from 12.5 to 12.6 N/mm²). The study by Snowman *et al* [177] demonstrated that moderate improvements (10.0-16.7%) in interfiber bond strength were achieved by delignifying a HW kraft pulp from a kappa number of 12 to 10 under mild reaction conditions of 1.5% NaOH charge and 90°C. Such an improvement was thought to be attributed to the initial removal of hydrophobic surface lignin, increasing hydrophilicity of fiber surfaces and improving conformability, resulting in increased bonding as compared to the brownstock pulp. However, interfiber bonding was essentially unaffected under the severe reaction conditions of 3.5% NaOH charge and 110°C, probably due to the degradation of carbohydrate fraction and the loss of hemicelluloses.

Ragauskas *et al* [139] conducted a study on oxygen delignification of low (30.0)- and high (48.0)- kappa SW kraft pulps to different kappa numbers. The paper physical properties were investigated. This study demonstrated that the low- and high- kappa pulps suffered 4.8-9.6% and 6.3 -15.6% zero-span strength loss respectively after oxygen delignification. On the contrary, the tensile index of paper samples made from these pulps increased by 4.6 – 8.3% and 3.6- 5.4 % respectively with lignin removal. This tensile enhancement was explained by the increase of fiber bonding. As residual lignin was removed, fiber became more flexible, which facilitated a more intimate contact between fibers. In addition, fiber surface fibrillation effect introduced during oxygen delignification identified by Hulten *et al* [163] may be another factor to improve fiber bonding and therefore increase tensile strength if fiber damage is not excessive.

2.5. Effect of Pulp bleaching on fiber charge

In last decades, a large amount of studies have been focusing on maximizing bleaching potential while minimizing bleaching costs and absorbable organic halogen generation [104, 178-182]. Accordingly, several typical ECF bleaching sequences such as DEDED and ODEDD, as well as the oxygen or/and peroxide reinforced alkaline extraction bleaching sequences D(EO)DED and OD(EOP)DD, have been developed to fully bleach kraft pulp to higher brightness (> 85% ISO). It was customary to evaluate pulp brightness ceiling/stability and viscosity after full bleaching [183, 184]. Recently, interest in wood fiber charge properties have been increasing due to its effect on fiber flexibility, fiber-fiber bonding, as well as wet-end chemistry [185, 186].

The effect of bleaching chemicals agents, such as oxygen, ozone, peroxide, and chlorine dioxide on fiber charge has been studied by Laine *et al* [56] and summarized in Table 2-20.

The data in Table 2-20 demonstrated that both total and surface fiber charge were strongly dependent on bleaching chemicals applied. Total and surface fiber charge was increased by 10% and 12% respectively after one stage oxygen delignification. This is probably due to the formation of some new carboxyl groups in both lignin and carbohydrate fractions [12, 58, 121]. Ozone treatment greatly reduced total fiber charge by ~50%. As seen in Table 2-20, ~ 50% of the fiber charge reduction (25 μ mol/g) was due to the removal of hexenuronic acids by ozone [32]. When a peroxide stage preceding the ozone stage (in OPZEP), the extent of HexA degradation from ozone treatment was greater. When a hydrogen peroxide stage was employed following an oxygen or alkaline extraction stage, total fiber charge was not significantly affected by peroxide treatment.

Neither did peroxide treatment change pulp hexenuronic acid content, which agrees with the observation that HexA is unchanged during a peroxide bleaching stage [32]. Chlorine dioxide treatment always reduced total fiber charge. However, the first D-stage seemed the most effective in this effect. More decrease in total fiber charge was found for the first D-stage following an oxygen delignification stage as in ODEDED.

Table 2-20. Fiber Charge of Bleached Kraft Pulps [56]

Sample	Kappa number	Viscosity (dm ³ /kg)	Total fiber charge (μeq/g)	Surface fiber charge (μeq/g)	HexA (μeq/g)
Reference	25.9	1060	100	25	37.0
O	13.2	940	110	28	44.8
OZ	7.0	750	60	21	21.9
OZE	4.9	725	58	21	13.9
OZEP	2.9	700	58	22	12.1
O	13.2	940	110	28	44.8
OP	8.6	890	108	27	40.7
OPZ	2.5	675	60	18	10.4
OPZE	1.2	650	56	18	4.8
OPZEP	0.8	650	56	20	4.0
O	13.2	940	110	28	44.8
OD	4.2	900	62	22	17.4
ODE	2.3	905	61	20	13.9
ODED	1.1	830	58	21	4.6
ODEDE	1.1	810	58	20	3.9
ODEDED	0.4	805	51	20	2.3
D	10.7	1050	82	25	17.0
DE	5.1	1060	78	16.6	13.1
DED	1.9	1055	66	16	7.1
DEDE	1.7	1040	64	16.5	5.3
DEDED	0.8	1005	57	16	3.2

In addition, hexenuronic acids were found to be significantly (>50%) degraded by chlorine dioxide. But, it is surprising to note that total fiber charge was not significantly affected by an alkaline extraction because the dissolution of oxidized lignin and concomitant removal of some degraded hemicelluloses usually occur at alkaline extraction stage.

It was also observed in Table 2-20 that fiber surface charge development in the different bleaching stages was similar to that of total fiber charge.

Table 2-21. Charged Characteristic of Bleached Kraft Pulps [160]

Sample	Pulp ISO brightness (%)	Viscosity (dm ³ /kg)	Total fiber charge (μeq/g)	HexA (μeq/g)
Reference	-	-	123	16.9
O	-	-	113	17.8
OD(EO)	-	840	86	9.7
OD(EO)DED	84.0	753	51	0.3
OD(EO)Q(PO)	87.5	773	73	10.3
O	-	940	113	17.8
OZ(EO)	-	-	76	6.7
O(DZ)(EO)	-	730	74	6.7
O(DZ)(EO)DED	87.5	745	49	0.3
O(DZ)(EO)Q(PO)	87.7	773	68	7.0

Toven [160] conducted a study on ECF bleaching of a SW kraft pulp (kappa number of 24.7) using bleaching sequences of D(EO)Q(PO), (DZ)(EO)DED, and (DZ)(EO)Q(PO) to ~87.5% pulp brightness. Total fiber charge of the bleached kraft pulps are summarized in Table 2-21. It is found from the results of OD(EO) and OZ(EO) bleaching that ozone degraded charged groups somewhat more efficiently than chlorine

dioxide did. Pressurized peroxide (PO) as a final bleaching stage reduced the amount of charged groups (e.g. from 86 $\mu\text{mol/g}$ at OD(EO) to 73 $\mu\text{mol/g}$ at OD(EO)Q(PO), but to a much lower extent than chlorine dioxide (e.g. from 86 $\mu\text{mol/g}$ at OD(EO) to 51 $\mu\text{mol/g}$ at OD(EO)DED). In addition, hexenuronic acids were not degraded in the pressurized peroxide stage.

Outside of these studies, a review of literature has presented limited data on fiber charge of fully bleached kraft pulps via different ECF and TCF bleaching protocols that have practical interest for utilization in existing bleaching operations.

2.6. Summary

This chapter provided detailed background on the origin of fiber charge/acidic groups in chemical pulps, their effects on fiber and paper physical properties, and the methodology for fiber charge/ carboxylic acid content measurements. It also provided fundamental understanding of lignin and carbohydrate chemistry during oxygen delignification and the mechanism for carboxyl group formation in residual lignin and polysaccharide. In addition, this chapter summarized the effects of different bleaching chemicals on pulp fiber charge.

CHAPTER 3 PROBLEM STATEMENT AND DISSERTATION OBJECTIVES

3.1. Problem statement

As discussed in CHAPTER 2, the latest efforts during oxygen delignification have mainly focused on extending the limitation of delignification such as double oxygen delignification, understanding the mechanism of residual lignin inactivity, the improvement of process efficiency by enhancing gas-liquid mass transfer, as well as the benefits of pulp yield and fiber quality from the integration of high kappa cooking and extended oxygen delignification. Based on the understanding of lignin and carbohydrate chemistry during oxygen delignification, carboxyl groups are formed in both lignin and polysaccharide fractions. However, fiber charge in oxygen delignified pulps was reported to either increase or decrease [56, 160]. The possible reason to cause this discrepancy needs further investigation. In addition, there is still lack of a detailed study on fiber carboxyl group formation during oxygen delignification. More practical questions to be accordingly addressed are: does oxygen delignification provide a viable approach to control fiber charge? Can a catalytic oxidation system be developed to dramatically increase carboxyl groups in polysaccharide during oxygen delignification? What percentage of carboxyl groups introduced by an oxygen delignification stage can be retained through a full bleaching sequence? How do different bleaching protocols affect carboxyl groups in bleached kraft pulps?

Therefore, knowing time-dependent profiles of carboxyl group content in bulk fibers and pulp polysaccharide during oxygen delignification will be helpful to understand fiber charge development, affecting factors, and possible ways of controlling fiber carboxyl

groups in polysaccharide by an early bleaching stage. Meanwhile, it is of significance to figure out the amount of carboxyl groups retained through a bleaching sequence and how bleaching protocols, particularly typical ECF and TCF bleaching sequences affect fiber carboxyl group content of fully bleached pulps differently.

3.2. Dissertation objectives

The focus of this study is to develop an understanding of fiber carboxyl group formation during typical oxygen delignification and full pulp bleaching protocols. With these understandings, it is anticipated to know whether oxygen delignification can provide a viable approach to control fiber carboxyl group formation and whether an optimization program or a catalytic oxidation system can be developed to dramatically increase fiber carboxyl groups during oxygen delignification. The early introduced carboxyl groups are anticipated to be partially retained through a bleaching sequence. Different effects of bleaching protocols on fiber carboxyl group content are also anticipated to be identified at comparable common pulp brightness. The objectives of this study are summarized as follows:

- Investigate dynamic change of fiber carboxyl group content in bulk fiber, polysaccharide, and residual lignin during one-stage oxygen delignification.
- Elucidate fiber carboxyl group content profiles for the integration of high kappa cooking and extended oxygen delignification.
- Develop a process optimization program to retain or a catalytic oxidation to increase carboxyl groups in polysaccharide of oxygen delignified pulps.

- A comparative study on fiber carboxyl group content of fully bleached kraft pulps during typical bleaching protocols
- Examine the effect of fiber carboxyl groups enhanced by oxidation of bleaching chemicals (oxygen and hydrogen peroxide) on fiber and paper sheet tensile strength/ stiffness.

CHAPTER 4 CHARACTERIZATION OF FIBER CARBOXYL GROUPS DURING ONE-STAGE OXYGEN DELIGNIFICATION OF A LOW KAPPA KRAFT PULP

4.1. Introduction

Oxygen delignification is widely used for lignin removal before bleaching and has become one of the dominant post-kraft pulping delignification technologies for both ECF and TCF operations [187]. In the past fifty years, the development and implementation of oxygen delignification technology has been achieved due to the contribution from discoveries in lignin/carbohydrate chemistry, improved reaction selectivity, energy, environmental concerns, and the desire for higher pulp yields [105]. Recently, the interests in this area have focused on extending the limit of delignification [139, 188] and oxygen mass transfer in gas-liquid interface [156, 157, 189].

Fiber charge has been found to be an important chemical property that can affect fiber swelling, water removal during wet pressing, the rate of refining, the adsorption of retention aids, and the strength and optical properties of the resultant papersheets [86, 185, 186, 190]. Carboxyl groups in cellulosic fibers are the main functional groups responsible for surface and bulk charge of kraft pulps. Therefore, the introduction of carboxyl groups into fiber by direct chemical and enzymatic modification of pulp, such as by grafting or the addition of polymers has been extensively studied [4-10, 191, 192]. In contrast, the parameters important to maximizing fiber charge in modern pulping and bleaching operations have only recently begun to be examined [193, 194].

As reported recently, oxygen delignification enhanced or slightly diminished fiber carboxyl groups of softwood kraft pulps [56, 160, 162]. An increase in fiber acidic groups

after an O-stage could be attributed, in part, to oxidative depolymerization reactions with lignin [137, 195]. Simultaneously, the reactive oxygen species in an O-stage have been shown to yield aldonic acids [12] that can either enhance overall fiber charge or contribute to pulp yield loss and a reduction in fiber charge. Therefore, changes in fiber charge/acidic groups after oxygen delignifications are anticipated to depend on process conditions and this has not been fully investigated. Additionally, the kinetic changes in fiber carboxylic acid content and its distribution between residual lignin and the carbohydrate fraction during oxygen delignification remain ill-defined and require further investigation. This study examines the changes in fiber carboxylic acid content during one-stage oxygen delignification of a SW kraft brownstock pulp and establishes to what extent total fiber carboxyl group content is associated with lignin and pulp carbohydrate.

4.2. Experimental

4.2.1. Materials

A commercial southern U.S.A pine unbleached kraft pulp with a kappa number of 32.5 (CSW) was used for the one-stage oxygen delignification studies. The pulp kappa number, viscosity, and main metal content are presented in Table 4-1. The sugar composition of this pulp is presented in Table A-1 in APPENDIX A.

Table 4-1. Pulp Kappa Number, Viscosity, and Metal Content of the Unbleached SW Kraft Pulp

Kappa number	Viscosity (mPa.s)	Major metals (ppm)			
		Mn	Mg	Cu	Fe
32.5	24.6	44.7	473.9	9.2	21.8

Note: Standard deviations of metal content are 1.496, 16.497, 0.306, 2.922 ppm, respectively

All other chemicals and solvents were commercially purchased from VWR or Sigma-Aldrich and used as received with the exception of 1, 4-dioxane which was freshly distilled over NaBH_4 prior to use.

4.2.2. Oxygen delignification

All one-stage oxygen delignification experiments were conducted in a 2.00-L inclined rotary stirred Parr reactor. The photograph of the Parr reactor and the safety of operation were presented in APPENDIX B. Typically, after preheated with water to 60 - 90 °C, the water was removed and the reactor was loaded with unbleached kraft pulp (30.00 g o.d.). Pulp consistency was adjusted to 10% using deionized water and required amount of NaOH (1.5 – 3.5% on o.d. pulp). A certain amount of MgSO_4 (0.1% w/w solution) was also added so that the molar ratio of Mg/Mn in the pulp was kept at 30-33: 1 mol/mol to offset the detrimental effects of Mn^{2+} [150]. After sealing the reactor, the vessel was heated to the desired temperature (85 – 115°C) and pressurized with O_2 (640 – 960 kPa). The reaction was terminated after 10-80 minutes, and the pressure in the reactor was released. The pulps were then washed, air dried, and stored at 2 °C for further use. The varied experimental parameters for one-stage oxygen delignification are presented in Table 4-2.

Table 4-2. One-Stage Oxygen Delignification Conditions

Parameter	Conditions
NaOH (wt %)	1.5, 2.5, 3.5
Temperature (°C)	85, 100, 115
Oxygen (kPa)	640, 800, 960
Time (min)	0, 10, 20, 30, 45, 60, 80

Note: 10% pulp consistency and the molar ratio of Mg : Mn = 31-33:1 [150]

4.2.3. Preparation of holocelluloses

Holocelluloses (holopulps) from the oxygen delignified pulps were isolated following a literature method [196] with slight modification. In brief, air dried pulp samples (2.00 g) were dispersed into 75.00 mL deionized water, treated with 0.60 g of NaClO₂ and 0.50 mL glacial acetic acid in a 250 mL Erlenmeyer flask. The resulting mixture was heated to 75 °C. After stirring for 1 hour, additional NaClO₂ (0.60 g) and glacial acetic acid (0.50 mL) were added and the reaction was continued for another 1 hour. This procedure was repeated for a total of 3 hours. Depending on the starting pulp kappa number, 92–98% yield of holocellulose was obtained from this procedure. The treated pulp was then cooled to 0 °C, filtered, washed with deionized water, and air-dried for further analysis.

4.2.4. Lignin isolation

Isolation of residual lignin from kraft brownstocks and O-stage delignified pulps was accomplished employing a standard literature method [197]. In brief, air-dried pulp (30 – 50 g o.d.) was added to an acidic *p*-dioxane prepared by adding 90% distilled *p*-dioxane to 10% 1.0 N HCl in a flask, yielding a final consistency of 4%. The pulp slurry was refluxed for 2 hours under an argon atmosphere, then cooled and filtered. The filtrate was concentrated under reduced pressure. The precipitated lignin was isolated by centrifugation, washed with acidic water (pH 2~3), and then freeze-dried. This procedure afforded, on average, 40–55% yield of residual lignin, based on mass recovery of lignin and starting pulp kappa number corrected for hexenuronic acid content. The detailed procedures were described in APPENDIX E.

4.2.5. Analytical methods

4.2.5.1. *Metal ion content in pulp samples*

Metal ion contents in pulp samples were analyzed using inductively coupled plasma emission spectroscopy following literature methods [198-200] (APPENDIX F).

4.2.5.2. *Pulp carboxylic acid content determination*

Carboxylic acid content in pulp samples was determined using Headspace Gas Chromatography with a modified pulp sample preparation procedure [201] (See APPENDIX G for details). In brief, 0.25 g air-dried pulp was treated with 50 mL 0.1 N HCl solution with magnetic stirring for 60 minutes at room temperature. The treated pulps were washed with 1.50 - 2.00 L deionized water until pH near neutral. The sample was air dried at least 24 hours. Weigh 0.05g air-dried pulp into a 20- mL headspace vial and accurately add 4.0 mL of a solution of 0.0025 M NaHCO₃ and 0.11M NaCl with pipette and cap the vial for HSGC measurement. The carboxylic acid content of fibers was calculated as follow:

$$RCOOH(\mu\text{mol} / \text{g}) = \frac{A_{CO_2} - A_{Control}}{f \times w} \times 1000 \quad (9)$$

where

A_{CO_2} and $A_{Control}$: CO₂ GC adsorption peak areas for sample and control

f: calibration constant (21718)

w: oven-dried sample weight in grams

The typical standard deviation for fiber carboxyl group content measurements of three replicates under the same oxygen delignification conditions was 1.05 $\mu\text{mol/g}$.

4.2.5.3. *Pulp hexenuronic acid content measurement*

Hexenuronic acid content in pulp samples was determined following a spectroscopic method [202]. Briefly, 0.05g air-dried pulp with known moisture content was accurately weighed and put into a 20 ml vial with 10 ml of hydrolysis solution (0.6% mercuric chloride and 0.7% sodium acetate trihydrate). The mixture was sealed in the vial with a septum and then heated for 30 min at 60-70 °C in a water bath with shaking. After cooling down of the sample, the UV adsorption of the filtrated was determined using a spectrophotometer (Hewlett-Packard UV-8453) at 260 and 290 nm. HexA content was calculated as fellow:

$$HexA(\mu mol / g) = \frac{0.287 \times (A_{260} - 1.2A_{290}) \times 10}{w} \quad (10)$$

where

A_{260}, A_{290} : peak areas of adsorption at 260 and 290 nm wave length, respectively

w: oven-dried sample weight in grams

The typical standard deviation for HexA measurement of three replicates under the same oxygen delignification conditions was 0.56 μ mol/g pulp.

4.2.5.4. ^{31}P NMR analysis

All NMR spectra were recorded on a 400 MHz Bruker Advance/DMX NMR spectrometer. The lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and analyzed by ^{31}P NMR following a literature method [203]. Cyclohexanol was used as the internal standard. ^{31}P NMR spectra were recorded using an inverse gated decoupling sequence, 90° pulse angle, 25-s pulse delay, and 150 transients at room temperature. All the NMR spectral acquisition and analyses were controlled by Bruker's XWINNMR 2.6 software running on an SGI (Silicon Graphics Indigo) server

using the Irix 7.0 operating system. The detailed procedures were described in APPENDIX H.

4.2.5.5. *Fiber surface charge measurement*

Polyelectrolyte titrations were used to determine surface charge on fibers as published by Wågberg *et al* [99]. A polymer with high molecular weight and high charge density, methyl glycol chitosan (MW > 1,000,000 Da, charge density 2.244×10^{-3} eq/g), was used as a cationic adsorption polymer for surface charge measurement. The concentration of unabsorbed chitosan was titrated with 2.688×10^{-4} N polyvinyl sulfate potassium using 0.1 % o-toluidine blue as an indicator, the color change was from blue to reddish purple. The detailed procedure and calculation were described in APPENDIX I.

4.2.5.6. *ESCA*

All pulp sample ESCA analyses were conducted on a Quantum 2000 instrument from a Physical Electronics using a monochromatic Al K α x-ray source (15 kV, 20.8 W, 100 μ m beam size, 500 μ m analysis areas) at Chalmers University of Technology, Goteborg, Sweden. The detailed procedures were described in APPENDIX J. The ESCA data were generated using a probe beam of focused, monochromatic Al-K α radiation. The photons cause electrons to be ejected from the sample, which are energy analyzed and counted to reveal atomic composition and surface chemistry of the sample. The escape depth of the electrons limited the analysis to the outer approximately 5.0 nm of the fiber surface by using a 45 ° take-off angle.

In addition, TAPPI standard methods [204] were used to determine pulp kappa number (T236 cm-85) and pulp viscosity (T230 om-94). The typical standard deviations

of three replicates for the measurements of pulp kappa number and viscosity under same oxygen delignification conditions were 0.25 kappa units and 0.58 mPa.s, respectively.

4.3. Results and discussion

4.3.1. Profiling carboxylic acid content in oxygen delignified pulps

A series of one-stage oxygen delignification experiments were conducted at varied reaction times, oxygen pressures, caustic charges, and temperatures. The development of total carboxylic acid content in oxygen delignified pulps is summarized in Figures 4.1-4.2.

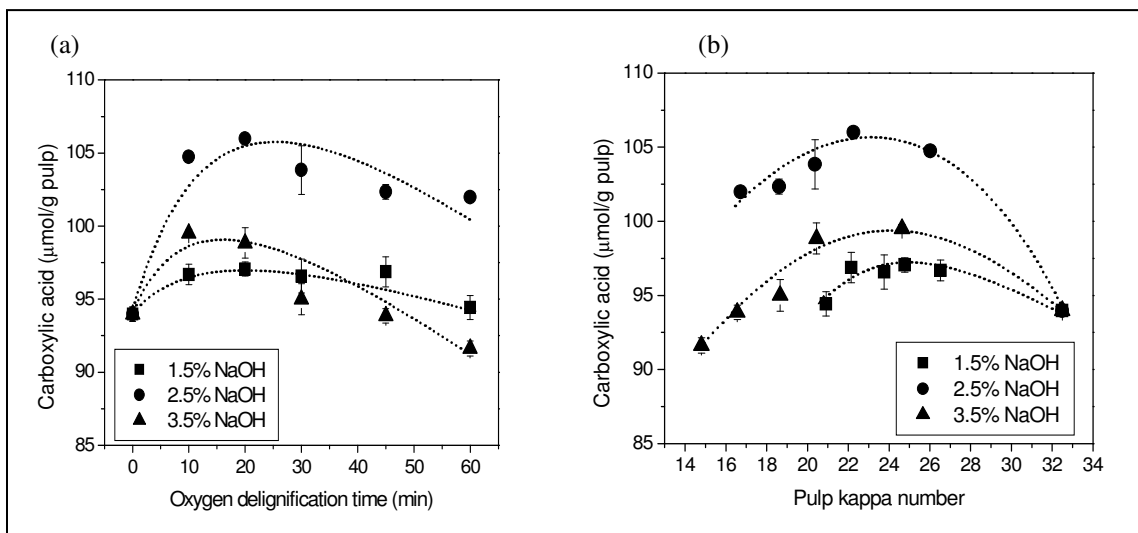


Figure 4.1. Fiber Carboxylic Acid Content Profiles at Three Different NaOH Levels during One-Stage Oxygen Delignification of a SW Kraft Pulp

Oxygen delignification conditions: NaOH: 1.5, 2.5, 3.5%, temperature: 100 °C, O₂ pressure: 800 kPa, and 10% pulp consistency

From Figure 4.1a, two distinct phases exist for total fiber carboxylic acid content profile in oxygen delignified pulps: an initial 4-13% rise in the first 10-30 minutes is followed by a slow decrease phase at three different initial NaOH levels. Figure 4.1b showed the maximum total fiber carboxylic acid content occurs at a kappa number of 22-

24 and further delignification is obviously not beneficial to total fiber carboxyl group increase.

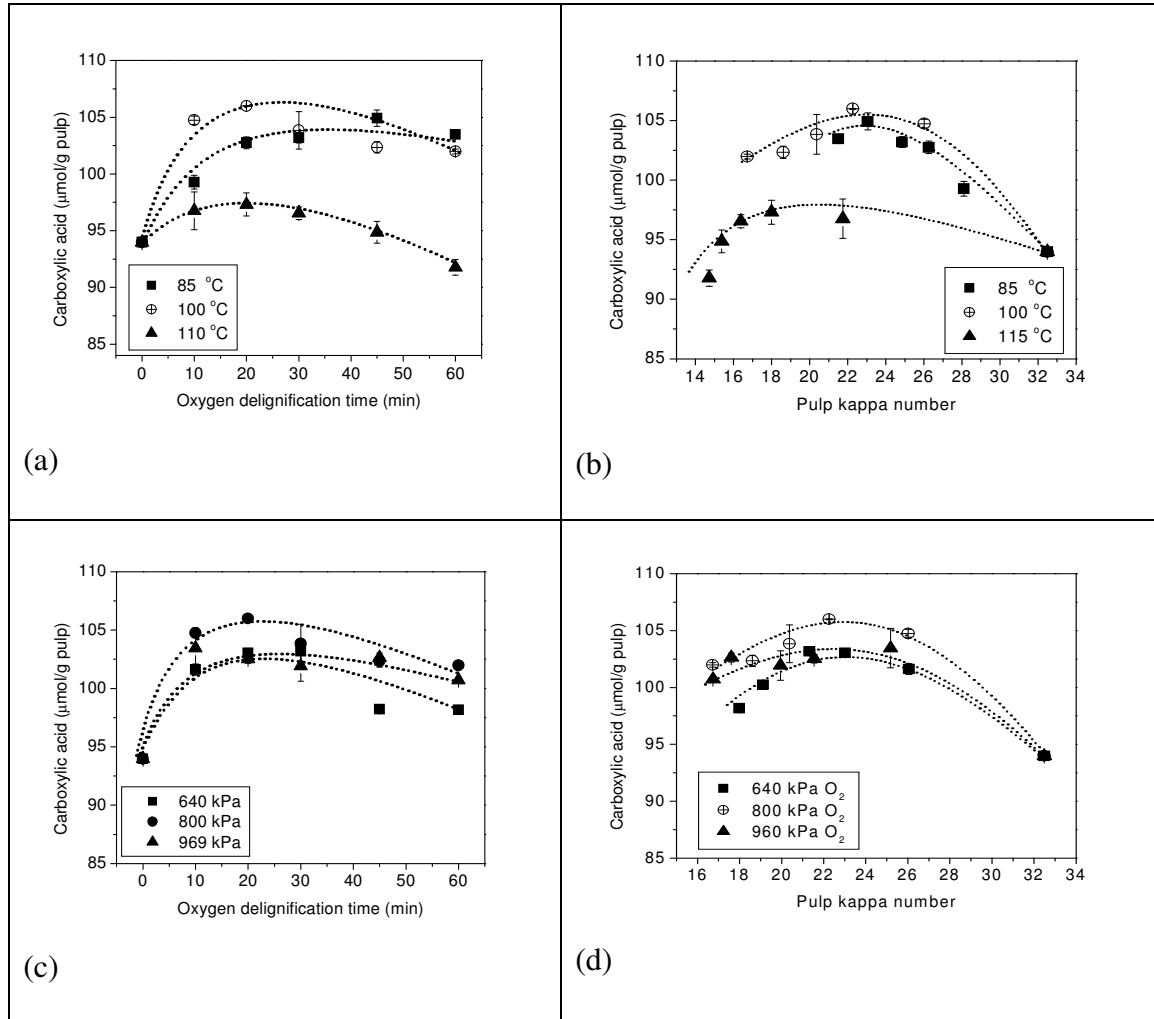


Figure 4.2. Fiber Carboxylic Acid Content Profiles at Different Temperatures (a-b) and O₂ Pressures (c-d) during One-Stage Oxygen Delignification of a SW Kraft Pulp

a-b: Temperature: 85, 100, and 115 °C; NaOH: 2.5%; O₂ pressure: 800 kPa; 10% consistency;
c-d: O₂ pressure: 640, 800, and 960 kPa; NaOH: 2.5%; Temperature: 100 °C; 10% consistency.

The same profile for total fiber carboxylic acid content was also found in oxygen delignified pulps at different temperatures and oxygen pressure as shown in Figure 4.2. Similarly, the maximum total fiber carboxylic acid content was found at a kappa number

of 21 - 24 under different reaction temperatures (Figure 4.2b) and varied oxygen pressure (Figure 4.2d). However, the maximum fiber carboxylic acid content does not occur at the maximum of delignification.

Previous oxygen delignification studies [105] have shown that residual lignin exhibits a rapid initial degradation followed by a slower delignification phase. The oxidized residual lignin in the pulps contributes to fiber acidic groups of oxygen delignified pulps. Likely, cellulosic and hemicellulose aldolic acids formed during oxygen delignification are also a source of fiber charge for oxygen delignified pulps. Therefore, total fiber carboxylic acid content in oxygen delignified pulps results from the formation of carboxylic acids in different chemical components of the fiber. The two-phase profile for fiber carboxylic acid content of oxygen delignified pulps should be ascribed to acid groups from these chemical components in each phase.

As shown in the literature [105], the degree of delignification increases with alkalinity and/or reaction temperature. However, Figure 4.1- 4.2 shows that higher NaOH (3.5%) and higher temperature (115°C) did not result in higher total fiber carboxylic acid content in oxygen delignified pulps. In addition, oxygen charge shows no significant effect on fiber carboxylic acid development under the experimental conditions studied. The optimal conditions for fiber carboxylic acid formation were found at 100 °C with 2.5% NaOH and 800 kPa oxygen.

4.3.2. Chemical component contributions

In general, the source of total fiber carboxyl groups consists of three parts: residual lignin, carbohydrate, and extractives. For oxygen delignified pulps, the contribution from extractives can be considered to be negligible. Therefore, the carboxylic acid in residual

lignin and carbohydrate are two major contributors to total fiber acid content in oxygen delignified pulps.

In unbleached kraft pulps, hexenuronic acids are an important contributor to fiber charge. However, there are few HexA remaining in holocellulose of oxygen delignified pulps due to the ClO₂ mild treatment during holopulping (see Table 4-3). The absolute amount of hexenuronic acids present in SW and HW kraft pulps has been reported to vary substantially depending on several parameters including wood furnish and pulping parameters [110]. For elemental chlorine free bleaching protocols, it is well established chlorine dioxide readily reacts with hexenuronic acids and these pulps typically contain only small amounts of these unsaturated sugars (<10% of HexA content in brownstock) [56, 169]. In this study, we separated carboxylic acid content in carbohydrate in oxygen delignified kraft pulp into two parts: HexA and other aldonic acids in holopulp.

Table 4-3. HexA in Oxygen Delignified Pulps and Corresponding Holopulps

Time (min)	0	10	20	30	45	60	average
HexA (μmol/g O- delig. pulp)	28.7	27.8	-	28.0	-	28.2	28.2
HexA (μmol/g holopulp)	3.5	2.9	2.8	2.2	2.0	3.5	2.8

Oxygen delignification conditions: NaOH: 2.5%, 100 °C, 800 kPa O₂, and 10% consistency.

As HexA content does not change during oxygen delignification (see Table 4-3) [56, 110, 169], accordingly, the carboxyl group content profiles of oxygen delignified pulps will be mainly affected by the carboxylic acid in residual lignin and fiber carbohydrate of the oxygen delignified pulps.

4.3.2.1. Carboxylic acid content in residual lignin of oxygen delignified pulps

Carboxylic acid content in residual lignin isolated from oxygen delignified pulps was determined using ^{31}P NMR analysis. The spectrum was shown in Figure 4.3.

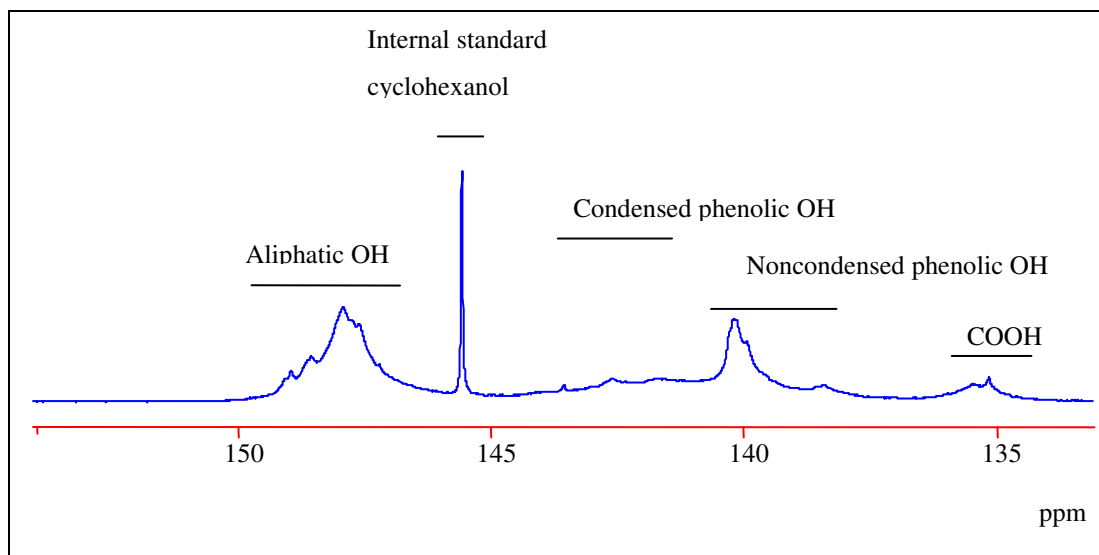


Figure 4.3. Typical ^{31}P NMR spectrum of SW Brownstock Residual Lignin

Figure 4.4 summarizes the change of carboxylic acid content in residual lignin isolated from oxygen delignified pulps treated at 100 °C with 2.5% NaOH and 800 kPa O_2 . A significant initial rise for carboxyl group content was observed in the first 10 minutes of oxygen delignification followed by a rapid decrease, after which the carboxylic acid profile exhibited a slow increase phase. The maximum carboxyl group content in lignin occurs at a kappa number of 25. The large increase in the carboxylic acid content of residual lignin in the first 10 minutes can probably be attributed to the oxidation of readily oxidizable residual lignin structures.

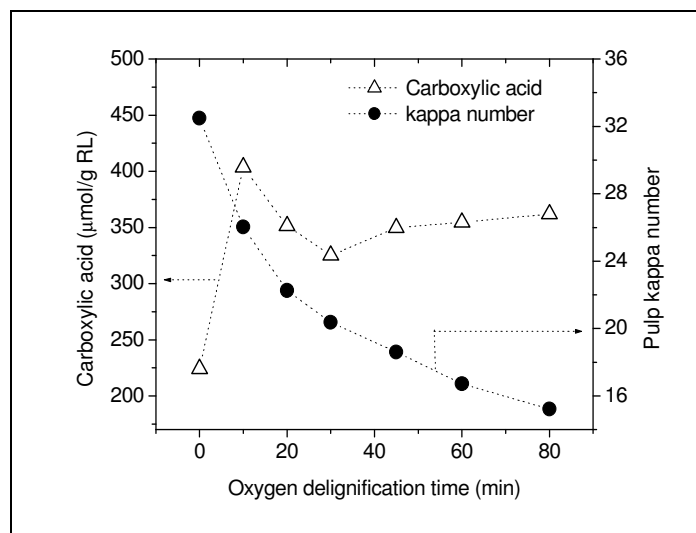


Figure 4.4. Carboxylic Acid Content Profile in Residual Lignin during One-Stage Oxygen Delignification of a SW Kraft Pulp

Oxygen delignification conditions: 2.5% NaOH, 800 kPa O₂, 100 °C, 10% consistency, 0-60 min

4.3.2.2. Time-dependent carboxylic acid profile in holopulps

Despite the changes in carboxyl group content of residual lignin during oxygen delignification, these acidic groups do not contribute to fiber charge of fully bleached pulps since subsequent bleaching stages remove these lignins. Therefore, fiber charge for fully bleached ECF pulp must originate primarily from carboxyl groups attached to polysaccharide. Previous research studies [56, 169] have reported total fiber charges of 56, 51, and 57 $\mu\text{mol/g}$ for softwood kraft pulps bleached via OPZEP, ODEDED and DEDED, respectively. The corresponding kappa numbers/HexA contents for the same fully bleached pulps were 0.8/4.0 $\mu\text{mol/g}$, 0.4/2.3 $\mu\text{mol/g}$, and 0.8/3.2 $\mu\text{mol/g}$ respectively. Since the remaining residual lignin and HexA contents in these fully bleached pulps are so low, the fiber charge of these pulps must predominantly come from carbohydrate.

To investigate carboxyl group formation in carbohydrate during oxygen delignification, instead of fully bleaching oxygen delignified pulps using ECF or TCF bleaching sequences, the oxygen delignified pulps were holocellulose pulped. These holocellulose pulps were used to evaluate the carboxyl groups in polysaccharide component of the oxygen delignified pulps after all lignin was oxidatively removed. Control experiments with oxygen delignified SW kraft pulp demonstrated that the holocellulose pulping did not result in any additional carboxylic acid formation in the oxygen delignified pulp as shown in Table 4-4.

Table 4-4. Carboxylic Acid Content in Holocelluloses of Oxygen Delignified SW Kraft Pulps at Different Holopulping Time

Treatment time (hour)	1.0	1.5	2.0	2.5	3.0
Carboxylic acid ($\mu\text{mol/g}$)	50.9	50.6	50.9	50.7	49.8

As summarized in Figure 4.5, three phases of carboxylic acid content appear in oxygen delignified holocellulose pulps. Initially, a 6-8 % of decrease in carbohydrate acid groups is observed during the first 10 minutes of oxygen delignification followed by a small increase and a final leveling off or slight decrease. Profiling the carboxylic acid content in the holocellulose oxygen delignified pulps established that a 6-8% increase in fiber carboxyl group content occurred after 26-42% oxygen delignification of the pulp. This small increase in fiber carboxyl group content limits the opportunities of engineering dramatic changes in fiber properties via a routine O-stage.

The initial rapid decrease of carboxylic acid content occurred most likely because of oxidative degradation of easily accessible hemicellulose and acidic amorphous cellulose. The gradual increase of carboxylic acid content with time should involve direct

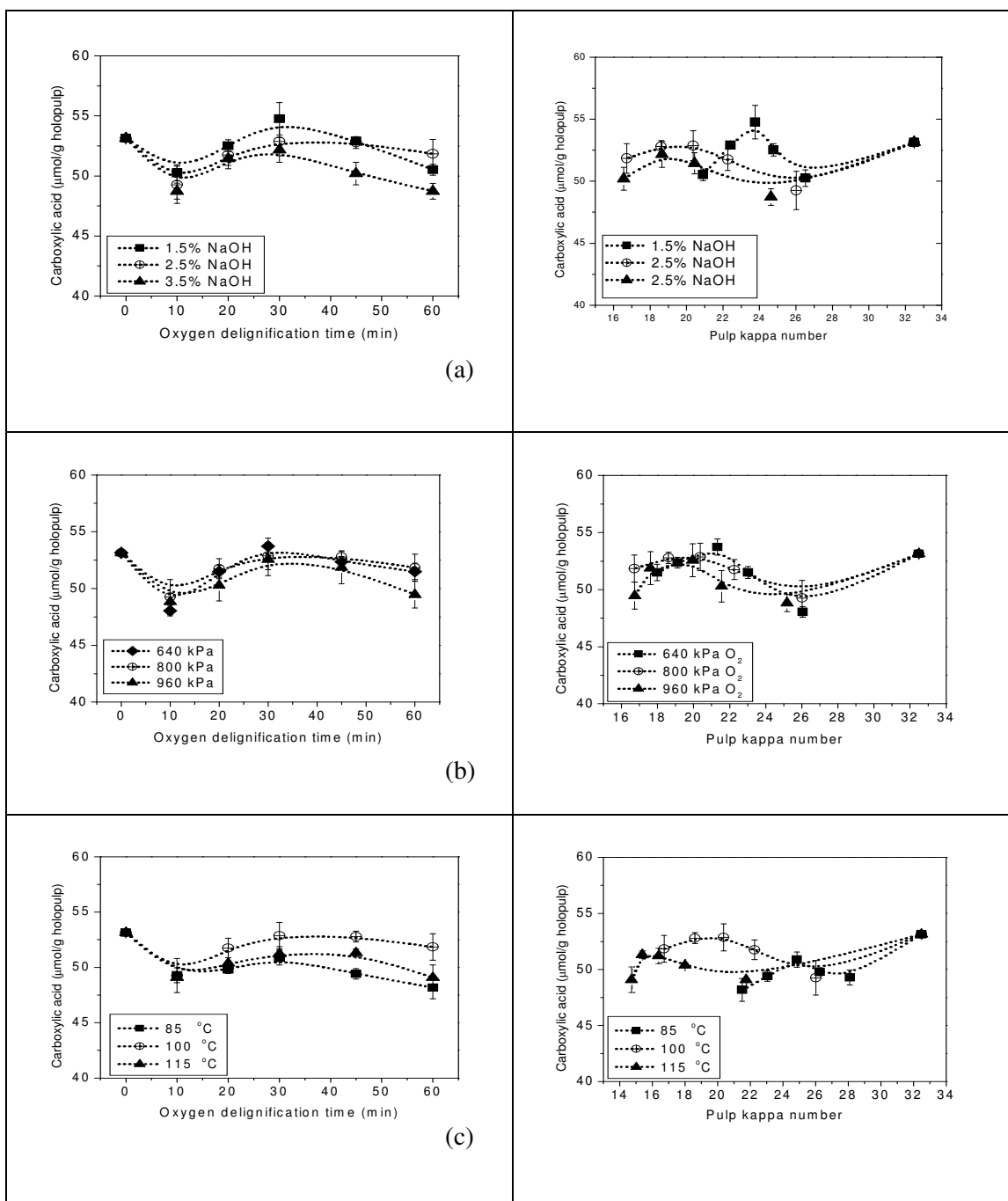


Figure 4.5. Carboxylic Acid Content Profiles in Holocelluloses of Oxygen Delignified Pulps during One-Stage Oxygen Delignification of a SW Kraft Pulp

a) NaOH: 1.5, 2.5, 3.5% at 100 °C and 800 kPa O₂; b) O₂ pressure: 640, 800, 960 kPa at 100 °C with 2.5% NaOH; c) Temperature: 85, 100, 115 °C with 2.5% NaOH and 800 kPa O₂.

oxidation of pulp carbohydrate via reactive oxygen species. This reaction is favored in the latter stages of oxygen delignification after the easily oxidizable fragments of lignin

are oxidized. The final phase consisting of a flat or slow decrease of acid group content is thought to be the oxidation and slow elimination of acid groups. These changes are supported by the reported changes of cellulose crystallinity during oxygen delignification [164].

The results in Figure 4.5 also indicate that both high alkalinity (3.5% NaOH) and high temperature (115 °C) do not favor carboxylic acid formation in holocellulose of oxygen delignified pulps. Generally, the appropriate parameters to obtain higher carboxylic acid in holocellulose of oxygen delignified pulps in this study are at 100 °C with 1.5-2.5% NaOH and 800 kPa oxygen.

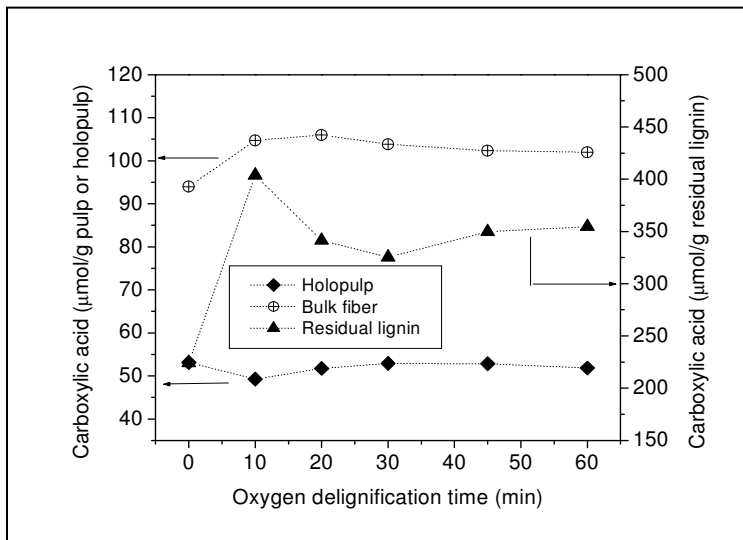


Figure 4.6. Carboxylic Acid Content in Bulk Fiber, Residual Lignin, and Holocellulose of Oxygen Delignified Pulps during One-Stage Oxygen Delignification of a SW Kraft Pulp. Oxygen delignification conditions: 2.5% NaOH, 800 kPa O₂, 100 °C, 10% consistency, and 0-60 min

As already discussed, total fiber carboxylic acid content profile during oxygen delignification is mainly influenced by carboxylic acid contents of residual lignin and pulp polysaccharide. Due to the different behavior of residual lignin and pulp

polysaccharide in an oxygen delignification stage, the relative contribution of carboxylic acid to total fiber charge from both residual lignin and holocellulose are different.

From Figure 4.6, it is obvious that the carboxyl groups in residual lignin have a significant effect on total fiber carboxylic acid content in the initial phase and the carboxylic acid content profile in carbohydrate fraction of oxygen delignified pulps influences total fiber charge behavior in the remaining phase.

Table 4-5. Fiber Charge of Oxygen Delignified Pulps and Holocelluloses

Pulp sample	Total charge ($\mu\text{mol/g}$)	Surface charge ($\mu\text{mol/g}$)	Charge ratio* (%)
Oxygen delignified pulps			
0	94.5	11.0	12.6
10	104.7	13.0	12.5
20	106.0	14.2	13.2
30	103.4	14.2	13.5
60	102.0	15.0	14.7
Holopulp			
0	53.0	7.9	16.2
10	49.1	9.0	18.3
30	53.9	8.7	16.1
60	48.6	8.6	16.3

*Charge ratio (%) = surface charge/ total charge*100; Oxygen delignification conditions: 2.5% NaOH, 100 °C, 800 kPa O₂, 10% consistency, and 0-60 min.

4.3.3. Fiber surface charge of oxygen delignified pulps

Table 4-5 shows the fiber surface charge of oxygen delignified kraft pulps and corresponding holocelluloses. It is noted that oxygen delignification increases surface fiber charge of oxygen delignified pulps by 16-26%. However, after removing residual lignin from these pulps by holopulping, the fiber surface charge of holocelluloses is

unchanged; suggesting that the surface fiber charge increase in oxygen delignified pulps is caused mainly by the oxidation of surface lignin.

Figure 4.7 shows the high resolution and curve-resolved ESCA spectrum of the C1s peak for unbleached SW kraft pulps and corresponding oxygen delignified pulps. The resolved (C1s) signal of a surface containing cellulose, hemicelluloses and lignin containing 4 bands (C1-C4), which correspond to carbons at different oxidation levels [100, 205]: C1 band represents unoxidized carbon (C-C), the C2 band carbon with one oxygen bond (C-O), the C3 band carbon with two bonds to oxygen (C=O or O-C-O), and C4 band carbon with three bonds to oxygen (O-C=O). The results are summarized in Table 4-6. It is observed that the O/C ratio increases with the extent of oxygen delignification and the carboxyl group (C4 band) increases significantly (41-43%), which is consistent with the fiber charge results in Table 4-5.

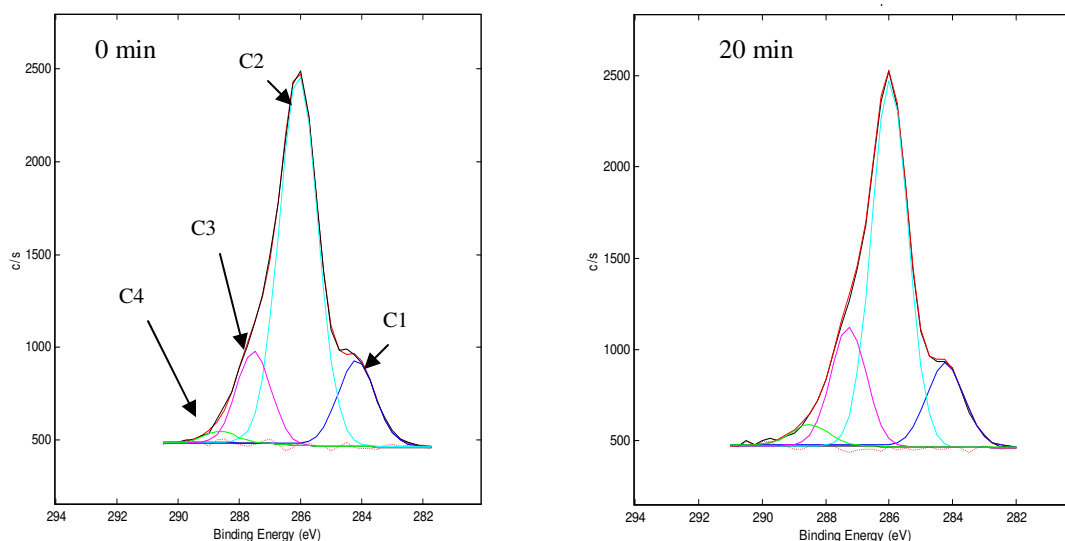


Figure 4.7.Curve-Resolved ESCA C1s Signal of Oxygen Delignified SW Kraft Pulps

Oxygen delignification conditions: 2.5% NaOH, 800 kPa O₂, 100 °C, and 10% consistency

Table 4-6. ESCA Atomic Composition and Functional Groups Present on the Surface of Oxygen Delignified SW Kraft Pulps

Sample (min)	O/C ratio (%)	C1(C-C,C-H) (%)	C2(C-O) (%)	C3(O-C-O,C=O) (%)	C4(O-C=O) (%)
0	0.690	15.91	67.71	14.65	2.73
20	0.728	15.63	61.10	19.40	3.87
60	0.773	11.50	68.65	19.54	3.91

Oxygen delignification conditions: 2.5% NaOH, 800 kPa O₂, 100 °C, and 10% consistency.

4.4. Summary

Based on the experimental results from a series of one-stage oxygen delignified pine kraft pulps, the following conclusions on carboxylic acid content in oxygen delignified pulps can be obtained.

- Total fiber carboxylic acid content profile exhibited an initial 4-13% increase in the first 10-30 minutes followed by a steady or slight decrease (2-7%).
- Holopulps in oxygen delignified pulps initially exhibited a 6-8% decrease in fiber charge in the first 10 minutes of an O-stage followed by a small increase (3-11%) and finally a slow decline (5-10%).
- The residual lignin exhibited a significant initial acid group content rise (79.9%) in the first 10 minutes of an O-stage and this was followed by a rapid decrease (19.2%) and then a slow increase (7.4-11.4%) in the remaining 50 minutes of oxygen delignification.
- The maximum carboxylic acid content for the pulp and holocellulose from oxygen delignified pulps during oxygen delignification occurred at a kappa number of 20-24 (~ 26-42% delignification), which does not match the maximum delignification.

- Under the oxygen delignification conditions studied, fiber carboxyl group content was maximized employing a reaction temperature of 100 °C with 2.5% NaOH and 800 kPa oxygen.
- Fiber surface charge was found to increase by 16-26% during oxygen delignification under the conditions of 2.5% NaOH, 100 °C, 800 kPa O₂, and 10-60 min.

These results suggest that carboxyl groups in carbohydrate fraction of softwood kraft pulps are formed and removed during an O-stage, concurrently. The dominant effect will determine the carboxylic acid content in pulp carbohydrate. However, the overall increase of carboxyl groups in total pulp fiber and carbohydrate fraction is limited during one-stage oxygen delignification.

CHAPTER 5 ELUCIDATING FIBER CARBOXYL GROUP CONTENT PROFILES DURING EXTENDED OXYGEN DELIGNIFICATION OF HIGH KAPPA SW KRAFT PULPS

5.1. Introduction

Conventionally, the production of softwood bleached kraft pulps is accomplished by cooking to a kappa number of 27-32 to reduce bleaching chemical costs and achieve higher target pulp brightness [206, 207]. Extended low kappa kraft cooking inevitably results in poor pulping selectivity, lower pulp yields, and higher recovery boiler loads in black liquor due to carbohydrate degradation caused by severe cooking conditions [131, 208, 209].

Since its introduction in 1970s, oxygen delignification has become a predominant delignification technology to produce ECF and TCF pulps due to its beneficial environment effects, reduced process costs, and energy savings [105, 106, 108, 210]. It has been demonstrated that one- or two- stage oxygen delignification can remove 35-50% of residual lignin in HW kraft pulp, and 40-70% in SW kraft pulp without significantly detrimentally impacting pulp physical properties [108, 113, 182]. Hence, extended oxygen delignification technology provides a simple and selective approach for production of high brightness bleached kraft pulps from high kappa kraft pulping. This has been recently described by Poukka *et al* [211]) as the integration of high kappa cooking and extended oxygen delignification into fiber line. The yield benefits, process selectivity, fundamental wood chemistry, and operational benefits have been extensively studied [108-111, 114, 139, 212, 213].

Recently, increasing practical interest has been drawn to understand the changes in fiber charge/acidic groups for oxygen delignified pulps [56, 160, 163]. In oxygen

delignified kraft pulps, the change in carboxylic acid content is primarily associated with the oxidation of residual lignin and polysaccharide [12, 105]. Varying cooking conditions not only affects the final pulp kappa number but also results in different structural properties for residual lignin and hemicelluloses. CHAPTER 4 reported a fundamental study on fiber carboxylic acid formation during one-stage oxygen delignification of a low kappa (32.5) SW kraft pulp, indicating maximum total fiber carboxylic acid content occurred after 26-42% delignification, depending on process conditions. It is unknown how the change of lignin content in incoming kraft pulps from high kappa cooking affect fiber carboxyl groups in the oxygen delignified pulps after extended oxygen delignification. This study elucidates the changes in carboxylic acid content for high kappa SW kraft pulps before and after extended oxygen delignification.

5.2. Experimental

5.2.1. Chemicals

All chemicals and solvents were commercially purchased from VWR or Sigma - Aldrich as reagent grade and used as received with the exception of *p*-dioxane which was freshly distilled over NaBH₄ prior to use.

5.2.2. Preparation of high kappa SW kraft pulps

Air-dried southern pine wood chips from a commercial U.S. kraft pulp mill were used for the pulping studies. Two SW kraft pulps with a kappa number of 49.5 (LSW) and 48.0 (HSW) were prepared by cooking in a M&K digester at 15% and 19% active alkali (AA) charges with 1650 and 1050 H-factors, respectively. Pulping sulfidity was kept at 25%, with cooking temperature at 170° C and a liquid/wood ratio of 4:1. After

kraft pulping, the pulps were disintegrated, screened, washed thoroughly with water, and stored at 2 °C. The pulp physical and chemical properties are presented in Table A-1 in APPENDIX A.

5.2.3. Two-stage oxygen delignification

One- and two-stage oxygen delignifications with inter-washing experiments were conducted using a 2.00-L inclined Parr reactor. Detailed oxygen delignification conditions as well as pulp kappa number and viscosity before and after oxygen delignification are summarized in Table 5-1.

Table 5-1. Oxygen Delignification Conditions and Pulp Properties

Sample	NaOH (%)	Temperature (°C)	Oxygen (kPa)	Kappa number	Viscosity (mPa.s)
LSW	-	-	-	49.5	36.8
LO	3.0	90	276	30.0	27.0
LOO1	3.0	70	276	25.0	25.2
LOO2	4.4	76	276	22.0	23.0
LOO3	1.6	105	276	19.3	20.2
LOO4	3.0	110	276	14.3	15.7
HSW	-	-	-	48.0	29.0
HO	3.0	80	276	31.0	25.0
HOO1	3.0	70	276	26.0	24.0
HOO2	1.0	90	276	24.0	23.0
HOO3	5.0	90	276	20.3	18.2
HOO4	3.0	110	276	14.8	14.5

LSW and HSW: Unbleached SW kraft pulp cooked at low AA and high AA, respectively

LO and HO: 1st stage oxygen delignification for LSW and HSW, respectively

LOO1-LOO4 and HOO1-HOO4: a series of 2nd stage oxygen delignifications for LO and HO, respectively

In a typical oxygen delignification experiment, the reactor was preheated to 60-90 °C and charged with kraft pulp (100.00 g o.d.), and the pulp consistency was adjusted to 10% using deionized water with 0.05% MgSO₄ and varying amounts of NaOH (1.0 – 5.0% on o.d. pulp). After sealing the reactor, the vessel was heated to the desired temperature (70–110°C) and pressurized with O₂ (276 kPa). The reaction was terminated after 60 minutes, and the pressure in the reactor was released. The pulps were then washed, air dried, and analyzed for pulp properties. For the OwO- stage experiment, the pulp was washed with deionized water between the first and second stage to a pH below 8 at room temperature.

5.2.4. Holocellulose preparation

Holocelluloses from the oxygen delignified pulps were isolated following a literature method [196] by treating the pulp with sodium chlorite at acidic condition.

5.2.5. Lignin isolation

Isolation of residual lignin from kraft brownstocks, O-, and OwO-stage delignified pulps was accomplished employing standard a literature method [197]. In brief, air-dried pulp (30 – 50 g o.d.) was added to an acidic *p*-dioxane prepared by adding 90% distilled *p*-dioxane to 10% 1.0 N HCl in a flask, yielding a final consistency of 4%. The pulp slurry was refluxed for 2 hours under an argon atmosphere, then cooled and filtered. The filtrate was concentrated under reduced pressure. The precipitated lignin was isolated by centrifugation, washed with acidic water (pH 2~3), and then freeze-dried. This procedure afforded, on average, 40–55% yield of residual lignin. The detailed procedures were described in APPENDIX E.

5.2.6. ^{13}C and ^{31}P NMR quantitative analysis

All NMR spectra were recorded on a 400 MHz Bruker Advance/DMX NMR spectrometer. Quantitative ^{13}C NMR spectra were acquired by using DMSO as a solvent for lignin with an inverse gated decoupling sequence, 90° pulse angle, 12-s pulse delay, and 10,000 scans [197, 214, 215]. The integration and carbon content calculation of the functional groups in the ^{13}C NMR spectra were performed in accordance with the literature method [214]. The lignin samples were also derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and analyzed by ^{31}P NMR following a literature method [203]. Cyclohexanol was used as the internal standard. ^{31}P NMR spectra were recorded using an inverse gated decoupling sequence, 90° pulse angle, 25-s pulse delay, and 150 transients at room temperature. All the NMR spectral acquisition and analyses were controlled by Bruker's XWINNMR 2.6 software running on an SGI (Silicon Graphics Indigo) server using the Irix 7.0 operating system. The detailed procedures for sample preparation and analysis were described in APPENDIX H.

5.2.7. Pulp carboxylic acid and hexenuronic acid determination

The carboxylic acid content in the pulp samples was determined by measuring CO_2 produced from the reaction of acid groups in fiber with bicarbonate solution using Headspace Gas Chromatography [201] with a standard deviation of three replicates at $1.05\ \mu\text{mol/g}$. The carboxylic acid in residual lignin was determined using ^{32}P NMR analysis as described in APPENDIX H. Hexenuronic acid content in pulps was

determined using a spectroscopic method [216] with a standard deviation for the measurements of three replicates at 0.56 $\mu\text{mol/g}$ pulp.

In addition, pulp kappa number was measured according to TAPPI method T-236 om-99 [204]. Typical experimental standard deviations for this procedure with three replicates of testing under the same conditions were determined to be 0.25 kappa units for the high kappa pulps. Pulp viscosity was determined in accordance with TAPPI standard T-230 om-89 [204] and standard deviation for pulp viscosity measurement of three replicates was 0.58 mPa.s.

5.3. Results and discussion

5.3.1. Total pulp fiber carboxylic acid content

For unbleached kraft pulps and the corresponding oxygen delignified pulps, residual lignin and pulp polysaccharide are the predominant constituents that contribute to total fiber carboxyl groups. The relationship between fiber carboxyl group content and extended oxygen delignification of high kappa SW kraft pulps has not been established. To address this issue, two SW kraft pulps with kappa numbers of 49.5 and 48.0 were prepared by conventional batch cooking with low active alkaline (LAA, 15% on o.d. pulp) and high active alkaline (HAA, 19% on o.d. pulp). These pulps were then oxygen delignified to kappa number values of 26.0-14.3 during one- and two-stage oxygen delignifications with inter-washing experiments in a Parr reactor. The pulp kappa numbers and viscosities before and after oxygen delignification conditions are summarized in Table 5-1. Obviously, the viscosities of LAA cooked pulp and corresponding oxygen delignified pulps is 5-10% higher than those of HAA cooked pulp and the oxygen delignified pulps.

The carboxylic acid content for the two SW kraft pulps and the corresponding oxygen delignified pulps were determined. These results are summarized in Figure 5.1.

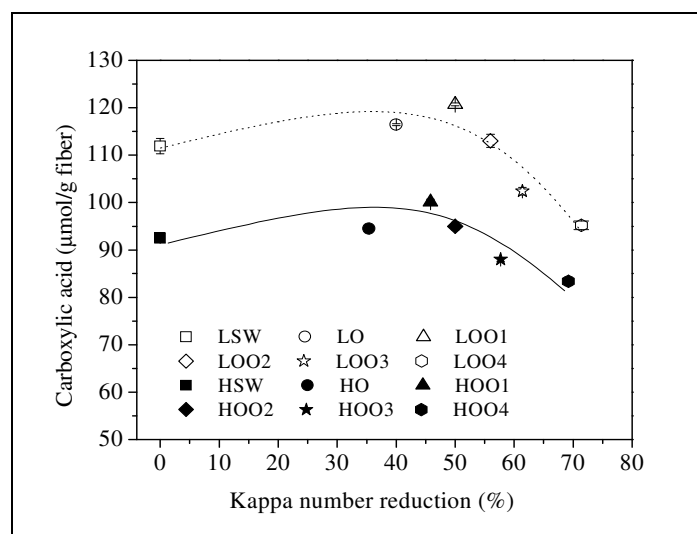


Figure 5.1. Carboxylic Acid Content in Total Fiber of High Kappa SW Kraft Pulps and the Corresponding Oxygen Delignified Pulps

It was observed that after the first stage of oxygen delignification, total fiber carboxylic acids content for both low AA and high AA cooked SW kraft pulps increased by 2-4%. However, further delignification via a second O-stage either slightly increased or decreased total fiber carboxylic acid content, depending on the degree of lignin removal, which is caused by either high caustic charge, or high temperature, or the combination of both. Generally, following the first O-stage, an additional 10-35% delignification by a second O- stage resulted in 3-18% decrease in total fiber carboxylic acid content. It is also of interest to note that the carboxylic acid content in the low AA cooked SW kraft pulp and the corresponding O- and OwO- delignified pulps was 13-23%

higher than that in high AA cooked SW kraft pulp and the corresponding O- and OwO-pulps.

5.3.2. Carboxylic acid content in polysaccharide

Since polysaccharide and residual lignin are the main chemical components to contribute carboxyl groups to total fiber charge of kraft pulps and oxygen delignified pulps, it was of interest to determine how extended oxygen delignification influenced the carboxylic acid group formation in these components. Pulp carbohydrates are known to experience two main types of reactions. One is degradation, the well-known alkaline peeling reaction [12] due to the oxidative formation of a C-2 carbonyl group on the cellulose chain. The second is the oxidative stopping reaction [105]. Both reaction pathways yield aldonic acids which are a source of new polysaccharide fiber charge for post O-delignified pulps. Polysaccharide fiber carboxyl groups are of tremendous practical interest as they represent the primary source of charge for fully bleached pulps. Furthermore, for fully bleached ECF pulps, the charge due to HexA plays a negligible role [56]. Hence, to evaluate polysaccharide fiber carboxyl groups before and after an oxygen stage, holocellulose was isolated by oxidatively removing residual lignin and HexA components from the pulps.

Figure 5.2 summarizes the carboxylic acid content for the holocellulose pulps of an O- and OwO delignified SW kraft pulps. The data in Figure 5.2 indicates that the carboxylic acid content in polysaccharide of low AA cooked SW kraft pulp and corresponding oxygen delignified pulps was 4-10% higher than that of high AA cooked SW kraft pulp and the corresponding oxygen delignified pulps. Generally, carboxylic acid content in holocellulose pulps decreased by 12-26% during oxygen delignification in

a near-linear relationship with lignin removal for both low AA and high AA cooked pulps.

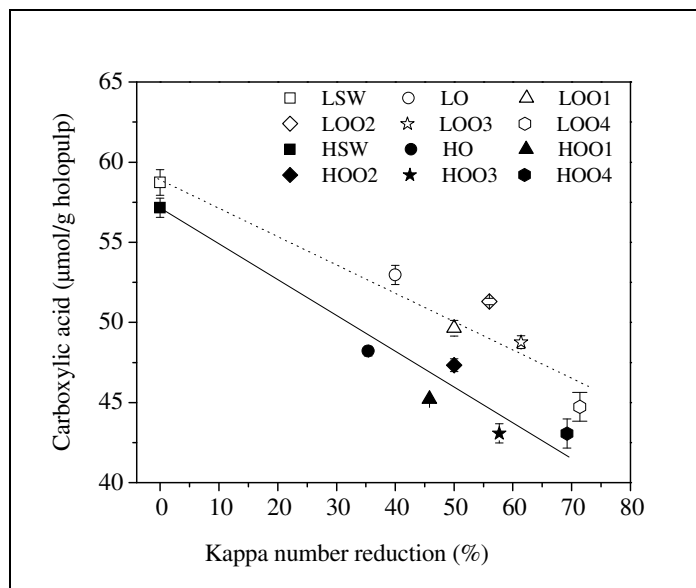


Figure 5.2. Carboxylic Acid Content in Holocelluloses of High Kappa SW Kraft Pulps and the Corresponding Oxygen Delignified Pulps

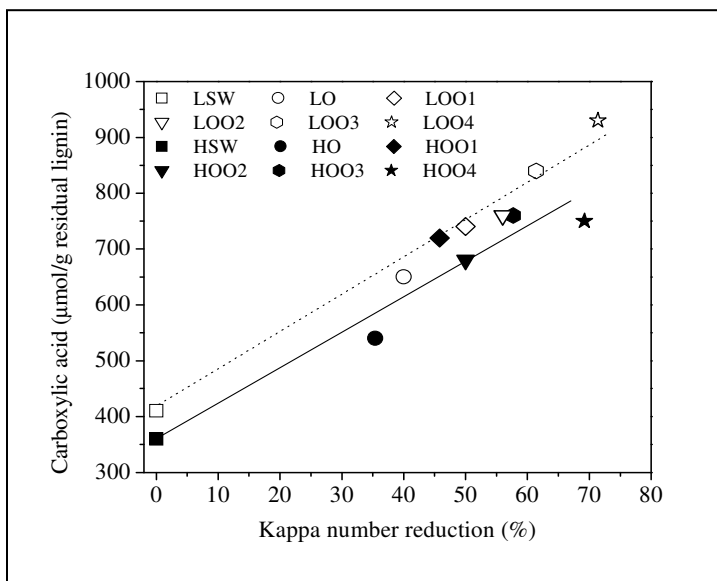


Figure 5.3. Carboxylic Acid Content Residual Lignin of High Kappa SW Kraft Pulps and the Corresponding Oxygen Delignified Pulps

5.3.3. Carboxylic acid content in residual lignin

Carboxylic acid content in the residual lignin isolated from an O- and OwO- stage delignified pulps was determined by quantitative lignin ^{31}P NMR analysis [203] and these results are presented in Figure 5.3. A 50-100% increase in the acid level of the oxidized residual lignin was found after an OwO-stage for both high AA and low AA cooked SW kraft pulps under the experimental conditions studied.

It is known that conjugated carboxylic acids can be formed by oxidative attack of oxygen species toward phenolic moieties in residual lignin to cause aromatic ring opening and generate muconic acids under alkaline conditions [12]. The cleavage of the $\text{C}_\alpha\text{-C}_\beta$ linkage of etherified structures containing an α -carbonyl group has been shown to yield benzylic-type ring-conjugated carboxylic acid [12, 139]. ^{13}C NMR analysis of residual lignin isolated from the SW kraft brownstocks and post-oxygen delignified pulps provided a facile means of measuring the ratio of conjugated: unconjugated carboxylic acids as shown in Figure 5.4.

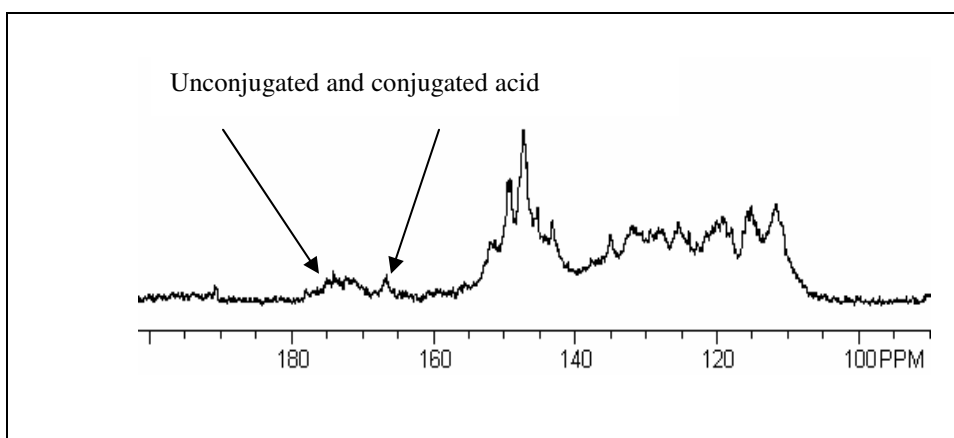


Figure 5.4. ^{13}C NMR Spectra of Isolated Residual Lignin from an Oxygen Delignified SW Kraft Pulp (HOO1)

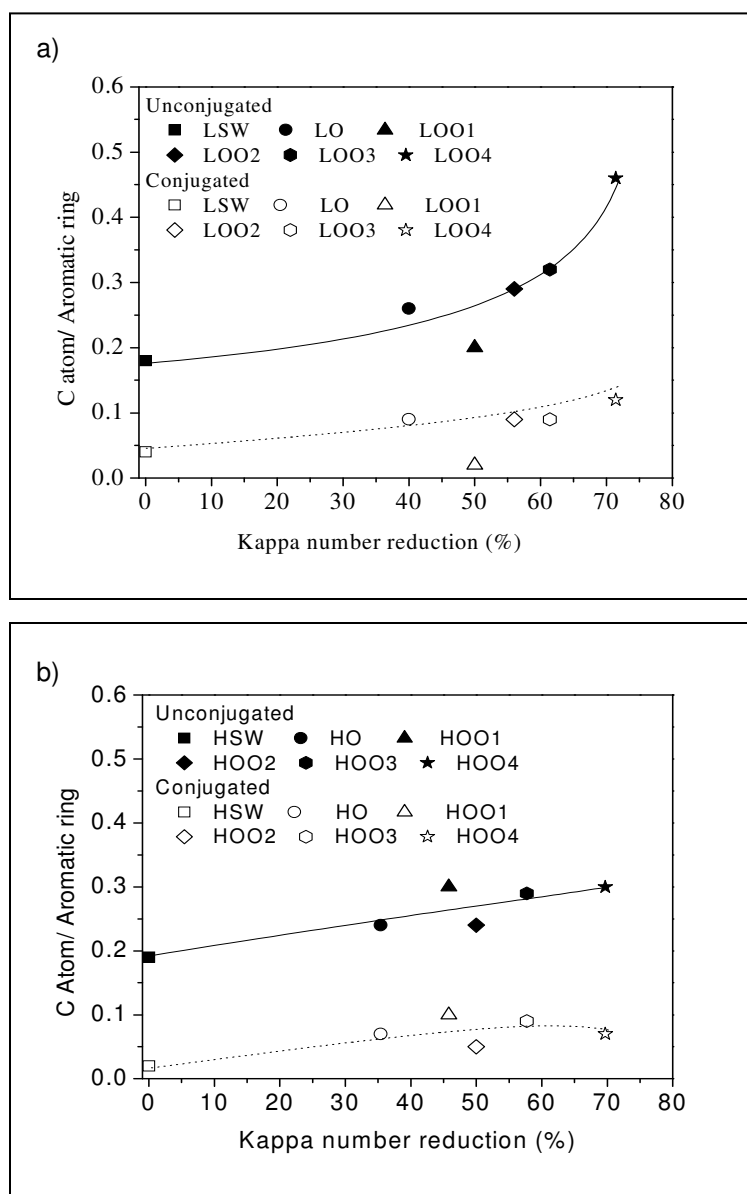


Figure 5.5. Conjugated and Unconjugated Carboxylic Acids in the Residual Lignins of (a) Low AA and (b) High AA Cooked SW Kraft Pulps and the Corresponding Oxygen Delignified Pulps

The ^{13}C NMR spectra data (Figure 5.5) demonstrated that the residual lignin from an O- and OwO- stage kraft SW pulps had an increase in carboxylic acid content similar to the results observed with ^{31}P NMR analysis. The residual lignin from the oxygen delignified pulps had a ratio of approximately 3-4:1 for unconjugated to conjugated acid

groups. Clearly, the unconjugated carboxylic acid groups dominate acid functional groups in the residual lignin of post-oxygen delignified SW kraft pulps. This suggests that most of the muconic acids or benzylic-type ring-conjugated carboxylic acids formed in residual lignin during oxygen delignification were further oxidatively fragmented.

5.3.4. Characteristic kappa number for maximum fiber carboxylic acid content

As oxygen delignification proceeds, carboxyl groups in both carbohydrate and residual lignin of the pulp are formed and removed simultaneously under alkaline conditions. As a result, a maximum in pulp carboxylic acid content can occur. The previous study (CHAPTER 4) on one-stage oxygen delignification of a 32.5 kappa SW kraft pulp indicated that maximum total fiber carboxylic acid content occurred after 24-42% delignification, corresponding to a kappa number of 20-24. From Figure 5.1, a maximum for total fiber carboxylic acid content was observed after 45-50% delignification under the experimental conditions studied, which corresponds to a kappa number of 24-25. These results suggest that a kappa number 20-25 for oxygen delignification of SW kraft pulps can be considered as a characteristic value range to obtain a maximum of total fiber carboxylic acid content.

5.3.5. Effect of cooking active alkali on carboxylic acid formation

As reported from the literature [56], HexA content in oxygen delignified pulps did not change before and after oxygen delignification. However, HexA analysis in this study indicated that low active alkali cooked kraft pulp had higher HexA content (~39.5 $\mu\text{mol/g}$ pulp) than that in high active alkali cooked SW kraft pulp (~28.0 $\mu\text{mol/g}$ pulp). After subtracting HexA from total fiber carboxyl group content, the remaining carboxylic acid

content in low AA cooked SW kraft pulp and the corresponding oxygen delignified pulps were still 3-10% higher than that in high AA cooked SW kraft pulp and the corresponding oxygen delignified pulps (Figure 5.6). The same trend was observed for acid group content in both holocelluloses (Figure 5.3). These results indicate it is likely to achieve higher or lower fiber carboxyl group content through high kappa cooking by changing active alkali followed by an extended oxygen delignification.

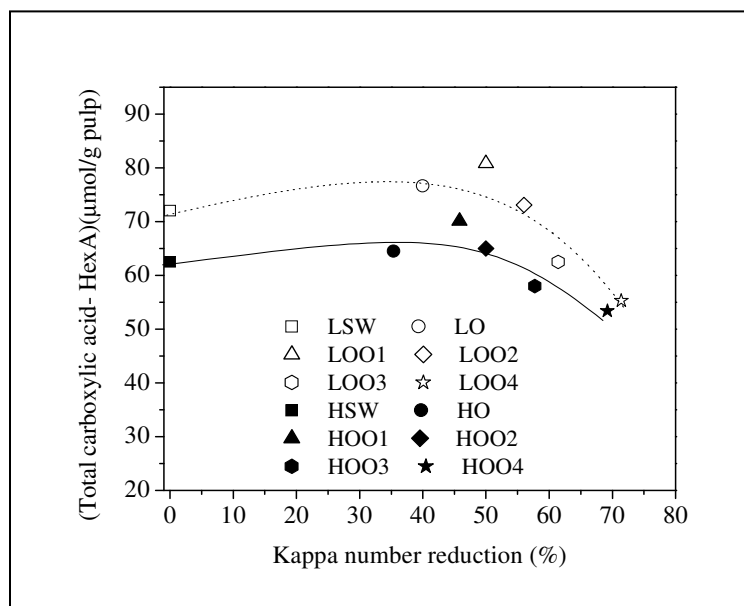


Figure 5.6. The Effect of Cooking Active Alkali on Carboxylic Acid Content of Oxygen Delignified SW Kraft Pulps Corrected for HexA Content

5.4. Summary

This study examined carboxylic acid content profiles during an O- and OwO- stage delignification for both high AA and low AA cooked SW kraft pulps. The results demonstrated that the first stage of oxygen delignification increased total fiber carboxylic acid content by 2-4%. Further delignification via a second O-stage either slightly

increased or decreased total fiber carboxylic acid content depending on the degree of lignin removal. Following first O-stage, additional 10-35% delignification from a second O-stage decreased fiber carboxylic acid content by 3-18%. The carboxylic acid content in the corresponding polysaccharides decreased by 12-26% with the extent of O- and OwO-stage delignification for both high AA and low AA cooked SW kraft pulps. However, a 50-100% increase of carboxylic acid content in residual lignin of oxygen delignified pulps was obtained after an OwO-stage delignification. The residual lignin from the oxygen delignified pulps had approximately 3-4:1 of unconjugated to conjugated acid groups. Generally, the carboxylic acid content in low AA cooked SW kraft pulp and the corresponding oxygen delignified pulps were systematically higher (13-23%) than that in high AA cooked SW kraft pulp and the corresponding oxygen delignified pulps. These results demonstrate that the integration of high kappa cooking and extended oxygen delignification provides a simple and direct approach to obtain higher or lower fiber carboxyl groups from kraft pulping and extended oxygen delignification.

The experimental results (combining with the results in CHAPTER 4) demonstrated that maximum carboxylic acid content in total fiber occurred at kappa numbers of 20-25, which can be considered a characteristic value range for oxygen delignification of a southern pine kraft pulp to obtain maximum carboxylic acid content in total pulp fiber.

CHAPTER 6 ENHANCEMENT OF FIBER CARBOXYL GROUPS BY CATALYTIC OXIDATION DURING ONE-STAGE OXYGEN DELIGNIFICATION

6.1. Introduction

The content and topological location of carboxyl groups attached to cellulosic fibers play a significant role in papermaking process. It has been reported that carboxyl groups in pulps are the principal sites involved in the retention of various wet-end additives in pulp suspensions [217]. Barzyk *et al* [4, 6, 61] have demonstrated that surface fiber charge exhibited unique properties, such as increasing specific fiber-fiber bond strength. Furthermore, bulk carboxyl groups in pulps affect aqueous fiber swelling and flexibility and inter-fiber bonding during the pressing and drying processes, and consequently influence the physical strength properties of dried paper sheets [64, 81, 218].

Typically, fully bleached kraft pulps have less than 0.1 mmol/g of carboxylic acid groups [219]. The charged groups originate, in part, from the hemicellulose fraction of the pulp.

The previous study (CHAPTER 4) profiled the changes in carboxylic acid content for softwood kraft fiber during one-stage oxygen delignification. This study clearly defined the amount of fiber carboxyl groups that could be attributed to residual lignin and polysaccharide. Maximum carboxylic acid content in total fiber and carbohydrate fraction of the pulp (holocellulose) was shown to occur after 26-42% oxygen delignification. Further extension of the oxygen delignification process to lower lignin content pulps decreased fiber carboxylic acid content for both total fiber and polysaccharide portion. Therefore, it is difficult to realize both a high degree of

delignification and maximum fiber carboxyl group formation under typical one-stage oxygen delignification treatments. In CHAPTER 5, although higher fiber carboxylic acid content can be obtained from the integration of high kappa cooking at low active alkali and extended oxygen delignification, obviously, the amount of fiber carboxyl group increase in polysaccharide is still low. For bleached kraft pulps, enhancement of acid groups in pulp polysaccharide is of primary importance since lignin acid groups are removed during sequential bleaching operations.

An alternative means of enhancing the formation of fiber carboxyl groups in an oxygen delignification stage is to develop novel chemical agents that could oxidatively increase fiber acidic groups. A review of the oxygen delignification literature [220-224] indicates that the use of a co-oxidant and/or catalyst in an O-stage is most frequently applied to extend delignification but not increase fiber charge/acidic groups. Nonetheless, several studies have reported the use of noble metal catalysts to selectively oxidize the hydroxyl groups of carbohydrate into the corresponding acid groups under reaction conditions similar to oxygen delignification [221, 225, 226]. For example, Felthouse reported [226] that ruthenium pyrochlore oxide could be employed as a catalyst to selectively oxidize alkyl alcohols and aldehydes to their corresponding alkyl acids using molecular oxygen as an oxidizing agent under alkaline conditions. Atr *et al* [227] successfully employed this catalyst to oxidize trans-1,2-cyclohexanediol and methyl α -D-glucopyranoside into corresponding di-acid at 50-75°C, with 15-29 bar of O₂ pressure. However, it is unknown whether this catalyst can catalytically oxidize the hydroxyl group into carboxylic acid in lignocellulosic fiber. This chapter summarizes our efforts at examining and optimizing the application of bismuth ruthenium pyrochlore oxide during

oxygen delignification to enhance carboxyl groups in pulp carbohydrate without significantly decreasing in pulp viscosity.

6.2. Experimental

6.2.1. Materials

A commercial southern U.S.A pine unbleached kraft pulp (CSW) with a kappa number of 32.5 was used for the study of catalytic oxidation during one-stage oxygen delignification. All chemicals and solvents were commercially purchased from VWR or Sigma-Aldrich and used as received.

6.2.2. Preparation of the catalyst

The catalyst, bismuth ruthenium pyrochlore oxide, was prepared following the procedure described by Harold *et al* [228]. In brief, 2.4729 g BiNO₃ and 1.0424 g RuCl₃ were added to 100 ml of water and 50 ml of concentrated nitric acid to obtain an equimolar bismuth ruthenium aqueous solution. This solution is then added, with stirring, to 600 ml of 9N KOH and kept at 77 °C for 16 hours. The resulting precipitate is then separated by centrifuging at 2500 g and reacted for another 16 hours in 600 ml of 6N KOH at 75 °C. The solid is then again separated by centrifuging and reacted for an additional 65 hours in 600 ml of 3N KOH at 85 °C. The product isolated by centrifuging was washed with deionized water (3 × 100 mL) and then dried in the oven at 105 °C.

6.2.3. Oxygen delignification and kraft lignin catalytic oxidation

All oxygen delignification experiments were conducted in a 2.00-L inclined rotary stirred Parr reactor. In a typical experiment, 30.00 grams oven-dried unbleached kraft pulp was adjusted to 10% pulp consistency, with deionized water and 1.00 N NaOH

solutions (2.5% NaOH mass on pulp). MgSO₄ was added to the reaction mixture so that the molar ratio of Mg/Mn in the pulp was kept at 33:1 [150]. The ruthenium pyrochlore oxide catalyst (0.00-0.50% on pulp) was added to the pulp slurry with stirring. The reaction mixture was then added to a pre-heated reactor, sealed, pressurized to 800 kPa with O₂ and rapidly (~ 5 min) heated to the target temperature. After 1 hour, the reaction was terminated and the vessel pressure was vented. The oxidized pulp was then filtered, washed with deionized water and stored at 2 °C until further analysis.

An orthogonal experimental design with 3-factor at 3-level (L₉3³) was also employed for parameters optimization. The experiment conditions are shown in Table 6-1.

Table 6-1. L₉3³ Orthogonal Experimental Design (3-Factor at 3-Level)

Level	Factor		
	NaOH (% o.d. pulp)	Temperature (°C)	Oxygen (kPa)
1	1.5	85	640
2	2.5	100	800
3	3.5	115	960

For kraft lignin oxidation, 0.50 g SW kraft lignin isolated from unbleached kraft pulps was mixed with 400 mL of deionized water. 0.28 g sodium hydroxide was then added, causing solubilization of the lignin. The mixture was oxidized by 800 kPa oxygen at 100 °C with and without 0.020 g catalyst (which was equivalent to 0.20 % based on pulp with kappa number of 32.5). The oxidized lignin sample was prepared for ³¹P NMR analysis following a literature procedure [198].

6.2.4. Holopulping

The oxygen-delignified pulps were holocellulose pulped (holopulp) following a literature described procedure [196].

6.2.5. Analytical methods

6.2.5.1. *Carboxylic acid content measurements*

Carboxylic acid content in pulp sample was determined based on the method developed by Chai *et al* [216] using Headspace Gas Chromatography to quantify CO₂ produced from the reaction of acid groups in pulp sample with NaHCO₂ at elevated temperature. The typical standard deviation for fiber carboxyl group measurements of three replicates under the same oxygen delignification conditions was 1.05 µmol/g.

Residual lignin was isolated from pulps by employing a mild acid hydrolysis procedure that had been described in the literature [197] and the carboxylic acid in residual lignin and oxidized lignin was determined using ³¹P NMR technique following a literature method [203].

6.2.5.2. *Pulp water retention value measurement*

Pulp WRV measurement was conducted according to a TAPPI testing method (Tappi um-256). In brief, a pulp mat of a fixed basis weight (0.63 o.d. g) was formed by draining a dilute pulp slurry (0.5% or less consistency) on a fine mesh screen in a centrifuging cup. The pulp pad was then centrifuged at 900g for 30 min. The wet pad after centrifuging was weighed then dried and weighed again. The water retention values were calculated from the following equation,

$$WRV(\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (11)$$

where

W_w : the weight of wet sample after centrifugation (g)

W_d : the weight of oven-dried sample (g).

Typical standard deviation for WRV measurement of three replicates under the same bleaching conditions was 2 g water/100 g pulp.

In addition, TAPPI standard methods [204] were used to determine pulp kappa number (T236 cm-85), pulp brightness (T452 om-92), and pulp viscosity (T230 om-94). The typical standard deviations for the measurements of these pulp properties of at least 3 replicates were 0.25 kappa units, 0.15 brightness units, and 0.58 mPa.s, respectively.

6.3. Results and discussion

6.3.1. Effect of catalyst dosage

To investigate the ability of bismuth ruthenium pyrochlore oxide to enhance fiber charge during oxygen delignification, a series of reactions were carried out at 10% consistency, 2.5% NaOH, 100 °C, and 800 kPa O₂, with 0.00 – 0.50% of catalyst added. In order to evaluate carboxylic acid content of pulp polysaccharide during catalytic oxygen delignification process, the oxygen delignified pulps were holopulped to obtain lignin-free pulps (holopulps). Table 6-2 summarizes carboxylic acid content in the oxygen delignified holocellulose pulps with different catalyst dosages. In addition, the kappa number and viscosity of oxygen delignified pulps were determined to examine the effects of the catalyst on fiber properties and these results are also presented in Table 6-2.

Table 6-2. Pulp Physical and Chemical Properties after Oxygen Delignification with the Addition of Catalyst

Catalyst (% o.d. pulp)	Carboxylic acid of holopulp ($\mu\text{mol/g}$)	Pulp kappa number	Pulp viscosity (mPa.s)
0	44.8	16.7	17.9
0.09	68.2	17.0	17.2
0.13	73.2	17.0	17.4
0.18	96.8	17.3	17.4
0.34	89.7	17.5	17.1
0.50	87.2	17.7	17.0

O-Conditions: 10% consistency, 2.5% NaOH, 100 °C, 800 kPa O₂.

These data indicate that carboxylic acid content in holocellulose pulps rises rapidly with increasing catalyst usage in an oxygen-stage. A 0.09 - 0.18% dose of catalyst in an O-stage leads to 40.3 - 116.0% carboxylic acid content increase in carbohydrate fraction of the oxygen delignified pulp. Additionally, there is no significant difference in the viscosity values for oxygen delignified pulps with and without the catalyst employed. This result indicates that the catalytic oxidation does not lead to significant carbohydrate chain cleavage. The pulp kappa number data in Table 6-2 demonstrates that a low charge of catalyst ($\leq 0.18\%$) has no negative effect on the degree of oxygen delignification. Application levels of the catalyst higher than 0.18% did not result in a net increase of fiber charge in the holocellulose pulps. Indeed, catalyst applications of more than 0.20% catalyst resulted in a net decrease of polysaccharide carboxylic acid groups.

As reported by Felthouse [226], under the alkaline oxygen conditions employed, it is believed that the ruthenium pyrochlore oxide results in in-situ formation of oxoruthenium (IV) complexes. This Ru^{IV} species is known to react with primary and secondary alcohol

groups to yield a reduced ruthenium (III)-alkoxide complexes. The reduced ruthenium species are unstable in alkaline solutions under oxygen pressure [229].

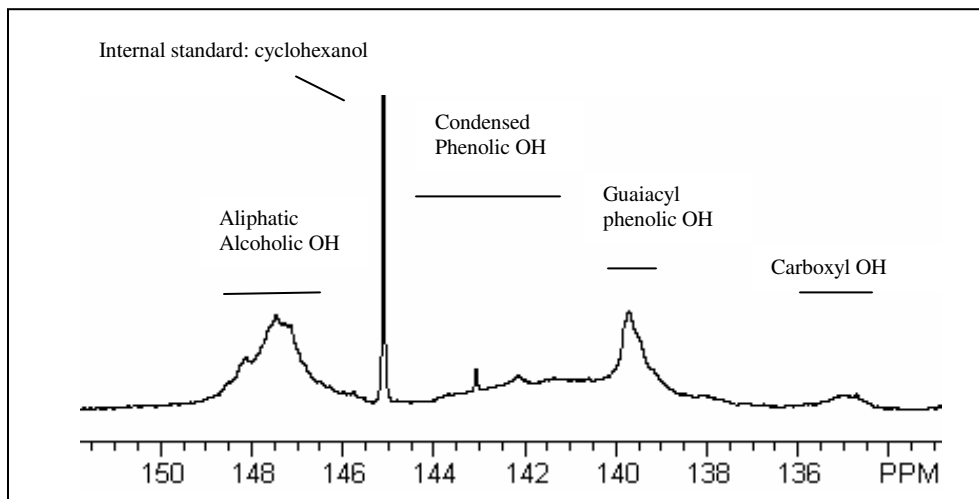


Figure 6.1. Typical ^{31}P NMR Spectrum for An Unbleached SW Kraft Lignin without catalyst employed.

To understand what components of the pulp are oxidized and contribute to the enhanced fiber carboxyl group formation, residual softwood kraft lignin was isolated from oxygen delignified pulps with and without the catalyst employed. This lignin was phosphitylated and quantitatively analyzed by ^{31}P NMR analysis. Figure 6.1 provides a typical ^{31}P NMR for the isolated SW kraft lignin. The integration region from δ 136.0 to 133.8 ppm was used to quantify carboxylic acid groups in the lignin samples. Figure 6.2 demonstrates that carboxylic acid content in residual lignin of oxygen delignified pulps with 0.18 % catalyst charge is 9.7 - 20.3% higher than that without the catalyst applied. When oxidizing kraft lignin isolated from the unbleached SW kraft pulp with and without catalyst, it was also found that the oxidized lignin with 0.020 g catalyst had 12.6% greater carboxylic acid content than the lignin sample oxidized without catalyst (Figure 6.3).

These results indicate that bismuth ruthenium pyrochlore oxide catalyst enhances carboxylic acid formation in residual lignin.

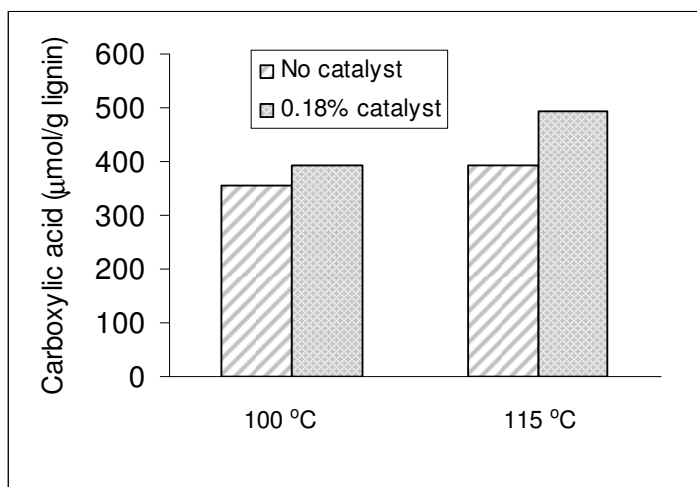


Figure 6.2. Carboxylic Acid Content in Isolated Lignin of Oxygen Delignified SW Kraft Pulps by ^{31}P NMR Analysis

Conditions: 10% pulp consistency, 2.5% NaOH, 800 kPa O_2 , 60 min

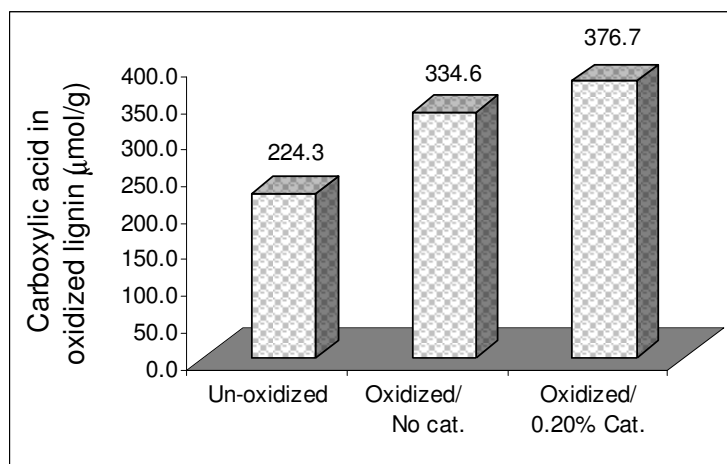


Figure 6.3. Carboxylic Acid Content in Oxidized Lignin by ^{31}P NMR Analysis

Conditions: initial pH > 13, 800 kPa O_2 , and 60 min

Table 6-3. Carboxylic Acid Content in Oxidized Softwood Kraft ECF Pulps

Pulp	NaOH (%)	Temp. (°C)	Oxygen (kPa)	Carboxylic acid (μmol/g)	
				Pulp	holocellulose
SW ECF	1.0	50	350	38.9	44.8
SW ECF + 0.18% cat.	1.0	50	350	36.0	44.3
SW ECF	1.2	100	640	36.7	43.1
SW ECF + 0.18% cat.	1.2	100	640	36.5	46.6
SW ECF	2.5	85	960	37.1	47.1
SW ECF + 0.18% cat.	2.5	85	960	36.8	45.7
SW ECF, 0.11% kraft lignin	2.5	85	960	37.8	42.4
SW ECF, 0.11% kraft lignin, 0.18% cat.	2.5	85	960	37.4	44.5

10% pulp consistency; reaction time: 60 min.

To further investigate how bismuth ruthenium pyrochlore oxide enhances polysaccharide carboxylic acid formation under oxygen delignification conditions, a commercial fully bleached ECF softwood kraft pulp (TAPPI brightness 88%) was chosen as a model to explore reactivity of the catalytic oxygen delignification treatment with pulp polysaccharide. The oxidative reaction conditions and results are summarized in Table 6-3.

Based on these results, employing 0.18% of catalyst under O-delignification conditions did not lead to a significant increase of polysaccharide carboxylic acid groups when a fully bleached pulp was employed. The addition of isolated kraft lignin to the reaction mixture prior to a catalytic O-stage did not increase carboxylic acid content in the pulp polysaccharides. These results can be readily attributed to a mechanism whereby the catalyst oxidizes carbohydrate attached to natural lignin fragments. Lignin-carbohydrate complexes (LCCs) are well known to exist in kraft pulps [230] and 85-90

% of the residual lignin in unbleached kraft pulps were reported to exist as LCCs. Based on the proposed “peeling delignification” mechanism involving LCCs [231], the carbohydrate in LCCs will be broken down from the attack of hydroxyl radical produced from phenonate delignification (Step I- IV in Figure 6.4) and a new reducing end in the carbohydrate will be formed. Generally, peeling reaction will start from this reducing end to decrease pulp DP and viscosity till a stopping reaction. However, when a catalyst like bismuth ruthenium pyrochlore oxide exists, it may catalytically oxidize the newly formed reducing end to corresponding carboxyl group (Step V in Figure 6.4). As a result, these oxidized fragments remain after residual lignin is removed and fiber carboxyl groups increase but the pulp viscosity does not decrease to an appreciable extent due to the oxidative stabilization, which are observed from the experimental results in Table 12.

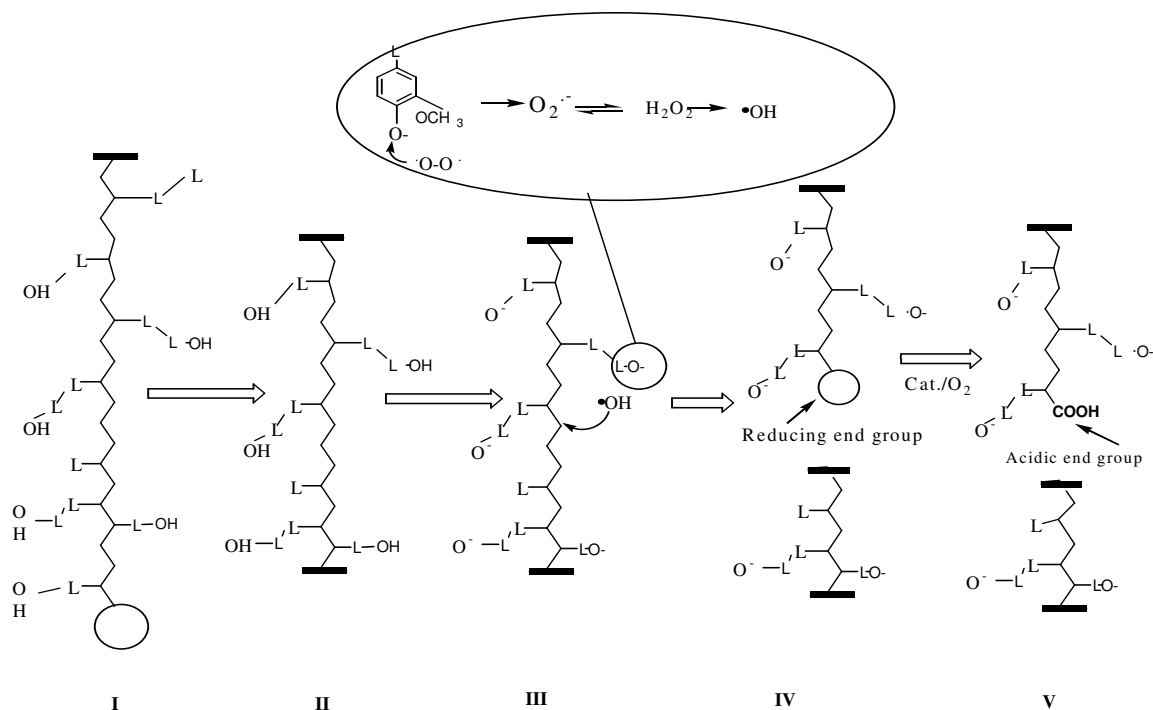


Figure 6.4. Proposed Mechanism for Carboxyl Group Formation in Carbohydrate Attached to LCCs through Catalytic Oxidation

Table 0-4. L_93^3 Orthogonal Experimental Design Employing 0.18% Catalyst in Oxygen Delignification and the Corresponding Results

Treatment	Factor			Response factor
	NaOH (%)	Temperature (°C)	O ₂ (kPa)	Carboxylic acid (μmol/g holopulp)
Group 1	1.5	85	640	70.4±0.14
Group 2	1.5	100	800	85.5±0.23
Group 3	1.5	115	960	80.7±0.56
Group 4	2.5	85	800	92.5±0.75
Group 5	2.5	100	960	85.4±0.32
Group 6	2.5	115	640	92.3±0.81
Group 7	3.5	85	960	94.4±0.93
Group 8	3.5	100	640	77.7±0.28
Group 9	3.5	115	800	75.5±0.54
K ₁ [*]	235.6	257.3	240.4	S ^{**} = 755.4
K ₂	271.1	249.5	253.5	
K ₃	247.7	248.6	261.5	
k ₁ (=K ₁ /3)	78.9	85.8	80.1	
k ₂ (=K ₂ /3)	90.4	83.7	84.5	
k ₃ (=K ₃ /3)	82.6	82.9	87.2	
R ^{***}	11.7	2.9	7.1	

Conditions: All reactions are conducted for 60 min with 0.18% catalyst; * K₁, K₂, and K₃: Sum of carboxylic acid content from three experiments with three level-1s, three level 2s, and three level 3s respectively; ** S: Sum of carboxylic acid content from 9 experiments; *** R = maximum k – minimum k.

6.3.2. Optimization

To further optimize reaction conditions to obtain high fiber carboxylic acid content during catalytic oxidation, an orthogonal experimental design with 3-factor at 3-level (L_93^3) was employed. Carboxylic acid content in polysaccharide was used as the response

factor. The experiment conditions are shown in Table 6-1 and the results are summarized in Table 6-4.

The R value in Table 6-4 indicates the effect of different experimental parameters on the formation of carboxyl groups in polysaccharides of the oxygen delignified pulps. The larger the R value, the more significant a factor it is for carboxyl group formation. Based on this analysis, the relative significance of the experimental factors influencing fiber carboxylic acid content is NaOH charge > oxygen pressure > reaction temperature. The parameter with the least significant effect in Table 6-4 is the experimental temperature, suggesting that the lowest temperature employed (85 °C) is high enough to provide the activation energy required for the catalytic oxidation of hydroxyl groups in pulp carbohydrate to the corresponding carboxylate groups.

6.3.3. Effect of individual parameter

6.3.3.1. *Alkalinity*

As a main factor, the effect of caustic charge on polysaccharide carboxylic acid formation in holocelluloses is illustrated in Figure 6.5. The carboxylic acid content in holocellulose pulps increases with the increasing NaOH charge from 1.5% to 2.5%, and subsequently decreases with additional NaOH charge. The same trend was found at three different temperatures with 800 kPa oxygen pressure, indicating that a medium caustic charge (*i.e.* 2.5% NaOH) is preferred for carboxylic acid formation during the catalytic oxidation.

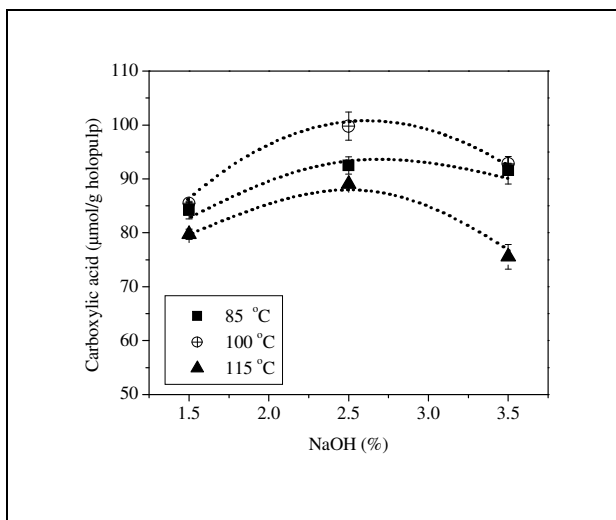


Figure 6.5. The Effect of Caustic Charge on Pulp Carboxylic Acid Formation from a Modified Oxygen Delignification with 0.18% Bismuth Ruthenium Pyrochlore Oxide

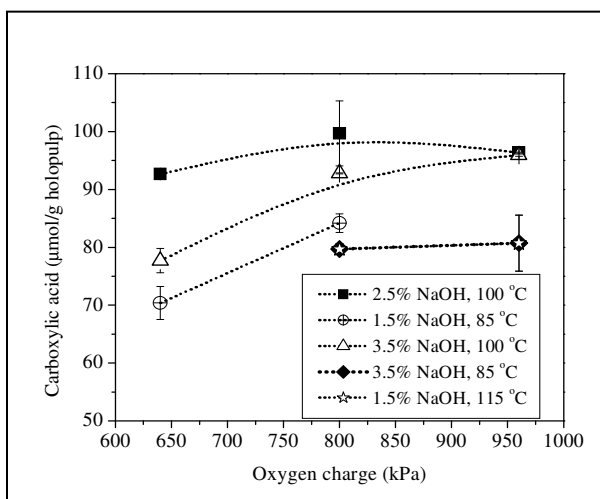


Figure 6.6. The Effect of Oxygen Pressure on Carboxylic Acid Formation from a Modified Oxygen Delignification with 0.18% Bismuth Ruthenium Pyrochlore Oxide

6.3.3.2. Oxygen pressure

The R value in Table 6-4 suggests that the effect of oxygen pressure on polysaccharide carboxylic acid formation is more significant than reaction temperature,

although less effective than caustic charge. The effect of oxygen pressure on catalytic oxidation of pulp polysaccharide was studied further, and these results are summarized in Figure 6.6. The results indicated that an increase in oxygen pressure beyond 800 kPa was not beneficial for fiber charge development.

6.3.3.3. *Temperature*

As summarized in Table 6-4 and Figure 6.7, the reaction temperature had the least effect on polysaccharide carboxylic acid formation for the conditions studied.

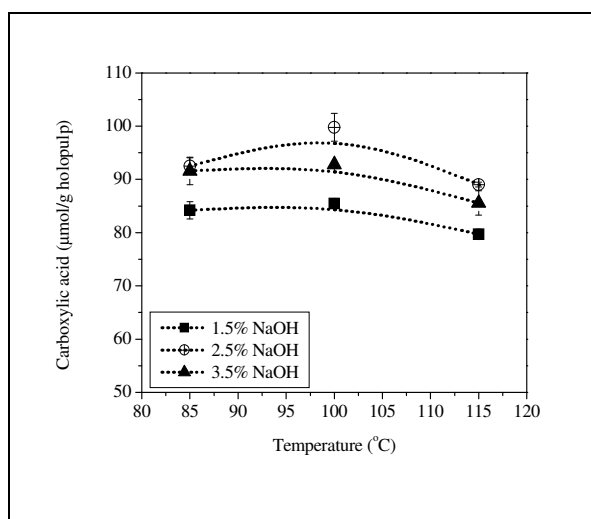


Figure 6.7. The Effect of Temperature on Pulp Carboxylic Acid Formation from a Modified Oxygen Delignification with 0.18% Bismuth Ruthenium Pyrochlore Oxide

Based on these studies, the optimal conditions for fiber carboxyl group formation were shown to be with 2.5% NaOH, 85 -100 °C, and 800 - 960 kPa with 0.18 % catalyst. The results of maximizing fiber carboxyl group formation with these parameters are summarized in Figure 6.8. These results indicate that it is possible to achieve ~100% increase in fiber carboxylic acid content under the optimal conditions during oxygen delignification.

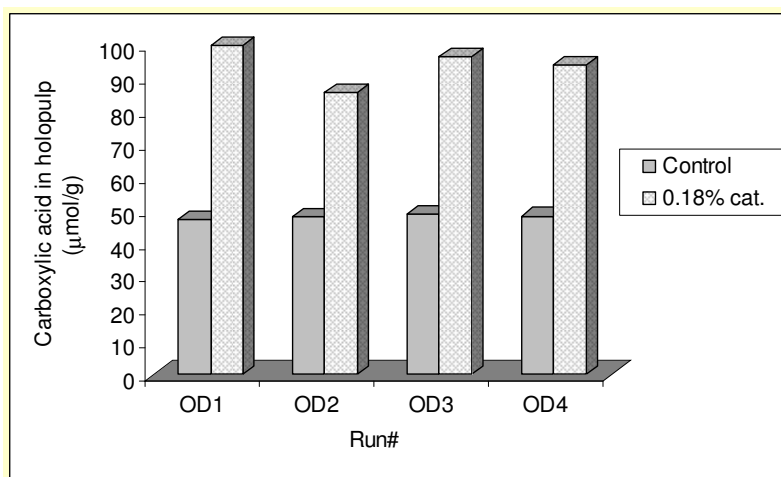


Figure 6.8. Carboxylic Acid in Polysaccharide of Modified Oxygen Delignified Pulp under Optimal Conditions

OD1: 2.5% NaOH, 100 °C, 800 kPa O₂, 60 min; OD2: 1.5% NaOH, 100 °C, 800 kPa O₂, 60 min; OD3: 2.5% NaOH, 100 °C, 960 kPa O₂, 60 min; OD4: 2.5% NaOH, 85 °C, 960 kPa O₂, 60 min

Table 6-5. Surface Fiber Charge of Polysaccharides of Oxygen Delignified SW Kraft Pulp with and without 0.18% Catalyst Employed

Reaction conditions	Total carboxyl groups (μmol/g holopulp)	Surface fiber charge (μmol/g holopulp)	Charge ratio (%)
1.5% NaOH, 100 °C, 800 kPa O ₂ , No catalyst	48.7	8.9	18.5
1.5% NaOH, 100 °C, 800 kPa O ₂ , 0.18% catalyst	85.5	15.5	18.1
2.5% NaOH, 100 °C, 800 kPa O ₂ , 0.18% catalyst	96.8	19.4	20.0
2.5% NaOH, 85 °C, 800 kPa O ₂ , 0.18% catalyst	92.4	18.1	20.3
1.5% NaOH, 85 °C, 640 kPa O ₂ , 0.18% catalyst	70.5	13.8	19.6

SW: Southern pine unbleached kraft pulp with kappa number of 32.5; 10% pulp consistency and 60 min reaction.

6.3.4. Fiber surface charge

Table 6-5 shows fiber surface charge of some holocellulose pulps isolated from oxygen delignified SW kraft pulps with and without 0.18% catalyst employed. It is observed that fiber surface charge was enhanced by 53.2 -115.6% when total fiber

carboxyl groups were increased by 45.1-99.2%. Therefore, both surface and bulk fiber carboxyl group enhancement was achieved through the catalytic oxidation during oxygen delignification.

6.4. Summary

The application of 0.09 - 0.18% bismuth ruthenium oxide catalyst during oxygen delignification effectively enhanced, by 52.2 - 116.0%, carboxylic acid content in the carbohydrate fraction of the pulps (holocellulose) without a significant decrease in fiber viscosity and delignification. Meanwhile, fiber surface charge was also enhanced significantly (>50%). The contributing factors and importance for acid group formation during oxygen delignification was shown to be NaOH charge > oxygen pressure > reaction temperature from the results of an orthogonal experimental design with 3-factor at 3-level. Optimal conditions for fiber carboxyl group formation in an O-stage was shown to occur with a 2.5% charge of NaOH, reaction temperature of 85 - 100 °C, and an oxygen pressure of 800-960 kPa. These results demonstrate a new strategy for engineering fiber charge in kraft pulps using a catalyst in the oxygen delignification stage. It also provides a new approach at enriching fiber carboxyl groups by directing oxidative chemistry toward carbohydrate attached to lignin fragments in the pulps.

CHAPTER 7 THE FATE OF PULP FIBER CARBOXYL GROUPS AFTER PULP BLEACHING

7.1. Introduction

The early studies by Lindstrom and Carlsson [185, 186] and Scallan and Grignon [3] established that pulp fiber in water behaved as a swollen polyelectrolytic gel provided sufficient charge exists. Since then, the benefits of fiber charge on fiber swelling of pulp fibers, inter-fiber bonding, and paper tensile strength have been extensively studied by enriching either surface or bulk fiber charge/acidic groups through grafting [8, 192], adsorption [9, 10], enzymatic modification [191], TEMPO-mediated oxidation [91], or oxidation during bleaching process [56, 160]. Despite these advances in fiber chemistry, paper physics, and fiber modification, our ability to practically control fiber charge in a kraft pulping and bleaching process is still in its early stages of development and needs additional research.

It has been known that bleaching agents such as oxygen, ozone, peroxide, and chlorine dioxide can result in the formation of carboxyl groups in residual lignin during pulp bleaching, which increases the solubility of oxidized lignin in an alkaline extraction stage [38, 59, 232]. The fiber carboxyl groups from lignin are largely reduced as lignin is removed during pulp bleaching. Some carboxylic groups are also introduced into carbohydrate by oxidative treatments [12, 47]. An elegant study by Laine [56] examined both total and surface fiber charge properties of bleached softwood (SW) kraft pulps after each bleaching stage in the sequences of OZEP, OPZEP, ODEDED, and DEDED with final pulp brightness values ranging from 74.1 to 86.8%. The experimental results from this study demonstrated that both total and surface fiber charge were strongly dependent

on the bleaching chemicals applied. For example, a 4-5% decrease in total fiber charge was shown to occur in the last E-stage for the bleaching sequences OZEP, OPZEP as well as first E stage in ODEDED and DEDED. However, the second E stage (E_2) in ODEDED and DEDED did not affect total fiber charge. Hydrogen peroxide employed in the last stage of OZEP and OPZEP following an alkaline extraction stage did not change the fiber charge whereas ozone and first chlorine dioxide stage (D_0) reduced fiber charge by 78-80%. A 10% increase of fiber charge was obtained when an unbleached SW pulp was oxygen delignified. It was also observed that the development of surface fiber charge in different bleaching stages was similar to that of total fiber charge [56]. A study by Toven [160] was conducted to bleach a SW kraft pulp via ECF bleaching sequences of OD(EO)DED, OD(EO)Q(PO), O(DZ)(EO)DED, and O(DZ)(EO)Q(PO) to ~87% pulp brightness. The results showed that ozone degraded charged groups somewhat more efficiently than chlorine dioxide. Pressurized peroxide (PO) as a final bleaching stage reduced the number of charged groups by 15%, but to a much lower extent than chlorine dioxide with a 40% reduction.

From the studies in CHAPTERS 4 - 5, different amounts of fiber carboxyl groups were found in different oxygen delignified SW kraft pulps depending on the pulping and oxygen delignification conditions. In CHAPTER 6, the enhancement of polysaccharide carboxyl groups was also obtained after one-stage oxygen delignification with the catalyst present. It was of interest to determine the degree of retention for the carboxyl groups introduced at the early bleaching stage (oxygen delignification) after the pulps were fully bleached. Additional studies are clearly needed to evaluate how different bleaching protocols influence fiber carboxyl groups of fully bleached pulps via ECF and

TCF bleaching sequences. This study first examines the amount of carboxyl groups in different oxygen delignified pulps retained through an ECF bleaching. Then a comparative study is conducted on fiber carboxylic acid content when a SW kraft is bleached to a target TAPPI brightness of 87-88% via different bleaching protocols.

7.2. Experimental

7.2.1. Materials

The pulps used in this study for bleaching were unbleached SW kraft pulps. These pulps were (1) Low kappa SW kraft pulp with kappa number of 32.5 (CSW) (2) Low AA and high AA cooked SW kraft pulps with 49.5 and 48.0 kappa number respectively (LSW and HSW) (3) Oxygen delignified pulps made from one-stage oxygen delignification of a SW kraft pulp (CSW) at 100 °C, 800 kPa O₂, 60 min, and 1.5% (LOD-5), 2.5% (MOD-5), 3.5 % (HOD-5) NaOH, respectively. A catalytically oxidized kraft pulp prepared during one-stage oxygen delignification at 100 °C, 800 kPa O₂, 60 min with 0.13% catalyst employed was also used in the bleaching study.

All chemicals except chlorine dioxide were commercially purchased from VWR or Sigma-Aldrich and used as received.

7.2.2. Pulp bleaching

Pulp bleaching via chlorine/chlorine dioxide, atmospheric alkaline extraction, and hydrogen peroxide was conducted in a water bath employing 4-mm-thick heat-resistant Kapak pouches. Oxygen delignification and oxygen/hydrogen peroxide reinforced alkali extraction were run in a 2.00-L inclined Parr reactor. Ozone bleaching was conducted in a CMS 2040 high intensity mixer with an ozone generator according to a procedure described in the literature [233]. The pulp was bleached with the sequences of

(D+C)EDED, (D+C)(EO)DED, DEDED, D(EPO)DED, OOD(EPO)D, OD(EO)DD, OD(EO)DP, and OQPZP. Following each stage, the treated pulp was thoroughly washed with deionized water till pH near neutral. The experimental conditions employed are summarized in Table 7-1. The detailed procedures for each stage bleaching were described in APPENDIX K.

Table 7-1. Experimental Conditions for Bleaching SW Kraft Pulps

Stage	Conditions
(D+C)	kappa factor (k.f.) = 0.20, 50% ClO ₂ substitution, 3.5% consistency, 50 °C, 45min, final pH 2.1.
D ₀	k.f.=0.20, 10% consistency, 50 °C, 60 min, final pH 2.4
O	0.274 or 0.80 MPa O ₂ , 2.2-2.5% NaOH, 0.1% MgSO ₄ , 100 °C, 60 min.
E ₁	3.0% NaOH, 90 °C, 10% consistency, 60 min.
(EO)	1.8% NaOH, 90 °C, 10% consistency, 0.1% MgSO ₄ , 35 psi O ₂ for 15 min, and 45 min at atmospheric, total 60 min.
(EPO)	1.8% NaOH, 90 °C, 10% consistency, 0.5% H ₂ O ₂ , 0.1% MgSO ₄ , 35 psi O ₂ for 15 min, and 45 min at atmospheric, total 60 min.
D ₁	0.8-1.0% ClO ₂ , 10% consistency, 75 °C, 180 min, final pH 3.8.
E ₂	0.5% NaOH, 10% consistency, 75 °C, 60 min.
D ₂	0.6-0.8% ClO ₂ , 10 % consistency, 75 °C, 180 min, final pH 4.0.
Q	0.6% EDTA, 2% consistency, 50 °C, pH 6.0, 60 min.
P(instead of E ₂)	1.0-1.2% H ₂ O ₂ , 1.5% NaOH, 10% consistency, 75 °C, 120 min.
P(instead of D ₂)	0.5-0.8% H ₂ O ₂ , 1.0% NaOH, 10% consistency, 75 °C, 120 min.
P ₁	2.5% H ₂ O ₂ , 3.5% NaOH, 10% consistency, 90 °C, 120 min
P ₂	1.5% H ₂ O ₂ , 1.8% NaOH, 10% consistency, 90 °C, 120 min.
Z	0.6% O ₃ , 10% consistency, 34 °C, pH 2.2, 20 min.

7.2.3. Pulp water retention value measurement

Prior to WRV testing, the pulp was treated with 0.1 N HCl for 60 min and washed with deionized water till near neutral to convert carboxyl groups into proton form.

Pulp WRV measurement was conducted according to according to a TAPPI testing method (Tappi um-256). In brief, a pulp mat of a fixed basis weight (0.63 g o.d.) was formed by draining a dilute pulp slurry (0.5% or less consistency) on a fine mesh screen in a centrifuging cup. The pulp pad was then centrifuged at 900g for 30min. The wet pad after centrifuging was weighed then dried and weighed again. The water retention value was calculated as follow:

$$WRV(\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (12)$$

where

W_w : weight of the wet sample after centrifugation

W_d : weight of the dry sample.

The typical standard deviation for pulp WRV measurement of three replicates under the same bleaching conditions was 2 g water/100 g pulp.

7.2.4. Analytical methods

Carboxylic acid content in samples was determined using Headspace Gas Chromatography to quantify CO_2 formed from the reaction of acid groups in pulp sample with NaHCO_2 at elevated temperature [98]. Hexenuronic acid content in pulps was determined using a spectroscopic method [202]. Typically the standard deviations associated with these measurements were 1.05 $\mu\text{mol/g}$ pulp and 0.56 $\mu\text{mol/g}$ pulp, respectively. In addition, TAPPI standard methods [204] were used to determine kappa

number (T231cm-96) and pulp viscosity (T-230 om-89) with standard deviations of 0.25 kappa units, 0.58 mPa.s, respectively.

7.3. Results and discussion

7.3.1. Enhanced fiber carboxyl groups retention after pulp bleaching

The study in CHAPTER 4 demonstrated relatively higher fiber carboxylic acid content was observed at certain conditions when delignifying a SW kraft pulp during one-stage oxygen delignification. It was interest to know whether the higher fiber carboxyl groups in oxygen delignified pulps could be retained through a bleaching process. Bleaching with the sequence of D(EO)DD was conducted for this purpose on the oxygen delignified pulps (LOD-5, MOD-5, and HOD-5). These results are presented in Figure 7.1. It was observed that the oxygen delignified SW kraft pulp with higher fiber carboxyl group content at 2.5% NaOH level ended up with 10-15% higher carboxylic acid content than at 1.5% and 3.5% NaOH levels after full bleaching.

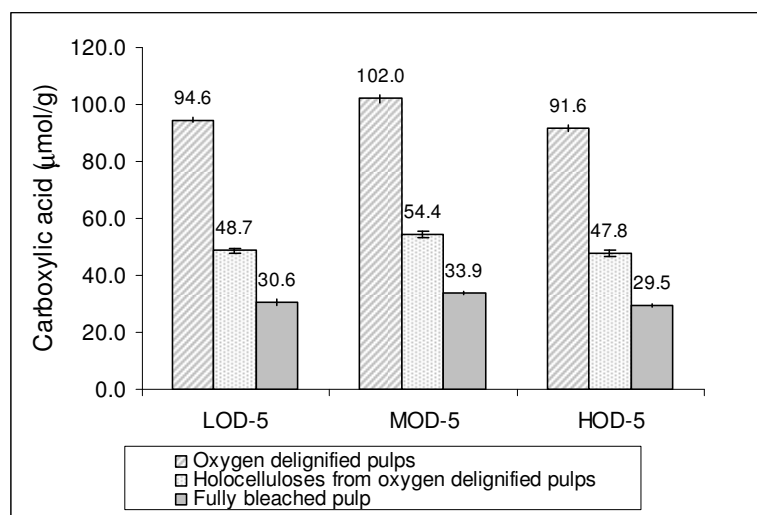


Figure 7.1. Carboxylic Acid Content in Total Fibers, Holopulps, and ECF bleached Kraft Pulps

Oxygen delignification conditions: 60 min, 10% consistency, 800 kPa O₂ at 1.5% NaOH (LOD-5), 2.5% NaOH (MOD-5), and 3.5% NaOH (HOD-5); Fully bleached pulp TAPPI brightness: 85.3-85.7%.

In CHAPTER 5, different amounts of fiber carboxylic acid were found for LAA cooked pulp (LSW) and HAA cooked pulp (HSW) as well as their respective oxygen delignified pulps. Full bleaching via an ECF bleaching sequence (OwOD(EPO)D) was conducted for LSW and HSW to a brightness of 85.0-85.5%. The carboxylic acid contents of these pulps are shown in Figure 7.2. The data demonstrated that fiber carboxylic acid content in LAA cooked SW kraft pulp was 8% higher than that in HAA cooked SW pulp, suggesting that fiber carboxyl groups introduced at kraft cooking was partially retained through a ECF pulp bleaching sequence.

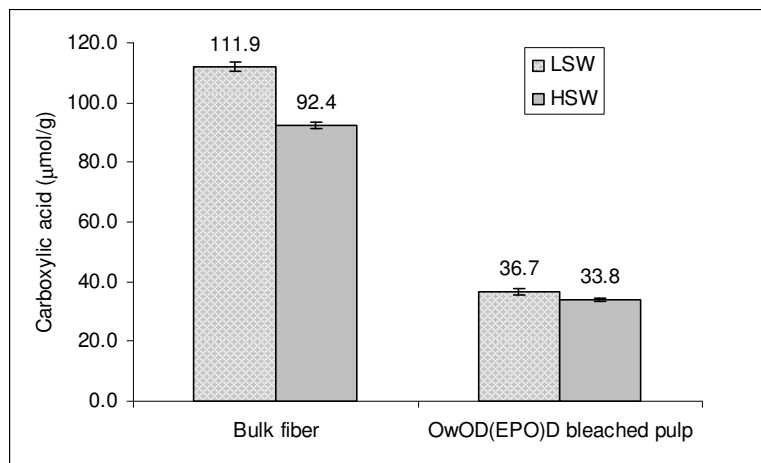


Figure 7.2. Carboxylic Acid Content in Total Fiber and Fully Bleached Pulps of LAA and HAA Cooked SW Kraft Pulps

Fully bleached pulp TAPPI brightness: 85.0-85.5%

In CHAPTER 6, the enrichment of polysaccharide carboxylic acid groups was obtained after one-stage oxygen delignification with the catalyst employed. To examine the degree of fiber carboxyl groups retention after the pulps were fully bleached, oxygen

delignified kraft pulps with and without catalyst employed were bleached employing a sequence D(EO)DD. These results of this study are presented in Figure 7.3.

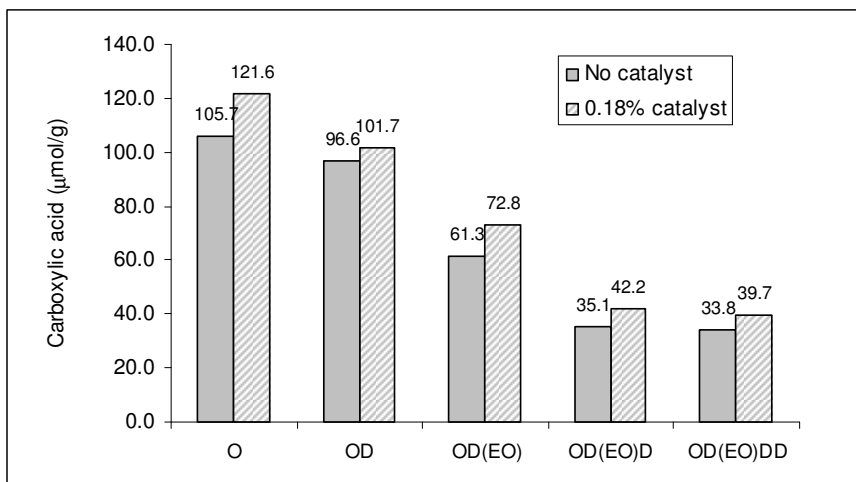


Figure 7.3. Carboxylic Acid Content of Bleached SW Kraft Pulps

Oxygen delignification conditions: 2.5 % NaOH, 800 kPa O₂, 100 °C, and 60 minutes, with and without 0.13% catalyst employed

The bleaching data indicates that carboxylic acid content in catalytically oxygen delignified pulp was systematically higher than that in non-catalytically oxygen delignified pulp through the bleaching stages. The final bleached kraft pulp with catalyst employed contained 17.5% higher carboxyl groups than the one without catalyst employed. The result of the full sequence bleaching data demonstrates the potential of utilizing a modified O-stage to increase fiber carboxyl groups in post-oxygen delignified and fully bleached pulps.

7.3.2. Effect of bleaching protocols

To investigate the effect of different bleaching protocols on fiber carboxyl groups, a mill produced pine kraft pulp with a kappa number of 32.5 (CSW) was employed in this

study. The kraft pulp was bleached to 87.1-88.4% brightness using a series of TCF and ECF bleaching sequences such as DEDED, D(EPO)DED, OD(EO)DD, OD(EPP)DP, and OQPZP. In addition, pulp bleaching was also accomplished using the bleaching sequence containing elemental chlorine such as (D+C)EDED, (D+C)(EO)DED for a comparison basis. The profiles of total fiber carboxylic acid content with the pulp kappa number are summarized in Figure 7.4. These results demonstrated that fiber carboxyl group content decreased from an initial 95.9 $\mu\text{mol/g}$ to a final 32.0-43.0 $\mu\text{mol/g}$ after bleaching the pulp (see Figure 7.4 and Figure 7.5), a 52-63% reduction in fiber carboxyl groups occurred dependent upon the different bleaching sequences and chemicals employed.

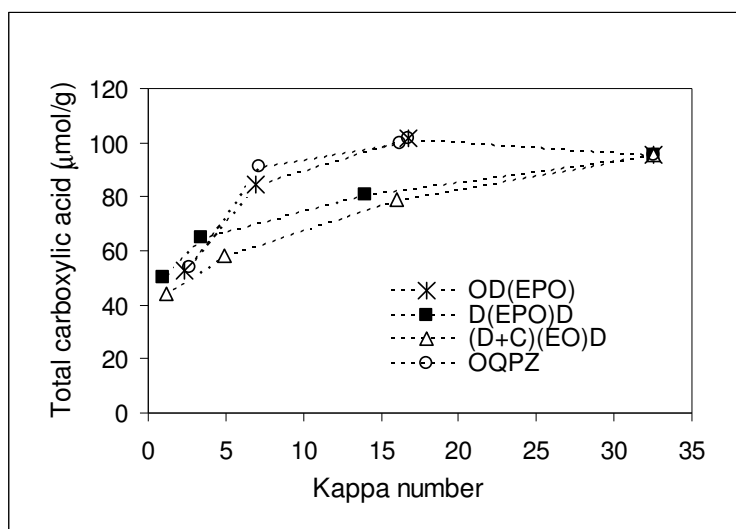


Figure 7.4. Total Fiber Carboxyl Group Content Development during ECF and TCF bleaching of a SW kraft pulp

From Figure 7.4, the oxygen delignification data indicates that fiber carboxylic acid content increased slightly (~7%) after an O-stage but this enhanced carboxyl groups were lost in subsequent stages. For bleaching post-oxygen delignified pulps, approximately 50% of the initial fiber carboxyl group content was lost after bleaching via OD(EPO) and

OQPZ. It was also observed that 54% of initial fiber carboxyl group content was lost from bleaching by (D+C)(EO)D, while 47% was lost after bleaching via D(EPO)D.

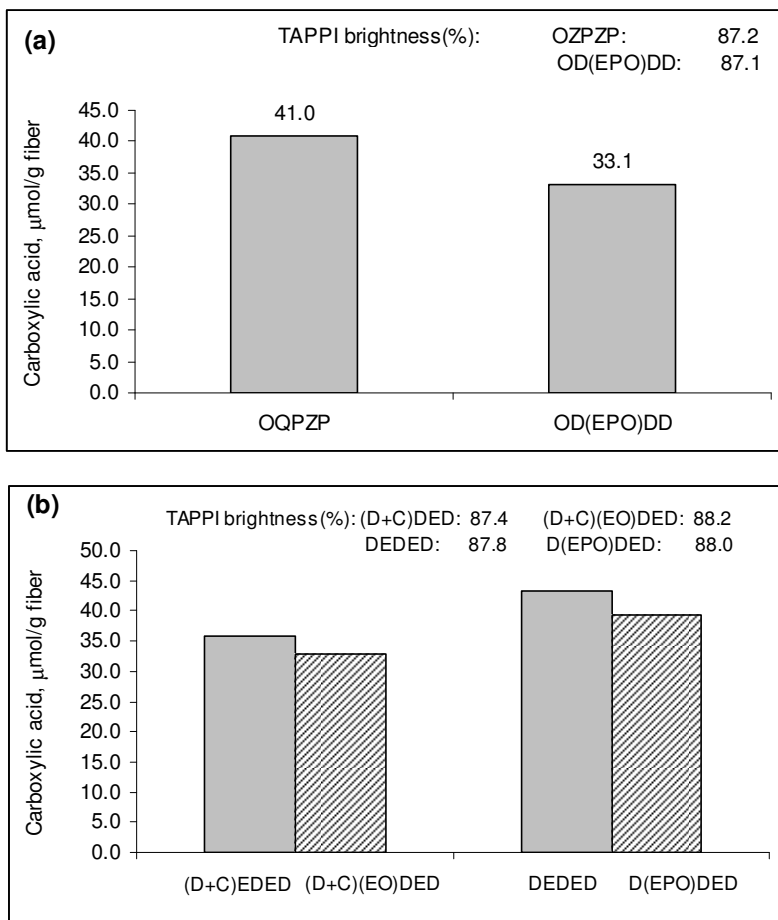


Figure 7.5. Total Fiber Carboxyl Group Content of Fully Bleached SW kraft Pulps

However, fiber carboxyl group content in final bleached pulp is of more practical interest. From Figure 7.5a, bleaching with an oxygen delignification stage followed by OQPZP yields a total fiber carboxyl group content 20.4% higher than that via OD(EPO)DD. Figure 7.6 demonstrates the change of fiber carboxyl group content caused by unit pulp kappa number reduction ($\Delta\text{Carboxylic acid}/\Delta\text{kappa number}$) for the fully bleached pulps. This relationship was employed to evaluate the effect of bleaching on fiber carboxyl acid content. It is noted that the pulp bleaching via OQPZP had a lower

value of fiber carboxyl acid content decrease per kappa number reduction (1.73 $\mu\text{mol}/\text{kappa number}$) than via OD(EPO)DD (1.95 $\mu\text{mol}/\text{kappa number}$). Therefore, bleaching via ozone and hydrogen peroxide is preferentially beneficial to fiber carboxyl acid formation for fully bleached pulps. The fiber carboxyl acid content of these pulps could be further increased through parameter optimization.

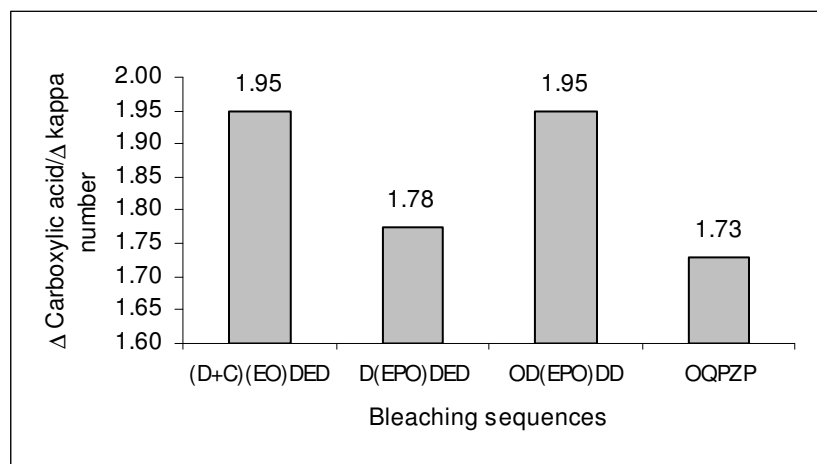


Figure 7.6. The Change of Fiber Carboxyl Group Content per Unit Pulp Kappa Number Reduction for Fully Bleached SW Pulps

When bleaching without using oxygen delignification (Figure 7.5b), total pulp fiber carboxyl acid content from the fully bleached pulp using D(EPO)DED or DEDED was higher (19.0-21.0%) than the pulps bleached using (D+C)(EO)DED and (D+C)EDED. From Figure 7.6, a lower value of fiber carboxyl acid content decrease per unit kappa number reduction was found for the pulp bleached via D(EPO)DED (1.78 $\mu\text{mol}/\text{kappa number}$) than (D+C)(EO)DED (1.95 $\mu\text{mol}/\text{kappa number}$). It is well known that chlorine is a chemical with greater economy but with lower bleaching selectivity than chlorine dioxide [44]. The lower selectivity may cause more fragmentation of some oxidized products that therefore dissolve in the subsequent washing or alkaline extraction.

When bleaching pulps to a final pulp brightness of approximately 88%, there is little residual lignin remaining in the fully bleached pulps as shown by very low pulp kappa number (< 0.4). Therefore fiber charge contribution from residual lignin can be negligible. Hexenuronic acid contents in these fully bleached pulps were found to be in the range of 2.8-3.6 $\mu\text{mol/g}$ fiber, which is only 10-13% of the initial HexA content ($\sim 28 \mu\text{mol/g}$ fiber) in the unbleached SW kraft pulp studied. HexA content reduction is known to be caused by the reaction with electrophilic bleaching chemicals like ClO_2 and O_3 [32, 56]. Accordingly, aldonic acids in carbohydrates are most likely the major contributors to the fiber carboxyl groups in fully bleached pulps studied.

7.3.3. Effect of second stage of alkaline extraction

Alkaline extraction (E_2) in the later stage of a multistage bleaching sequence is not a delignification stage, instead it serves to remove colored and degraded products and activate the pulp to further oxidation, which allows the amount of oxidant in the following stage to be decreased [40]. Typical caustic charge at this stage is 0.5% (on o.d. pulp). However, it was observed in Table 7-2 that the E_2 stage did not lead to a significant increase in pulp brightness but decreased total fiber carboxyl group content by 10.9-13.0% for (D+C)EDED and (D+C)(EO)DED sequences, and 14.9-15.0% for DEDED and D(EPO)DED sequences. When removing the second alkaline extraction stage, the lost fiber carboxyl group content from the E_2 stage was retained in the fully bleached pulps (Figure 7.7). Therefore, when evaluating the benefit of a second alkaline extraction in a bleaching sequence, the tradeoff for pulp brightness, fiber carboxyl group loss, and cost of facility and operation needs to be considered.

Table 7-2. Pulp Brightness and Carboxylic Acid Content of Bleached Kraft Pulp

Bleaching sequence	Brightness (%)	Carboxylic acid ($\mu\text{mol/g fiber}$)
(D+C)ED	68.2	46.7
(D+C)EDE	68.7	41.7
(D+C)(EO)D	77.6	43.9
(D+C)(EO)DE	77.6	38.2
DED	75.1	54.9
DEDE	74.6	46.7
D(EPO)D	81.4	49.5
D(EPO)DE	80.2	42.0

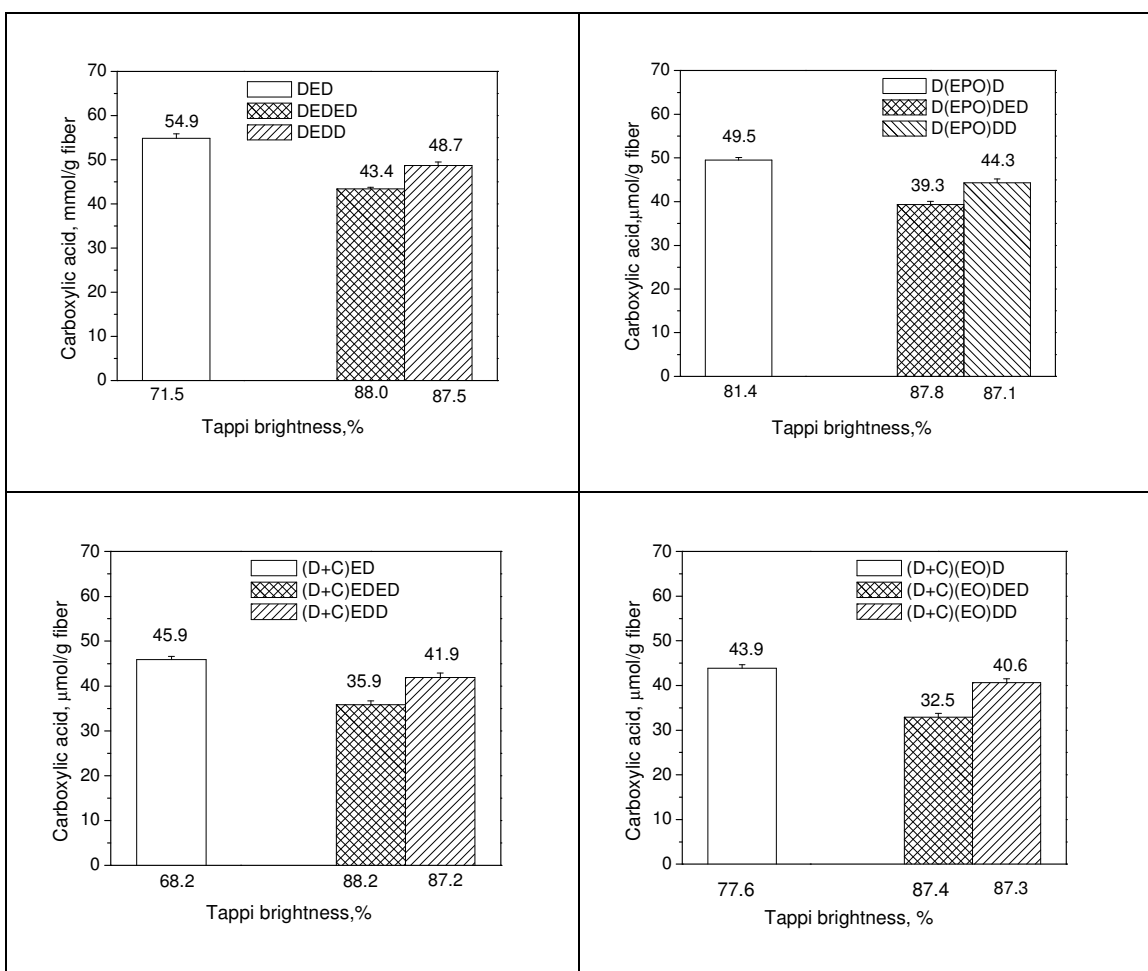


Figure 7.7. Fiber Carboxylic Acid Content of Fully Bleached Pulp with and without Using a Second Alkaline Extraction Stage

7.3.4. Effect of hydrogen peroxide bleaching

The growth in the use of hydrogen peroxide in chemical pulp bleaching since the late 1980s is attributable largely to environmental constraints in the operation of bleach plants. Hydrogen peroxide is often used in the later stages of bleaching due to its greater selectivity [40]. Additionally, use of hydrogen peroxide to reinforce the oxidative extraction stage is frequently employed to enable the preceding chlorination chlorine dioxide stage to be operated at a lower kappa factor and can allow some softwood kraft mills to re-gain their final brightness and reduce chemical costs. Accordingly, typical modern ECF bleaching sequences have developed such as D(EPO)DPD, and OD(EPO)DP [234].

Previous studies by Barzyk *et al* indicated that an alkaline peroxide stage could effectively increase fiber charge of kraft pulps [61]. Our recent study [204, 235] demonstrated that the carboxylic acid content could be increased up to 24% when a fully bleached ECF SW kraft pulp was bleached with 1% peroxide, 2% NaOH, at 80 °C for 60 minutes at 10% consistency. These results show the potential of increasing pulp fiber carboxyl groups using an alkaline hydrogen peroxide stage.

During pulp bleaching, when a hydrogen peroxide stage is used for brightening pulp either to replace the later alkaline extraction (E₂) or last chlorine dioxide (D₂) stages in the sequences DEDED, D(EPO)DED, (D+C)EDED, and (D+C)(EO)DED, it did not show the effect of increasing fiber carboxylic acid content as indicated in Figure 7.8, which is consistent with the result reported by Laine [56]. However, when hydrogen peroxide was used to replace the D₂ in OD(EPO)DD as OD(EPO)DP, an increase of approximately 20.0 % in fiber carboxylic acid content of the fully bleached SW kraft

pulp was obtained compared with the sequence using chlorine dioxide in the last two stages (OD(EOP)DD) (Figure 7.8b). An altering arrangement of acidic and basic bleaching stage may be the reason for this phenomenon.

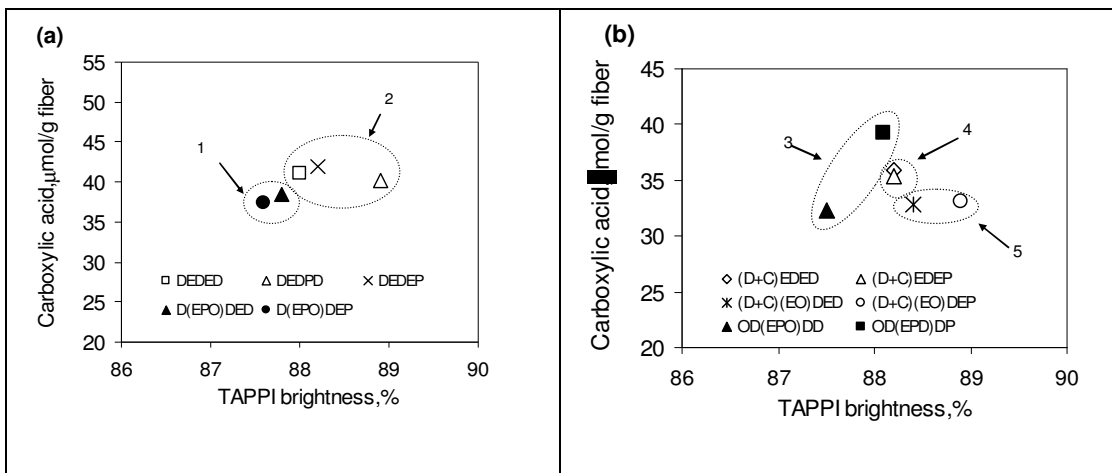


Figure 7.8. The Effect of Hydrogen Peroxide Bleaching at a Different Stage on Pulp Fiber Carboxylic Acid Content

Note: Circle 1: in D(EPO)DED, replace last D by P to get D(EPO)DEP; Circle 2: In DEDED, replace E2 or last D by P and then get DEDPD or DEDEP; Circle 3: In OD(EPO)DD, replace last D by P and then get OD(EPO)DP; Circle 4: In (D+C)EDED, replace last D by P and then get (D+C)EDEP; Circle 5: In (D+C)(EO)DED, replace last D by P and then get (D+C)(EO)DEP

7.4. Summary

The pulp bleaching study demonstrated that fiber carboxyl groups enhanced at early stages by either kraft pulping or oxygen delignification with and without catalyst employed could be partially retained through an ECF bleaching sequence, which provides a possibility to introduce fiber carboxyl groups at early bleaching stage.

In this study, several full sequence pulp bleaching treatments were employed to bleach a mill produced SW kraft pulp to a target brightness of 87.1 - 88.4%. Fiber carboxylic acid content of the pulps during bleaching was monitored and was shown to

be dependent upon specific bleaching protocols. Although oxygen delignification was found to increase fiber carboxylic acid content by 8%, overall, 52.0-63.0% of initial pulp fiber carboxyl groups were lost in subsequent bleaching stages. The decrease in fiber carboxyl groups was shown to be due primarily to the removal of oxidized lignin, HexA, and some aldonic acids.

Generally, total fiber carboxylic acid content in the pulps bleached with DEDED, D(EPO)DED, and OQPZP was shown to be 18.0-21.0% higher than those bleached with (D+C)EDED, (D+C)(EO)DED, and OD(EPO)DD. It was also found that the second alkaline extraction stage in (D+C)EDED, (D+C)(EO)DED, DEDED, and D(EPO)DED caused a decrease (10.9-15.0%) in pulp fiber carboxylic acid content. When removing the second alkaline extraction stage from these bleaching sequences in (D+C)EDD, (D+C)(EO)DD, DEDD, and D(EPO)DD, the lost fiber carboxyl groups due to the later alkaline extraction were retained. When hydrogen peroxide was employed as a terminal bleaching stage, it increased fiber carboxylic acid content 20.0% as shown for the fiber acidic content for pulps bleached via OD(EPO)DP vs. OD(EPO)DD. These observations provide mills a simple and directed approach to retain or reduce fiber carboxylic acid content for fully bleached kraft pulps.

CHAPTER 8 EFFECT OF FIBER CARBOXYL GROUPS ENHANCED BY CHEMICAL OXIDATION ON FIBER AND PAPER STRENGTH PROPERTIES

8.1. Introduction

Research studies over the past decades have indicated that fiber charge was one of the primary factors influencing final physical sheet properties. It has been established from the early studies [3, 186, 236] that pulp fibers with sufficient charge in water behave as a swollen polyelectrolytic gel and have the ability to swell due to electrostatic repulsion between existing like charges. The effect caused by anionically charged groups in a fiber and resulting counter cation groups causes additional water to enter the fiber wall by osmotic pressure and the accompanying swelling and plasticization increases the fiber conformability and bonding. The investigation by Engstrand *et al* [62] demonstrated that charged groups introduced into mechanical pulps from 90 $\mu\text{mol/g}$ to 250 $\mu\text{mol/g}$ using 4% hydrogen peroxide treatment at pH of 9 -13 for 120 min at 60 °C. As a result, paper tensile index and specific elastic modulus were found to increase 33.3 - 177.7% and 17.6 - 117.6%, respectively.

Studies by Barzyk, Page, and Ragauskas demonstrated that surface acid groups for chemical pulps play a key role in determining the strength of specific fiber-fiber bonding [4-6]. Employing well controlled laboratory procedures fully bleached SW kraft pulps were prepared with a uniform distribution of carboxyl groups across the fiber cell wall and with carboxyl groups located primarily at the fiber surface. Their studies demonstrated that fiber specific bond strength could be enhanced by approximately 50% dependent upon the degree of surface enrichment of acid groups. The mechanism of strength enhancement by surface carboxylic acid groups has not fully defined but it has

been generally attributed to an ionic effect or possibly due to increased localized surface swelling that allows more molecular flexibility and more intimate molecular contact and inter microfibril diffusion/bonding.

Laine *et al* [10, 83] explored alternative technologies for increasing the amount of fiber surface charge involving the adsorption of carboxyl methylcellulose (CMC) with different molecular weight (2.8×10^5 and 1.0×10^6) and degree of substitution (0.71 and 0.52) to the surface of bleached softwood kraft pulp at an elevated temperature (80 °C). Physical strength studies demonstrated that such a CMC topochemical modification of pulp provided 21.4 – 100.0 % increase in paper tensile index and 17.1-34.3% increase in paper tensile stiffness from 59 - 96% total fiber charge enrichment with 5.6 – 7.4 mg/g CMC attached [83]. Neither the sheet density nor the light scattering coefficient was affected by the attachment of CMC onto fiber. The effects were interpreted in terms of improved specific bond strength. The paper tensile strength improvement (18.2- 36.4%) was also obtained by Zhang *et al* [93] through absorbing 10-35 mg/g of Dextran (MW: 2 million Da; charge density: 0.161-0.484 meq/g) on the bleached kraft pulp.

Paper stiffness, a measure of the initial resistance of the paper sheet to strain, is a property of paper to resist bending and its ability to support its own weight when handled. The dry stiffness of paper affects its feeding ability and its ability to avoid distortion due to the pull of ink during the printing process. Therefore, paper dry stiffness is important to the converting operations for forms and envelopes.

The effect of lignin on the tensile and stiffness of paper or composite materials has been acknowledged [237-239]. The influence of pore structure on different strength properties of papers from unbleached kraft fibers at different pulp yields (45-60%) was

investigated by Forsstrom *et al* [240] using NMR relaxation measurements of water to determine the pore structure of the fibers. Their results demonstrated that paper tensile stiffness increased from 6.4 kN.m/kg to 9.1 kN.m/kg when fiber pore size increased from 12nm to 15 nm. It was suggested that fibers with larger pores allowed for a larger molecular contact area between fibers, stronger fiber/fiber joints, and consequently a higher strength of the formed sheets. Paper tensile stiffness was also increased by high molecular weight xylan addition during kraft pulping [241] and application of hydrophilic dry-strength resins/polymers/starch [242, 243]. One study by Agnew *et al* [244] showed that the addition of Kevlar polyamide into pulp fiber at a volume fraction of 0.05-0.5% was found to increase paper apparent elastic modulus from 1.19 kg/m to 1.9-5.31 kg/m. As previously described, by attaching CMC onto bleached kraft pulp, Laine *et al* [83] reported a 17.1 - 60.0% increase in tensile stiffness with 5.6 – 10.3 mg/g of CMC attached. The paper stiffness can be also improved by refining process [245]. While refining a mixture of mechanical and chemical pulp in a conical lab refiner, Tunen *et al* [246] found that paper tensile stiffness increased 25.4 – 45.8% when increasing refining energy to 25-140 kwh/t. In addition, enzymatic (cellulase, laccase, and proteinase) treatment of long fiber-rich fraction of the pressurized refiner mechanical pulp and fines was found to lead to higher (> 3%) tensile strength, tensile stiffness (elastic modulus) and Scott bond [247]. However fibers deformations that changed the direction of fiber axis (kinks, folds, and twists) were found to be detrimental to tensile strength and tensile stiffness due to the decrease of fiber segment activation in fiber network compared to undeformed fibers [248, 249]. Vander Wielen and Ragauskas [250] reported that wet-tensile stiffness of the thermomechanical and kraft pulp sheets

increased by 138-144% respectively with increased dielectric-barrier discharge treatments but little improvement was found for dry-tensile stiffness.

A report by Kitaoka *et al* [91] has shown that TEMPO-oxidation of bleached hardwood kraft fibers could increase fiber charge by a factor of 7.8 and this increased the Young's modulus of the sheet by 18.5%. However, the ability to enhance paper stiffness by oxidative bleaching has been understudied in light of the reported benefits derived from enriched fiber charge on pulp fiber. Our recent studies [235] have reported that a peroxide stage can increase fiber carboxylic acid content by 20.0 – 25.0%; alternatively the application of 0.09-0.18% bismuth ruthenium pyrochlore oxide in an oxygen stage can increase fiber carboxylic acid content in holocelluloses by 52.2 – 116.0%. This study examines the effect of fiber carboxyl groups enhanced by oxidation of bleaching chemicals on fiber and paper tensile strength and stiffness.

8.2. Experimental

8.2.1. Pulp sample preparation

A commercial southern U.S.A southern pine (*Pinus taeda*) unbleached kraft pulp with a kappa number of 32.5 as well as mill produced ECF bleached softwood (BSW), mixed hardwood (BMHW), and Acacia (BAHW) kraft pulps were used in this study.

Holocelluloses (holopulps) with fiber carboxylic acid content of 61.9 - 90.3 $\mu\text{mol/g}$ were prepared following the procedure in the previous study (CHAPTER 6) by holopulping catalytically oxygen delignified SW kraft pulps. Meanwhile, the catalytically oxygen delignified SW kraft pulps were bleached through D(EO)DD to 84.0-84.6% TAPPI brightness. The BSW, BMHW, and BAHW pulps were each treated in a water bath employing 4-mm-thick heat-resistant Kapak pouches with 1.0% H_2O_2 at 1.5%

NaOH, 90 °C, and 10 % pulp consistency for 60 min. The treated pulps were washed thoroughly with deionized water until pH near neutral.

8.2.2. Pulp analysis

Carboxylic acid content in the pulp samples was determined [201] by measuring CO₂ produced from the reaction of acid groups in fibers with bicarbonate solution using Headspace Gas Chromatography with a standard deviation for the measurement of three replicates at 1.05 µmol/g .

Pulp WRV measurement was conducted according to a TAPPI testing method (Tappi um-256) with a typical standard deviation for WRV measurement of three replicates under the same bleaching conditions at 2 g water/ 100 g pulp.

In addition, TAPPI standard methods [204] were used to determine kappa number (T231cm-96), pulp viscosity (T-230 om-89), and pulp brightness (T452 om-92) with standard deviations of 0.25 kappa units, 0.58 mPa.s, and 0.14 brightness units, respectively.

Fiber length was measured by Fiber Quality Analyzer (OpTest Equipment Inc. 1999). Typical standard deviations for fiber mean length and mean curl measurements of three replicates under the same oxygen delignification and bleaching conditions were 0.03 mm and 0.005, respectively.

8.2.3. Handsheet making and paper tensile strength testing

All the control and modified pulps/holocelluloses were pretreated with 0.1 N HCl solutions to convert carboxyl groups into proton form followed by a thorough washing with deionized water until pH near neutral prior to making handsheets.

Handsheets were prepared using a British sheet mold according to TAPPI Method T-205 [204] after the treated pulp was disintegrated for 20,000 revolutions in the British disintegrator. The handsheets made were dried in restraint rings at room temperature (RT) and in a flat plate dryer at elevated temperature (105 °C) and then conditioned normally (23 °C, 50% relative humidity) at TAPPI standard conditioning testing room for at least 24 hours before physical testing.

Paper tensile strength was measured according to TAPPI Standard T 494 om-01 on an Instron Model 1122 testing apparatus using an Instron 1000 lb reversible load cell for 15 mm width paper strips. The average tensile strength and stiffness of strips cut from 10 sheets were converted to the average tensile index and tensile stiffness index with typical standard deviations of 0.50 N.m/g and 0.08 kN.m/g, respectively. In addition, paper tear strength and dry zero span were measured according to TAPPI Standard methods (T414 and T 231 respectively).

The SEM pictures were taken using a JSM-6400 SEM (JEOL Inc., Japan).

8.3. Results and discussion

To explore the relationship between fiber carboxyl groups and fiber properties as well as paper tensile properties, a series of holocellulose kraft pulps were prepared with differing levels of carboxylic acid groups. The differing levels of fiber charge were readily accomplished employing a recently discovered catalytic oxygen delignification [235] that enhances fiber carboxyl groups without altering the overall O-delignification process. The oxygen delignified pulps were then holocellulose pulped to remove residual lignin and hexenuronic acids providing a fully bleached pulp. Meanwhile, the catalytically oxidized pulps were bleached to a brightness of 84.0-84.6%. As an

alternative to this methodology, an alkaline peroxide stage on fully bleached pulps was employed to enhance fiber carboxyl groups [235]. The results of these oxidative treatments in terms of fiber carboxylic acid content and other pulp physical properties are summarized in Table 8-1.

Table 8-1. Fiber Carboxyl Group Content and Physical Properties for Holopulps, ECF Bleached Kraft Pulps, and Chemically Modified ECF Bleached Kraft Pulps

Fiber source	Carboxylic acid ($\mu\text{mol/g}$)	Fiber* length (mm)	Fiber curl	Viscosity (mPa.s)	WRV (%)	Brightness (%)
Holopulp-0	61.9	2.28	0.139	11.2	147	86.1
Holopulp-1	75.8	2.28	0.132	10.8	155	86.2
Holopulp-2	88.6	2.23	0.129	10.6	162	86.1
Holopulp-3	90.3	2.31	0.125	10.6	166	86.2
OD(EO)D-0	31.7	2.36	0.170	12.7	158	84.6
OD(EO)D-1	43.0	2.35	0.166	11.8	159	84.2
OD(EO)D-2	45.1	2.38	0.159	11.1	161	84.2
OD(EO)D-3	51.4	2.37	0.154	11.2	169	84.1
BSW-c	38.4	2.25	0.143	15.6	175	88.9
BSW-p	45.1	2.32	0.109	15.0	178	89.2
BMHW-c	31.8	0.95	0.142	10.6	130	88.9
BMHW-p	38.9	1.06	0.123	10.8	136	89.3
BAHW-c	32.4	0.72	0.094	11.4	178	90.1
BAHW-p	38.2	0.77	0.074	10.5	188	90.9

BSW: mill produced ECF bleached SW kraft pulp; BMHW: Mill produced ECF mixed HW kraft pulp; BAHW: mill produced ECF bleached Acacia kraft pulp; c: control; p: treated with 1% H_2O_2 at 1.5% NaOH, 10% consistency, and 90 °C for 60 min; * Length weight weighted

8.3.1. Pulp fiber properties

This data in Table 8-1 demonstrated that pulp viscosity and fiber length were comparable regardless of the degree of fiber carboxyl group enhancement by chemical oxidation. However, it is noted that fiber curl decreases with an increase of fiber

carboxylic acid content as shown in Figure 8.1, which is likely caused by the electrostatic repulsion between the negatively charged carboxylate anions in the same fiber [251].

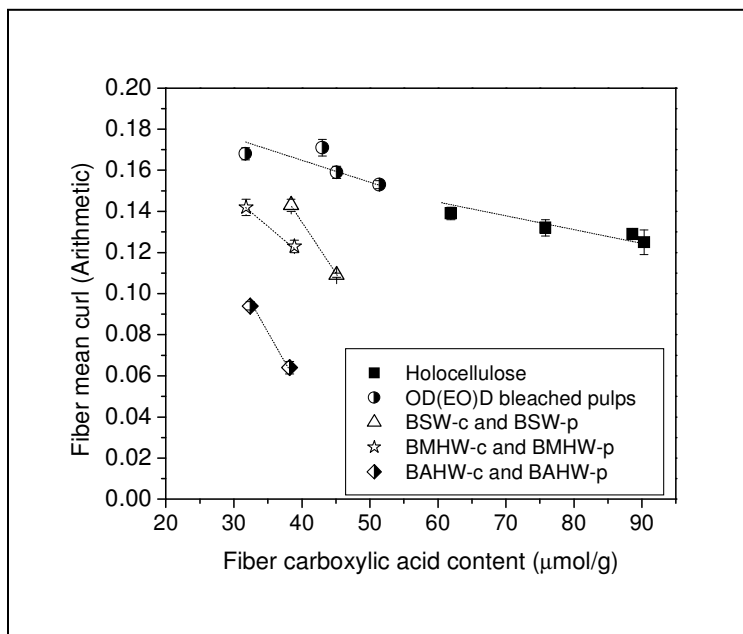


Figure 8.1. The Relationship between Fiber Carboxylic Acid Content and Fiber Curl

It has been reported by Laine and Lindstrom [83] that pulp WRVs increase 13.2-50.0 % when total fiber carboxylic acid content increases by 59 - 96% with CMCs attached onto an ECF bleached kraft pulp. From Figure 8.2, fiber WRVs increase 5.3-12.9% with pulp fiber carboxyl group enhancement through chemical oxidation by 21.2-45.9% in holopulps. The increase of fiber WRVs was also observed in bleached catalytically oxidized kraft pulps and modified ECF bleached kraft pulps (Figure 8.2). The similar results were found in fully bleached kraft pulps by Toven [160] that WRVs increased only from 1.14 mg/ml to 1.21 mg/ml with fiber carboxylic acid content increase from 51 μmol/g to 73 μmol/g.

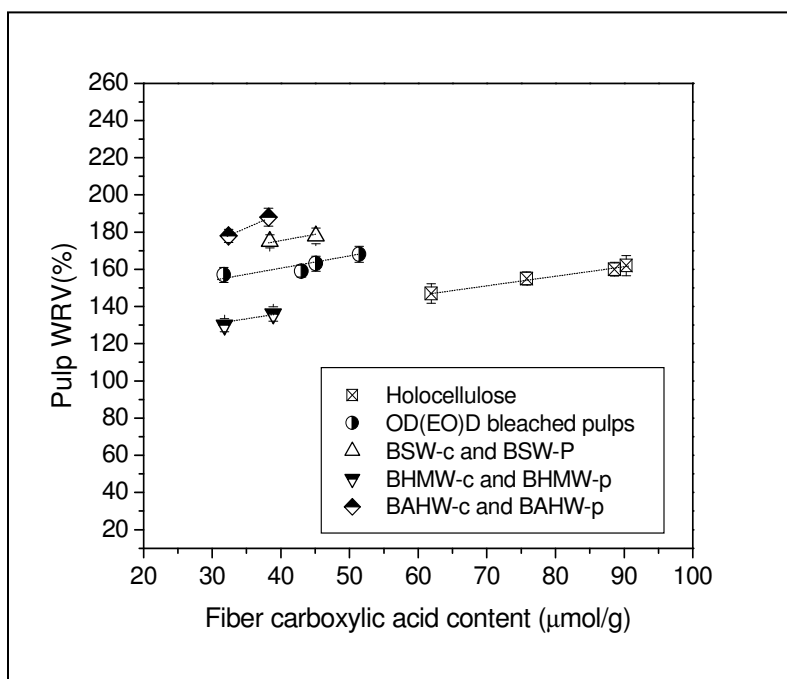


Figure 8.2. The Relationship between Fiber Carboxylic Acid Content and Pulp WRVs

8.3.2. Physical strength of the paper sheets

The physical strength analysis of the pulps reported in Table 8-1 was conducted. Sheet density, zero-span index, and paper tear index are summarized in Table L-1 in APPENDIX L. The relationship between pulp carboxylic acid content and papersheet tensile index are presented in Figure 8.3.

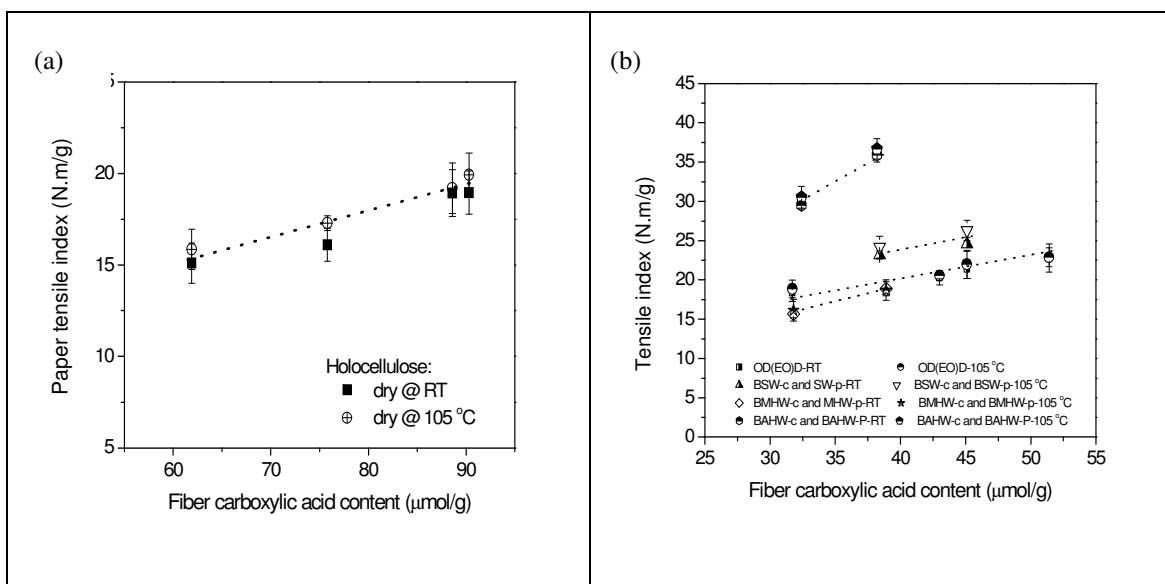


Figure 8.3. The Relationship between Fiber Carboxylic Acid Content and Paper Tensile Index

(a) Holocelluloses (b) Fully bleached pulps

Generally, when paper sheets were dried at room temperature, an increase of fiber carboxylic acid content by 22.5-45.9% in holocelluloses and 35.6-61.2% in OD(EO)D bleached kraft pulps resulted in 6.6 - 25.7% (Figure 8.3a) and 10.6-24.2% (Figure 8.3b) increase in the paper tensile index at comparable pulp viscosity. And 4.3 - 21.7 % of increase in tensile strength was obtained for paper sheets made from modified ECF bleached kraft pulps (BSW-p, BMHW-p, and MAHW-p) with 17.4-22.3% of fiber carboxyl groups increase (Figure 8.3b). In addition, drying the sheets at an elevated temperature (105 °C) resulted in a little higher paper tensile strength than at room temperature (Figure 8.3).

The data in Figure 8.4 demonstrates that fiber carboxyl groups have a significant effect on paper sheet dry-tensile stiffness. For paper sheets made from holocelluloses isolated from catalytically oxidized SW kraft pulps and dried under the same conditions, the enhanced fiber carboxyl groups by 22.5 - 45.9% resulted in 8.1 - 30.1% increase in

dry-tensile stiffness (Figure 8.4a). And 14.2-22.4% increase in tensile stiffness is achieved when fiber carboxylic acid content increase 35.6-62.1% in the OD(EO)D bleached pulps (Figure 8.4b). When pulp fiber carboxyl groups increases by 17.4 - 22.3% through hydrogen peroxide oxidation, an increase of 4.4-11.0% in paper dry-tensile stiffness index is obtained for paper sheets dried at room temperature. It is also observed from Figure 8.4 that the paper dry-tensile stiffness was 4.7 - 24.8% higher when the handsheets were dried at 105 °C under the flat plate dryer than at room temperature.

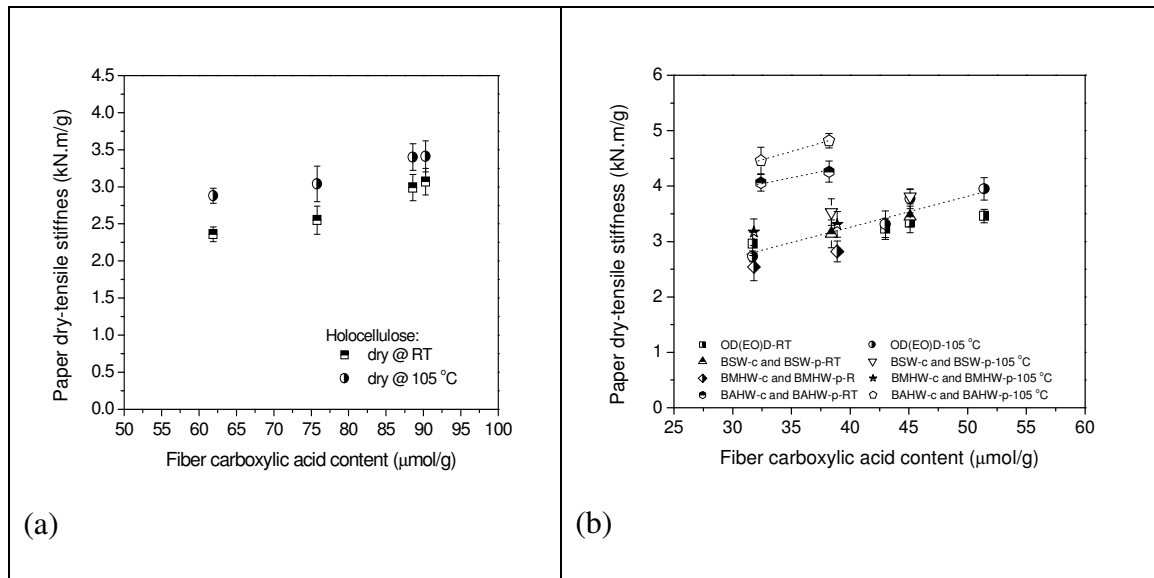


Figure 8.4. The Relationship between Fiber Carboxylic Acid Content and Paper Tensile Stiffness Index

(a) Holocelluloses (b) Fully bleached pulps

From Figure 8.5, the effect of fiber carboxylic acid content on paper sheet dry-tensile stiffness correlates very well with paper tensile strength enhancement. Therefore, a possible explanation for the effect of fiber carboxylic acid on paper dry-tensile stiffness improvement is that the enhanced fiber charge improves fiber bonding, which further improves paper tensile strength and stiffness.

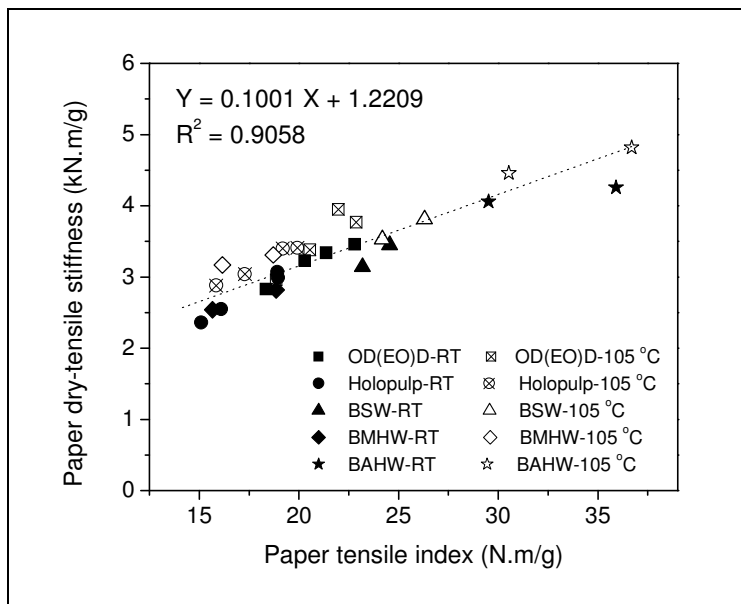


Figure 8.5. The Relationship between Paper Tensile Index and Paper Dry-Tensile Stiffness Index

Figure 8.6 shows SEM pictures of the paper sheet strips along the broken edges after tensile testing. It is noted that less fibers are pulled out for stiffer and stronger papers (right) along the broken edges after tensile testing, indicating more strong fiber-fiber bonding for the pulps with high fiber charge.

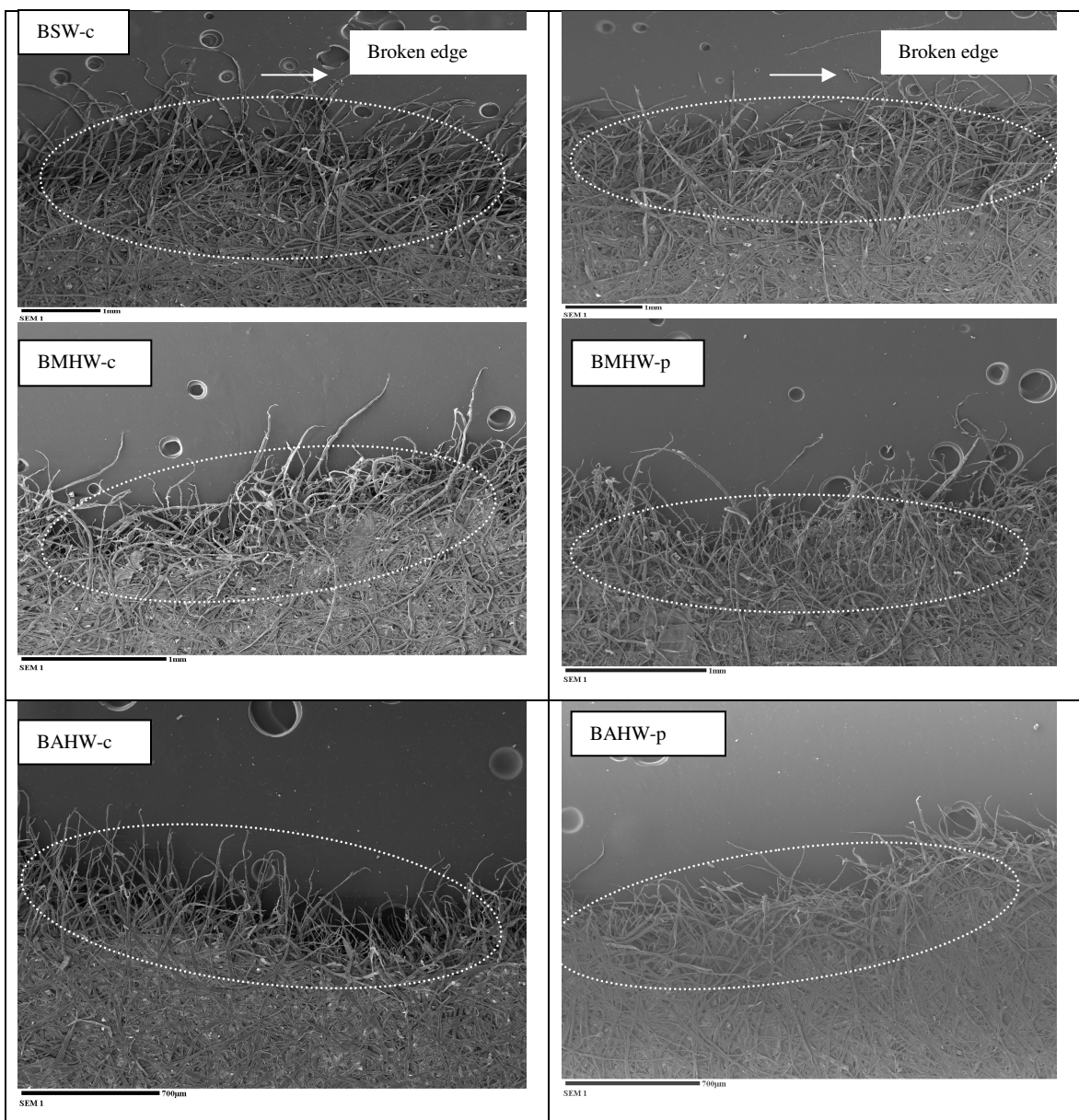


Figure 8.6. SEM Pictures of the Paper Sheet Broken Edges

Note: The circles in the pictures highlight the areas along the broken edges with fibers pulled out

8.4. Summary

This study examined fiber and paper tensile properties of the pulps with different amount of fiber carboxyl groups introduced by oxidation of bleaching chemicals (oxygen and hydrogen peroxide). The results demonstrated that the increase of fiber carboxyl groups by chemical oxidation reduced fiber curl index but resulted in marginal increase

in fiber WRVs. An increase of fiber charge by 17.4-61.2% resulted in 4.3-25.5 % of increase in paper tensile index at comparable pulp viscosity. The tensile strength increase is likely to be caused by the improvement of fiber-fiber bond strength rather than bond areas due to the fiber charge enhancement by chemical oxidation.

It was found that paper dry tensile stiffness could be improved by 4.4-11.0% with 17.4-22.3% fiber carboxyl group enhancement through peroxide chemical oxidation on fully bleached kraft pulps. For the paper sheets made from holocelluloses isolated from catalytically oxidized SW kraft pulps, the enhanced fiber carboxyl groups by 22.5 - 45.9% resulted in 8.1-30.1 % increase in dry-tensile stiffness. And 14.2-22.4% increase in tensile stiffness was achieved when fiber carboxylic acid content increase 35.6-62.1% in OD(EO)D bleached pulps. Paper dry-tensile stiffness was 4.7-24.8% higher when drying the sheets at an elevated temperature (105 °C) than at room temperature. The benefits of fiber carboxylic acid content on sheet dry-tensile stiffness correlates well with the improvement of paper tensile strength, indicating fiber-fiber bond might be one of the contributors for this improvement.

CHAPTER 9 OVERALL CONCLUSIONS

This study first examined the dynamic profiles of carboxyl group formation in bulk fiber, polysaccharide, and residual lignin during one-stage oxygen delignification a SW kraft pulp with a kappa number of 32.5. The results demonstrated that maximum of carboxylic acid content for both total fiber and polysaccharide were found at a kappa number of 20-24 (26-38% kappa number reduction), which does not match the maximum delignification that usually occurs at 60 minutes reaction. Comparably, the optimal conditions to achieve higher fiber carboxylic acid content for one-stage oxygen delignification are found at 1.5-2.5% NaOH, 800 kPa O₂ at 100 °C.

Carboxyl group formation from high kappa pulping and extended oxygen delignification was also examined in this study. Generally, carboxylic acid content in low AA cooked SW kraft pulp (49.5 kappa number) and the corresponding oxygen delignified pulps were systematically higher (13-23%) than those in high AA cooked SW kraft pulp (48.0 kappa number) and the corresponding oxygen delignified pulps. The same profile was also found for polysaccharides of both oxygen delignified pulps. The experimental results demonstrated that maximum carboxylic acid content in total fiber occurred at kappa numbers of 24-25. Combining with the findings during one-stage oxygen delignification, kappa number of 20-25 can be considered the characteristic values for oxygen delignification to achieve maximum carboxylic acid content in southern pine kraft pulp fiber.

Due to the limitation of fiber carboxyl group increase during typical oxygen delignification, an early stage fiber carboxyl group enhancement was developed by catalytic oxidation of lignocellulosic fiber during one-stage oxygen delignification. The

results indicated that the application of 0.10 - 0.18% bismuth ruthenium pyrochlore oxide catalyst during oxygen delignification effectively enhanced, by 52.2 – 116.0%, the carboxylic acid content in carbohydrate fraction of the pulps (holocellulose) without a significant decrease in pulp viscosity and delignification. The contributing factors and importance for carboxyl group formation in carbohydrate pulp fraction was shown to be NaOH dosage > oxygen pressure > temperature. Optimal conditions for fiber carboxyl group formation in an O-stage was shown to occur with a medium caustic charge (2.5%), lower temperature (85-100 °C), and high oxygen pressure (800-960 kPa) under the experimental conditions studied.

The pulp bleaching study demonstrated that fiber carboxyl groups enhanced during pulping and early bleaching stages (oxygen delignification) was partially retained through an ECF bleaching sequence. In addition, a comparative study on total fiber carboxylic acid content of fully bleached SW kraft pulps at final pulp brightness value of 88.0% was conducted. Although oxygen delignification was found to increase fiber carboxyl groups slightly, overall, 52.0-63.0% of initial pulp fiber carboxyl groups were lost in subsequent bleaching stages. The decrease in fiber acidic groups was shown to be primarily due to the removal of oxidized lignin, HexA, and some aldonic acids. Generally, fiber carboxylic acid content in the pulps bleached via DEDED, D(EPO)DED, and OQPZP was shown to be 18.0-21.0% higher than those bleached via (D+C)EDED, (D+C)(EO)DED, and OD(EPO)DD. It was also found that the second alkaline extraction stage (E₂) in (D+C)EDED, (D+C)(EO)DED, DEDED, and D(EPO)DED caused a decrease (10.9-15.0%) in pulp fiber carboxylic acid content. When removing the second alkaline extraction stage from these bleaching sequences as (D+C)EDD, (D+C)(EO)DD,

DEDD, and D(EPO)DD, the lost fiber carboxylic acid content due to the later alkaline extraction was retained. When hydrogen peroxide was employed as a terminal bleaching stage, it increased fiber carboxyl groups by 20.0% as shown for pulps bleached via OD(EPO)DP vs. OD(EPO)DD. These observations provide mills a simple and directed approach to retain or reduce fiber carboxylic acid content for fully bleached kraft pulps.

The effect of fiber carboxyl groups introduced by oxidation of bleaching chemicals such as oxygen and hydrogen peroxide on fiber and paper physical properties was examined. The results demonstrated that the increase of fiber carboxyl groups by chemical oxidation reduced fiber curl index but resulted in marginal increase in fiber WRVs. An increase of fiber carboxyl groups by 17.4-61.2% resulted in 4.3-25.5 % of increase in paper tensile index at comparable pulp viscosities and 4.4-30.1% increase in paper dry tensile stiffness. Paper dry-tensile stiffness was 4.7-24.8% higher when drying the sheets at an elevated temperature (105 °C) than at room temperature. The benefits of fiber carboxylic acid content on sheet dry-tensile stiffness correlates well with the improvement of paper tensile strength, suggesting fiber-fiber bonding might be one of the contributors for this improvement.

CHAPTER 10 RECOMMENDATIONS FOR FUTURE WORK

Although the benefits of fiber charge have been acknowledged and surface fiber charge modification has been achieved, controllable technology for total fiber carboxyl group enrichment is still under development.

This study was the first time to demonstrate employing a catalyst to increase fiber carboxyl groups in carbohydrate at an early bleaching stage (oxygen delignification). However, the mechanism of carboxyl group enhancement via the catalytic oxidation and the retention of enhanced carboxyl groups through bleaching require further investigations.

The effect of fiber carboxyl groups enhanced by chemical oxidation on paper dry-tensile stiffness has been presented in this study. The mechanism of this effect is still less understood and needs more investigations.

In addition, more research works need to be focused on the following aspects:

1. Develop a simple, rapid, and accurate methodology to determine fiber surface charge and further investigate how total and surface fiber charge function differently.
2. Further develop controllable fiber carboxyl group enhancement technology to address the following issues:
 - How does total and surface fiber charge affect fiber and paper physical properties differently?
 - How much total or surface fiber charge should be introduced into fiber to obtain desirable fiber or paper physical properties? Is there an equation to quantify the relationship between fiber charge and fiber and paper strength properties?

- How does fiber charge affect wet-end chemistry?
- How much refining energy saving can be achieved for 10% total fiber charge increase?

APPENDIX A PROPERTIES OF UNBLEACHED SOFTWOOD KRAFT PULPS

A commercial southern U.S.A southern pine (*Pinus taeda*) kraft pulp with a kappa number of 32.5 (CSW) was kindly donated by International Paper, Franklin Mill, VA. The pulp was thoroughly washed with deionized water prior to use.

Two SW kraft pulps with a kappa number of 49.5 (HSW) and 48.0 (HSW) were prepared at the laboratory by cooking the southern pine wood chips in a M&K digester at 15% and 19% active alkali charges with 1650 and 1050 H-factors, respectively. Pulping sulfidity was kept at 25% with cooking temperature of 170° C and a liquid/wood ratio of 4:1. After kraft pulping, the pulps were disintegrated, screened, washed thoroughly with water, and stored at 2 °C.

Table A-1 summarizes metal content, physical and chemical properties of the brownstock kraft pulps used in this study.

Table A-1. Pulp Metal Content, Physical and Chemical Properties

Pulp	Kappa No.	Viscosity (mPa.s)	Major metals (ppm)				Sugar composition (%)				
CSW	32.5	24.6	Mn	Mg	Cu	Fe	Arab.	Gal.	Glu.	Xyl.	Man.
			44.7	473.9	9.2	21.8	0.68	0.46	81.13	11.47	6.09
LSW	49.5	36.8	22.1	283	17.3	19.9	0.50	0.50	75.30	9.00	6.70
HSW	48.0	29.0	19.6	299	24.7	27.5	0.50	0.50	75.30	7.50	7.00

APPENDIX B EQUIPMENT AND SAFETY OF OPERATION

All one- and two- stage oxygen delignification experiments were conducted in a 2.00-liter inclined rotary stirred Parr reactor as shown in Figure B.1. The Parr reactor was constructed from 316 stainless steel and was equipped with a stirrer and a pressure gauge. The reactor was connected to a 4842 temperature controller.

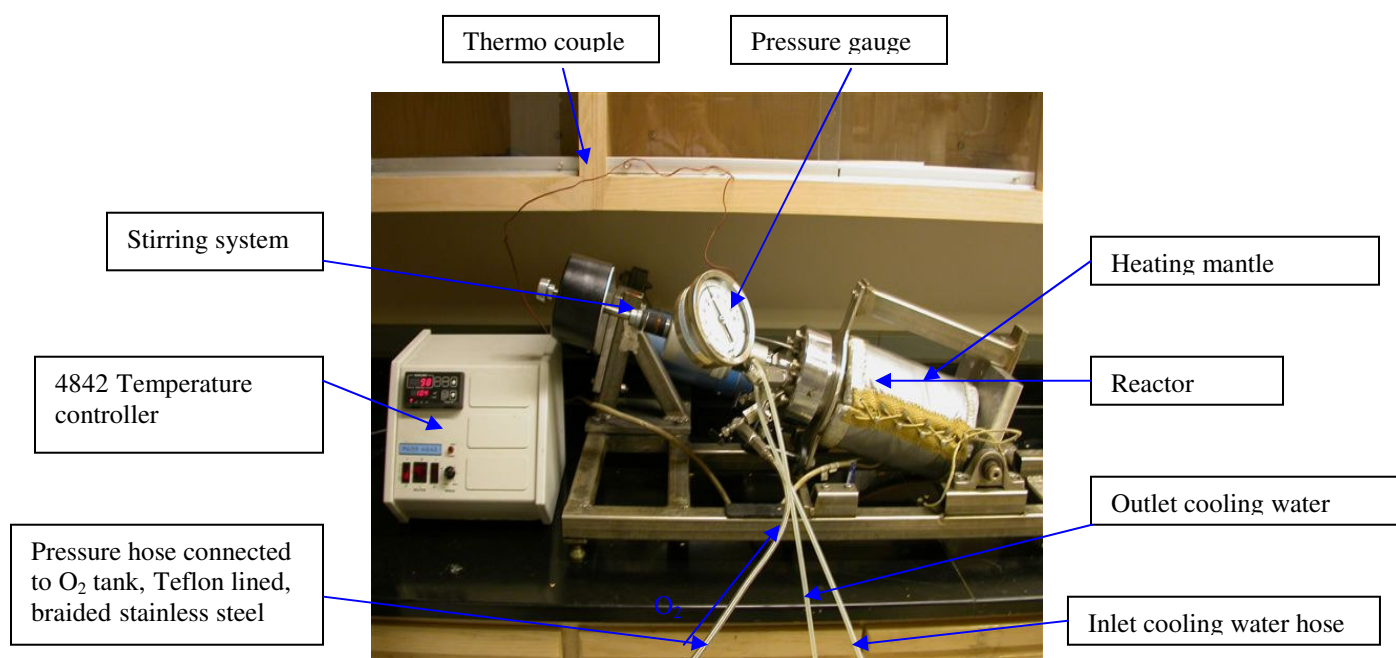


Figure B.1. Photograph of a 2.00-Liter Inclined Parr Reactor with a Thermo-Couple Controlled Heater

Preliminary study was also conducted to obtain optimal mixing conditions that did not detrimentally influence the results. Pulp kappa number was used to evaluate how the amount of pulp used and the rotating speed of mixer affect the mixing result. Table B-1 shows the effect of the amount of pulp used and the mixing speed on the pulp kappa

number of oxygen delignified pulps under the conditions of 2.5% NaOH, 100 °C, 800 kPa O₂, and 10 min. It is noted that the optimal mixing effect was found using 30.00 grams o.d. pulp and the rotating speed was to set the speed controller at scale 30.

Table B-1. The Effect of the Amount of Pulp Used and Mixing Speed on Pulp Kappa Number of Oxygen Delignified Pulps

Amount of pulp used (Grams, o.d.)	Rotating speed control scale	Pulp kappa number
20	30	26.8
30	30	26.1
50	30	27.1
80	30	28.2
30	9	27.5
30	20	26.7
30	30	26.1
30	50	27.0
30	80	27.9

Safety of operation for the Parr reactor requires that the operator be trained prior to use and familiar with all aspects of its operations and aware of all the potential hazards.

First, bare skin should be covered with appropriate personal protective equipment such as gloves and goggles/safety glasses. Before turning on the temperature controller for heating, thermocouple must be inserted into the reactor appropriately for temperature control and avoiding overheating. Before charging oxygen, make sure the reactor is sealed completely. During the reaction, the operator must check the set/actual temperature and vessel pressure at least once every 10-minute. When the reaction is completed, close the valve of oxygen tank, turn off the heater, and then release the reactor pressure to zero. Wait for at least 1 minute before opening the reactor. Using insulated

gloves is recommended while taking sample from the reactor. Always keep the equipment in a clean and well maintained condition after completion of the reaction.

APPENDIX C REPRODUCIBILITY AND REPLICABILITY

The error bar value in each data point through the whole thesis was calculated from at least three replicates of sample testing under the same conditions.

Reproducibility and replicability of oxygen delignification and carboxyl group content determination were critical for this study. For this purpose, three oxygen delignification reactions under the same conditions (2.5% NaOH, 0.80 MPa O₂ and 100 °C for 30 min) were performed. The sample from each run was analyzed with three replicates for pulp kappa number, fiber carboxyl group content, and carbonate content in the corresponding effluent. The average values for pulp kappa number, fiber carboxyl group content, and filtrate carbonate content in each run and three replicates are shown in Table C.1. Their corresponding standard deviations for three replicates under the same conditions are less than 0.05, 1.40, and 0.03, respectively.

Table C-1. Pulp Properties Measured with Three Replicates at Three Different Treatments under the Same Conditions

Run	Test replicate	Pulp kappa number		Fiber carboxyl group (μmol/g)		Carbonate in the effluent (g/L, Na ₂ O)	
		Average	Stdev.	Average	Stdev.	Average	Stdev.
1	3	20.8	0.03	105.6	1.35	0.62	0.02
2	3	20.9	0.02	102.2	1.08	0.61	0.03
3	3	20.4	0.05	103.8	1.40	0.64	0.03

APPENDIX D CARBOXYL GROUP GENERATION CATALYST SCREENING

To screen a carboxyl group generating catalyst to enhance fiber carboxyl groups in polysaccharide, a series of inorganic, organic, and complexes were added to the oxygen delignification system. After oxygen delignification, the oxygen delignified kraft pulps were holopulped to isolate holocellulose. Fiber carboxyl groups in these holocelluloses were measured. Figure D.1 summarizes carboxyl group content in the holocelluloses of oxygen delignified pulps with some different catalysts (*i.e.* Sodium molybdate(VI) dehydrate, Anthraquinone (AQ), Tungsten (VI) oxide, 1,10-phenanthroline, Bismuth (Bi)-ruthenium(Ru) pyrochlore oxide, Cr_2O_3) employed. It is observed that bismuth ruthenium pyrochlore oxide has the highest effect of fiber carboxyl group enhancement. Control testing showed that the bismuth ruthenium pyrochlore oxide did not contribute the analysis of acid groups in the pulp. The further study of this catalyst on fiber carboxyl group enhancement during oxygen delignification was reported in CHAPTER 6.

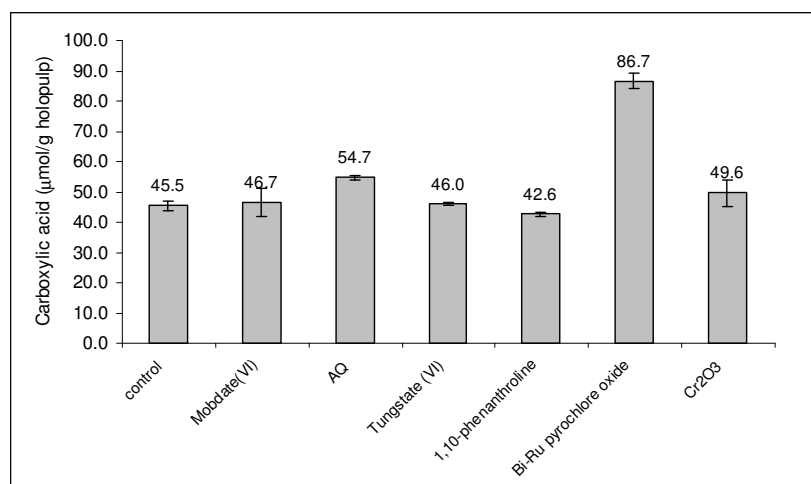


Figure D.1. Carboxyl Group Content of Holocelluloses Isolated in Catalytically oxygen delignified SW Kraft Pulps

Conditions: 30 o.d. pulps, 2.5% NaOH, 800 kPa O_2 , 100 °C, 60 min, and 0.12-0.15% catalyst (on o.d. pulp)

APPENDIX E PULP RESIDUAL LIGNIN ISOLATION

Residual lignin from kraft brownstocks, O-, and OwO-stage delignified pulps was isolated employing an acid hydrolysis technique that has been commonly used to isolate lignin from kraft pulps [197]. Prior to acid hydrolysis, *p*-dioxane was freshly distilled with NaBH₄. The isolation setup was shown in Figure E.1 and the procedure was as follows:

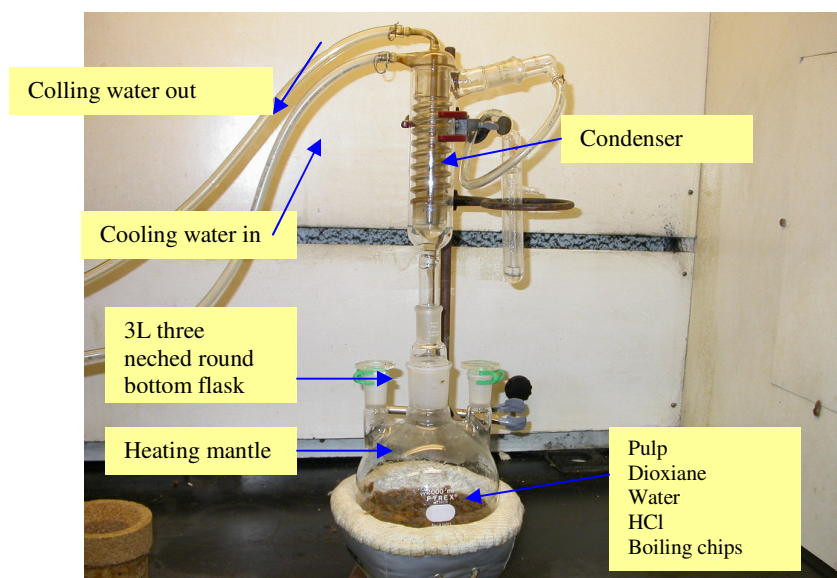


Figure E.1. Acid Hydrolysis Apparatus for Residual Lignin Isolation

A 3-L, three-necked round-bottom flask containing boiling chips and fitted with a condenser was charged with 30 g of air-dried pulp (o.d. basis). A 0.1 N HCl solution mixture of *p*-dioxane/water (9:1) was added to the pulp so that the final consistency of the slurry was 4%. The reaction mixture was refluxed for two hours under an argon atmosphere before it was cooled and filtered through a 4-L-capacity coarse fritted-glass Buchner funnel covered with filter paper (to avoid plugging). The resulting filtrate was

passed through a fine-fritted-glass Buchner funnel packed with celite to remove any pulp fines. The lignin/water/dioxane mixture was then neutralized with an aqueous saturated solution of sodium bicarbonate to an apparent pH value of 5.0-5.5 and concentrated under reduced pressure to approximately 10% of the initial volume. Deionized water (approx. 400 mL) was added and the mixture was concentrated again under reduced pressure to remove the last traces of *p*-dioxane. The resulting lignin-water mixture was transferred to a 1.00-L beaker, diluted with deionized water to a volume of approximately 800 mL, acidified to a pH of 2.0-2.5, and transferred to 250-mL-capacity centrifuge bottles. The bottles were frozen, thawed, and centrifuged. The supernatant was siphoned, and fresh acidified water was added. This step was repeated three times, each time combining the lignin into fewer bottles so that in the third wash one bottle contained all the lignin. The lignin was then freeze-dried for 1-2 days, after which it was characterized with NMR.

APPENDIX F PULP METAL ION CONTENT ANALYSIS

Metal ion content in pulp samples were analyzed using inductively coupled plasma emission spectroscopy following literature methods [198-200]. A summary of the digestion method was as follows:

1. An oven dried pulp (0.5-2.0 g) was accurately weighed in a clean, labeled, pre-cleaned griffin beaker and covered with a watch glass. The weight of the sample specimen was recorded to the nearest 0.1 mg.
2. The sample was transferred to a hot plate in a fume hood. To the beaker, 5 mL of 1:1 HNO₃/water was added, swirled, and recovered with the watch glass.
3. The sample was heated slowly for 10-15 minutes to a gentle reflux. After 10 to 15 minutes the beaker was removed from heat and allowed to cool.
4. 2.5 mL of concentrated HNO₃ was added to the beaker.
5. The beaker was returned to the hot plate to reflux for 30 minutes. The volume was not allowed to drop below 5 mL. After 30 minutes, the beaker was removed from the hot plate and allowed to cool.
6. Step 4 and 5 was repeated.
7. To the cooled beaker, 1 mL of deionized water and 1.5 ml of 30% H₂O₂ was added. The watch glass was placed back on the beaker.
8. The beaker was returned to the hot plate on reduced heat. The samples began to effervesce. When the sample effervescence subsided, the beaker was removed to cool.
9. 0.5 mL of 30% H₂O₂ solution was added to the beaker. The beaker was covered with the watch glass and returned to hot plate until effervescence subsided.

10. Step 9 was repeated until the general appearance of the digest was unchanged, or a total of 5 mL of 30% H₂O₂ was added.
11. To the beaker, 2.5 mL of concentrated HCl was added along with 5 mL of deionized water. The beaker was returned to the hot plate, heated for 15 minutes, and then removed to cool.
12. Once cool, the under surface of the watch glass was rinsed into the sample beaker with deionized water. The digest was filtered through a pre-rinsed Whatman 41 filter paper into a 50 mL graduated cylinder. The sides of the beaker were rinsed with deionized water to ensure quantitative transfer of the sample digest. Do not exceed a final volume of 50 mL.
13. The final volume of the filtrate was brought up to 50 mL with deionized water.
14. The digests were transferred to appropriately labeled, pretreated sample bottles and submitted for ICP analysis.

Analysis of the sample digest was accomplished using a Perkin Elmer Optima 3000 DV Emission Spectrometer. This instrument, equipped with an autosampler and integral computer workstation, was configured to detect up to 30 elements simultaneously in less than 5 mL of sample digest solution. The principal analysis was the detection of characteristic ultraviolet and visible light emission from metallic elements injected in a high temperature argon plasma torch. To improve instrument performance, an yttrium internal standard was added to each sample, standard, and blank to compensate for small variations in sample flow rate, sample viscosity, acid concentration, and other instrumental and chemical parameters. Quantification of the sample analysis was based

on the measurement of specific wavelength intensities and comparison against multi-point calibration standards for each element.

APPENDIX G PULP FIBER TOTAL CARBOXYLIC ACID CONTENT MEASUREMENT

Carboxylic acid content in pulp samples was determined using Headspace Gas Chromatography (HSGC) with a modified pulp sample preparation procedure [201] as follows: 0.25 g air-dried pulp was treated with 50 mL 0.1 N HCl solution with magnetic stirring for 60 minutes. The treated pulps were washed with 1.50-2.0 L deionized water until pH near neutral. The sample was air dried at least 24 hours. Weigh 0.05g air-dried pulp into a 20-mL headspace vial and accurately add 4.0 mL a solution of 0.0025 M NaHCO_3 and 0.11M NaCl with pipette and cap the vial for HSGC measurement.

All measurements were carried out using an HP-7694 automatic headspace sampler and model HP-689 capillary gas chromatograph equipped with a thermal conductivity detector (Agilent Technologies, Palo Alto, CA) (Figure G.1.) .



Figure G.1. Headspace Gas Chromatographic Instrument

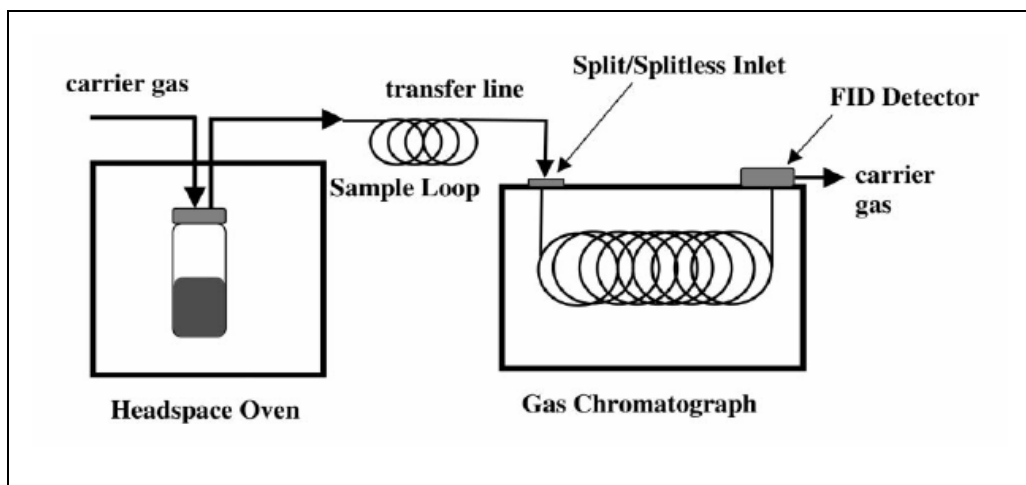


Figure G.2. The Diagram of the Headspace GC

GC conditions were as follows: Capillary column (model S-Q, J&W Scientific Inc. Folsom, CA) with I.D. 0.53 mm \times 30 m at 30 °C, carrier gas helium flow rate of 3.1 ml/min. The GC was run in splitless mode. Headspace sample operating conditions were as follows: Oven temperature of 60 °C, vial pressurized by helium and pressurization time of 0.2 min, sample-loop fill time of 0.2 min, loop equilibration time of 0.05 min, via equilibration time of 10 min with strong shaking, and loop fill time of 1.0 min. The scheme of the headspace GC was shown in Figure G.2 and the gas chromatogram was shown in Figure G.3. The carboxylic acid content of fiber can be calculated as follow:

$$RCOOH(\mu mol / g) = \frac{A_{CO_2} - A_{Control}}{f \times w} \times 1000 \quad (13)$$

where

A_{CO_2} and $A_{Control}$: CO₂ GC adsorption peak areas for sample and control

f: calibration constant (21718)

w: oven-dried sample weight in grams

The typical standard deviation for three replicates under the same oxygen delignification and bleaching conditions was 1.05 $\mu\text{mol/g}$ pulp.

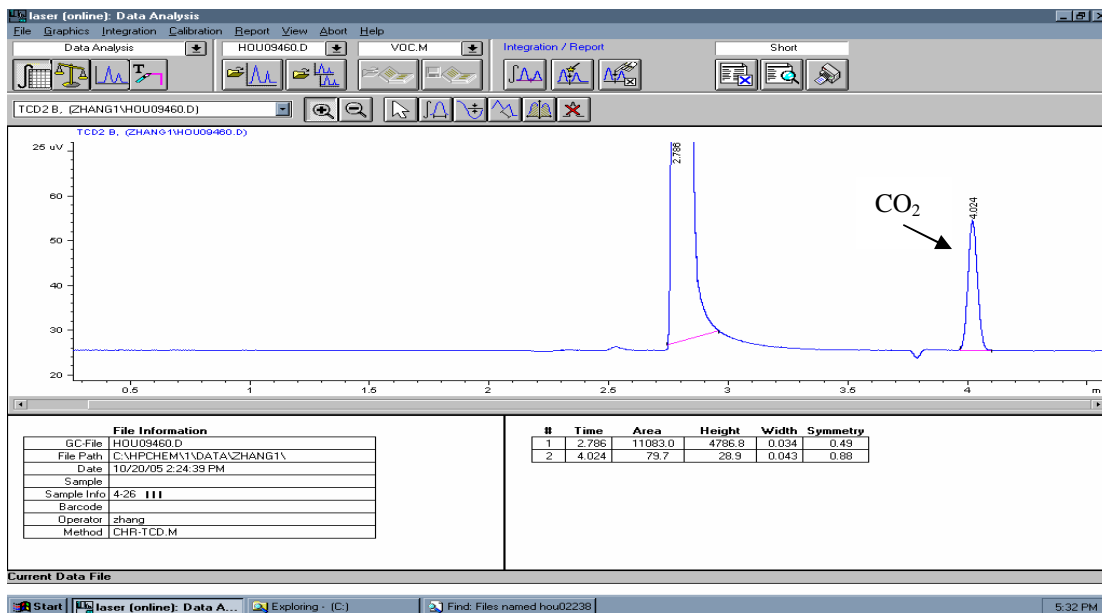


Figure G.3. Gas Chromatogram of Carbon Dioxide from Headspace GC

APPENDIX H CHARACTERIZATION OF RESIDUAL LIGNINS BY ^{13}C and ^{31}P NMR ANALYSIS

^{13}C NMR analysis of carboxyl groups

The ^{13}C -NMR sample was prepared by adding 100 mg of dry lignin to 0.45 ml of DMSO- d_6 in a 4 mL vial. The solution was transferred to a 5-mm NMR tube using a pipette. The quantitative ^{13}C experiments were performed using a 90° pulse with an inverse gated decoupling (IGD) pulse sequence, which is needed to remove the nuclear Overhauser effect (nOe). An 11 s pulse delay value, obtained from the literature, was used to insure complete ^{13}C nuclei relaxation between pulses [36]. Between 10,000 and 20,000 transits were acquired for every sample at a temperature of 50°C and a sweep width of 200 ppm (TD=32768, LB=10 Hz). The integration regions used for the analysis of the spectra were shown in Table H-1 [214, 215]. Manual phasing and a 3-point manual base line correction were performed on each spectrum along with a chemical shift calibration using the DMSO signal ($\delta 39.5$ ppm) as a reference.

Quantitative ^{31}P -NMR analysis of carboxyl groups

^{31}P -NMR is an efficient and facile technique for quantifying lignin hydroxyl groups and carboxylic acid groups. The lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and analyzed by ^{31}P NMR following literature methods [203] as described as follows:

1. A solvent mixture composed of anhydrous pyridine and deuterated chloroform in a 1.6:1 ratio was prepared.

2. The solvent mixture was used to prepare a solution of approximately 4.0 mg/mL of cyclohexanol (internal standard) and 3.6 mg/mL of chromium acetylacetonate (relaxation agent).
3. Approximately 25 mg of dry lignin was weighed. The lignin was dried under vacuum (~ 20 mm Hg) for a minimum of 24 hrs.
4. A 400 mL aliquot of the pyridine/chloroform solvent was added to the dry lignin.
5. A 150 mL aliquot of the internal standard/relaxation agent solution was added the lignin and solvent mixture.
6. The mixture was stirred for several minutes, and 75-100 mL of 2-chloro-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaphospholane was added. The sample was mixed for 1 min and then immediately transferred into a 5 mm NMR tube.
7. The NMR spectrum was recorded immediately.

Each ^{31}P NMR acquisition was performed with a 25 s delay between 90° pulses. The inverse gate decoupling pulse sequence was used to obtain quantitative spectra. A minimum of 150 transients was acquired for each sample. The acquisitions were performed at room temperature, using a 61.9 ppm sweep width (TD=32,768) and a 4 Hz line broadening. All the chemical shifts were calibrated to the product of the phosphitylating agent with water which gives a sharp ^{31}P signal at $\delta 132.2$ ppm. Integration regions used to analyze the spectra were obtained from literature and listed in Table H-2.

Table H-1. Integration Regions for ^{13}C -NMR Analysis of Lignin Samples [214, 215]

Structure	Integration region (δ ppm)
Unconjugated COOH	178.0-167.5
Conjugated COOH	167.5-162.5
C3,C4 Aromatic ether or hydroxyl	154.0-140.0
C1, Aromatic C-C bond	140.0-127.0
C5, Aromatic C-C bond	127.0-123.0
C6, Aromatic C-H bond	123.0-117.0
C5, Aromatic C-H bond	117.0-114.0
C2, Aromatic C-H bond	114.0-106.0
Aliphatic C-O bond, C β in β -O-4; C α in β -5 and β - β	90.0-78.0
Aliphatic C-O bond, C α in β -O-4	79.0-67.0
Aliphatic COR	67.0-61.0
Aliphatic C-O C γ in β -O-4	61.0-57.0
Methoxyl OCH ₃	57.0-54.0
C β in β - β and C β in β -5	54.0-52.0
OCH ₃ in MAME structure	52.0-49.0
CH ₂ in Diaryl methane	29.0-27.0
Aromatic C total	154.0-106.0
Aromatic C-R (substituted)	52.0-49.0
Aromatic C-R (unsubstituted)	29.5-27.0

Table H-2. ^{31}P NMR Integration Regions Used to Quantify Functional Groups in Lignin Samples [203]

Functional group	Integration region (δ ppm)
Cyclohexanol (internal standard)	145.6-144.4
Aliphatic OH	149.0-145.6
Condensed phenolic OH	144.4-140.4
Guaiacyl phenolic OH	140.4-137.6
Carboxyl OH	136.0-133.8

NMR error analysis

NMR error analysis was established by isolating residual lignin either from brownstock samples or oxygen delignified pulp samples and analyzing the spectroscopic data three separate times. Least significant difference ($LSD = 2 \cdot t \cdot s$), where t is the critical student t value at the 95% confidence level, and s is the standard deviation, were calculated. LSD values were obtained for carboxyl groups by ^{31}P NMR and ^{13}C NMR analysis. These values were then used to determine if the differences in the measured lignin functional groups were statistically significant.

APPENDIX I FIBER SURFACE CHARGE DETERMINATION

Polyelectrolyte titrations were used to determine surface charge on fibers as published by Wågberg *et al* [99]. A polymer with high molecular weight and high charge density, methyl glycol chitosan (MW > 1,000,000 Da, charge density 2.244×10^{-3} eq/g), was used as a cationic adsorption polymer for surface charge measurement. The procedure was described as follows:

1. 1.5 g (o.d. basis) pulp was weighed out into a 400 mL beaker.
2. 300 mL 0.1 M HCl was added to the pulp and stirred for 60 min.
3. The pulp was filtered using a vacuum flask and glass filter funnel and washed with at least 400 mL DI water.
4. The filtered pulp was transferred into the 400 mL beaker with addition of 250 mL 0.005 N NaHCO₃. The pH of solution was adjusted to 9.0 with 0.05 N NaOH and stirred for 20 minutes.
5. The pulp was filtered and washed thoroughly with 1400-1600 mL DI water.
6. Different volume of 2.42×10^{-3} N chitosan solutions (12.5, 25.0, 37.5, and 50 mL) was added to the pulp, DI water was added to bring the final volume of pulp slurry to 300 mL, and the mixture was stirred for 40 minutes.
7. The pulp was filtered into a clean container and the filtrate was collected for titration.
8. The concentration of unabsorbed chitosan was titrated with 2.688×10^{-4} N polyvinyl sulfate potassium (PVSK) using 0.1 % o-toluidine blue as an indicator, the color change was from blue to reddish purple.

9. The equivalent of chitosan adsorbed to pulp was calculated using the following equation:

$$(\mu\text{eq/g pulp}) = \frac{V_{Blank} - V_{Sample}}{1.5} \times N_{PVSK} \times \frac{300}{V_{Titrated}} \quad (14)$$

where

V_{blank} and V_{sample} : PVSK consumed volume (mL) for titration of control and sample filtrates

N_{PVSK} : Normal concentration of PVSK

$V_{Titrated}$: titrated filtrate volume (20.00 mL)

1.5: oven-dried pulp sample used (g)

300: solution volume (mL) after chitosan addition, which was 301.5 g by weight (solution +pulp).

APPENDIX J ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

To prepare samples for ESCA work, great care for cleanliness was taken. The drying plates and handsheet molds used for sample preparation were cleaned exhaustively with water, ethanol, and acetone. The samples were touched only at the edges with clean forceps, and sterile, power-free gloves were used. Samples mailed for analysis in Sweden were wrapped in sterile aluminum foil, sandwiched between clean XPEDX blotter papers, and placed in air-tight sterile bags prior to transport and analysis.

All ESCA data were generated using a probe beam of focused, monochromatic Al-K α radiation. The photons cause electrons to be ejected from the sample, which are energy analyzed and counted to reveal the atomic composition and surface chemistry of the sample. The escape depth of the electrons limited the analysis to the outer approximately 5.0 nm of the fiber surface by using a 45 ° take-off angle. All ESCA analysis were conducted on a Quantum 2000 instrument from A Physical Electronics using a monochromatic Al K α x-ray source (15 kV, 20.8 W, 100 μ m beam size, 500 μ m analysis areas) at Chalmers University of Technology, Goteborg, Sweden.

Prior to analysis samples were cut into rectangles of approximately 0.5 by 1.0 cm and mounted under metal forms on sample mounts using clean tweezers and scissors. The samples were then placed into a vacuum chamber and analyzed.

The data generated include low-resolution survey scans to identify the elements present in relative proportion, which give the full spectrum between 0 and 1000 to 1400 eV binding energy. Peaks used to compare relative abundances of oxygen to carbon on the sample surface include a C(1s) and O(1s) peak (Figure J.1.). Chemical shifts for the

carbon C (1s) peak were deconvoluted to provide spectra (Figure J.2.) with peaks identified as four separate classes of carbon by their oxidation levels.

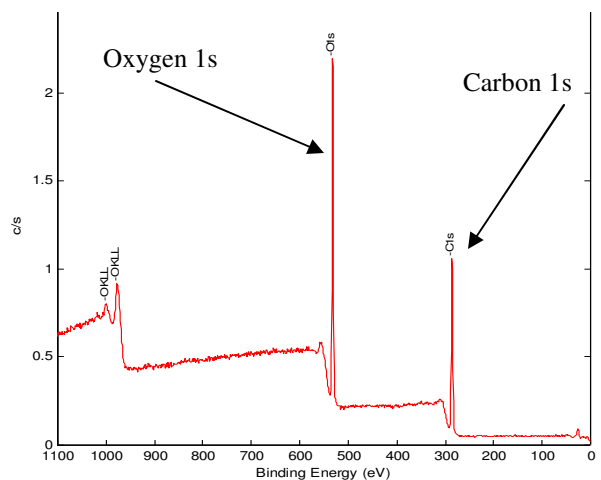


Figure J.1. Carbon (C1s) and Oxygen (O1s) Peaks Detected by ESCA of a SW Kraft Pulp

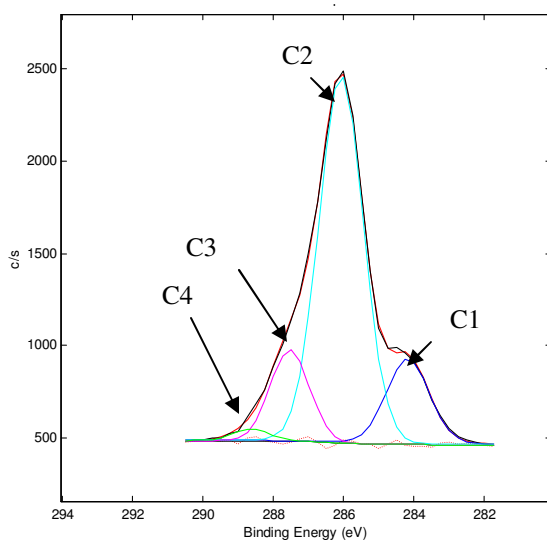


Figure J.2. Curve-Resolved ESCA C1s Signal of A SW Kraft Pulp

APPENDIX K PULP BLEACHING PROCEDURES

Pulp bleaching via chlorine/chlorine dioxide, atmospheric alkaline extraction, and hydrogen peroxide was conducted in a water bath employing 4-mm-thick heat-resistant Kapak pouches. Oxygen delignification and oxygen/hydrogen peroxide reinforced alkali extraction were run in a 2.00-L inclined Parr reactor. Ozone bleaching was conducted in a CRS reactor with CMS 2040 high intensity mixer and an ozone generator according to the procedure described in the literature [252]. The main bleaching procedures were described as follows:

Chlorine (C) and/or chlorine dioxide (D) bleaching

1. The pulp was placed in a Kapak pouch and the required deionized water was added.
2. The chlorine solution and/or chlorine dioxide solution was introduced into the bag.
3. The pouch was sealed, kneaded, and placed in a water bath.
4. The bag was kneaded every 10-15 minutes throughout the duration of the treatment.
5. After the treatment, the pulp was neutralized with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, removed from the pouch, filtered, and thoroughly washed with the deionized water.

Chelating treatment (Q)

1. The pulp was placed in the Kapak pouch
2. The deionized water (some was saved for rinsing) and the EDTA solution were mixed in a beaker.
3. The EDTA solution was introduced into the bag and the beaker was rinsed, and that solution was added to the slurry.
4. The slurry pH was adjusted with 1.0 NaOH to ~6.0

5. The pouch was sealed, kneaded, and placed in a water bath.
6. The bag was kneaded every 10-15 minutes throughout the duration of the treatment.
7. After the treatment, the pulp was removed from the pouch, filtered, and thoroughly washed with the deionized water.

Alkaline extraction (E)

1. The pulp was placed in the Kapak pouch.
2. The deionized water (some were saved for rinsing) and the 1.0N NaOH were mixed in a beaker.
3. The water/NaOH solution was introduced into the bag.
4. The beaker was rinsed and that solution was added to the slurry.
5. The pouch was sealed, kneaded, and placed in a water bath.
6. The bag was kneaded every 10-15 minutes throughout the duration of the treatment.
7. After the treatment, the pulp was removed from the pouch, filtered, and thoroughly washed with the deionized water.

Peroxide reinforced alkaline extraction (EP) stages were performed in accordance with the procedure above, except hydrogen peroxide (0.5% o.d. basis) was introduced in Step 2.

Hydrogen peroxide bleaching (P) was also performed in accordance with the procedure as (EP) except more NaOH and hydrogen peroxide were employed.

Oxygen reinforced extraction stages (EO)

4. Required amount of deionized water mixed with 1.0N NaOH solution was added to the pulp.

5. The reaction mixture was placed in the preheated (85 °C) 2-L Parr reactor.
6. The reactor was immediately and quickly sealed, heated to the target temperature (90 °C), and pressurized with oxygen.
7. After the treatment, the treated pulp was filtered and thoroughly washed with deionized water.

Oxygen and peroxide reinforced alkaline extractions (EPO) were performed identically with the procedure described above, except hydrogen peroxide (0.5%; o.d. basis) was introduced in Step 1.

Note: The hydrogen peroxide (30% solution) should be handled with an ice/water bath in order to reduce the degradation of the chemical. The bottle should be placed back in the refrigerator as soon as possible.

The terminal (or exit) pH after each extraction and reinforced extraction was determined. Measured pH values were always greater than or equal to 10.5.

Ozone bleaching (Z)

1. Pulp sample of 90 grams (o.d. basis) was stirred with sulfuric acid at 1% consistency in a British disintegrator to decrease the pH of the stock to 2.2-2.5.
2. The pulp stock was dewatered without washing to 10% consistency and placed in the bowl of the reactor and the lid was secured.
3. Ozone was generated using an ozone generator connected to the CRS reactor.
4. Upon injection of the ozone gas (0.6% on o.d. pulp) to the pulp, the mixing impeller was engaged at a speed of 2000 rpm for an interval 20 seconds.

5. The pulp was then mixed for 8-10 seconds every 5 minutes at 550 rpm for the remainder of the 20-minute retention time. The temperature was kept at 36-40 °C.
6. At the end of the 20-minute reaction, the remaining gas was evacuated through a potassium iodide solution.
7. The pulp was washed thoroughly before proceeding the next stage.

APPENDIX L PAPER SHEET DENSITY, ZERO-SPAN INDEX, AND TEAR INDEX

Table L-1. Paper Sheet Density, Zero-Span Index, and Tear Index

Fiber source	Fiber Carboxyl acids ($\mu\text{mol/g}$)	Density (g/cm^3)		Zero-span index (N.m/g)		Tear index ($\text{mN.m}^2/\text{g}$)	
		RT	105 °C	RT	105 °C	RT	105 °C
Holopulp-0	61.9	0.392	0.395	113.1	116.2	16.21	14.90
Holopulp-1	75.8	0.391	0.391	112.3	113.9	15.96	14.72
Holopulp-2	88.6	0.392	0.401	110.5	114.8	15.32	14.73
Holopulp-3	90.3	0.401	0.412	112.9	114.9	15.01	14.16
OD(EO)D-0	31.7	0.392	0.397	-	-	-	-
OD(EO)D-1	43.0	0.384	0.394	-	-	-	-
OD(EO)D-2	45.1	0.401	0.408	-	-	-	-
OD(EO)D-3	51.4	0.392	0.403	-	-	-	-
BSW-c	38.4	0.402	0.413	122.4	120.6	20.52	18.83
BSW-p	45.1	0.410	0.420	123.8	122.6	20.14	18.75
BMHW-c	31.8	0.402	0.423	112.1	113.9	6.86	4.48
BMHW-p	38.9	0.420	0.431	115.4	112.1	6.59	4.68
BAHW-c	32.4	0.480	0.478	150.9	152.2	5.76	5.30
BAHW-p	38.2	0.475	0.490	152.9	152.8	5.52	5.09

CSF: Holopulps: ~720 ml; OD(EO)D pulp: ~720 ml; BSW-c and BSW-p: 710 ml and 705 ml; BMHW-c and BMHW-p: 680 ml and 675 ml; BAHW-c and BAHW-p: 625 ml and 620 ml.

APPENDIX M Experimental and Modeling of Carbonate Formation in the Effluent of Oxygen Delignification

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A quantitative model of carbonate formation in the effluent of one-stage oxygen delignification for a softwood kraft pulp was developed and experimentally validated. This model quantitatively described carbonate formation in the effluent of oxygen delignified SW kraft pulps and its kinetic characteristics. It could be used as an approach to predict pulp kappa numbers in the solid phase (fiber) from carbonate content in the liquid phase (filtrate). From the kinetic behavior of carbonate formation and its relationship to pulp kappa number, a control strategy was suggested. Constant kappa number curves used for parameter selection were developed to achieve target pulp kappa number while retaining pulp viscosity and total fiber charge properties.

Keywords: carbon dioxide, carbonate, effluent, kappa number, kraft pulp, kinetics, oxygen delignification, viscosity

Introduction

The pulp and paper industry is a global industry that converts low-cost wood lignocelluloses into high-value fiber-based products in a sustainable manner. Energy efficiency, environment compatibility, and enhanced process efficiency have been the main research drives for pulp and paper industry over the past three decades. Molecular

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oxygen, as the most abundant, inexpensive, energy-efficient, and environment-friendly oxidant, is a particularly attractive choice for many large-scale oxidative processes [253]. The industrial application of oxygen delignification (O) for pulp bleaching has expanded very rapidly since the first commercial system started in 1970s. It has become the dominant operational technology to produce elemental chlorine free (ECF) and totally chlorine free (TCF) bleached pulps [105, 106, 108, 187, 210]. The main benefits for an oxygen delignification stage are its low process costs and environmental compatibility. The latter benefits are derived from the fact that both the chemicals applied in an O-stage and the materials removed from the pulp can be incinerated in the kraft chemical recovery system. Furthermore, the lignin removed in O-stage reduces the levels of chlorinated organic by-products formed in subsequent chlorine dioxide bleaching operations [105]. In light of these benefits, extensive research efforts have been conducted to enhance the efficiency and selectivity of oxygen delignification. Several aspects of this process have been examined including lignin/carbohydrate chemistry, process selectivity improvements, pulp yield retention, extended delignification, the efficiency of oxygen mass transfer, and pulp fiber modification [111, 112, 114, 115, 138, 153, 157, 212, 254]. Additionally, the large amount of dissolved lignin fragments and carbohydrate degradation products formed during oxygen bleaching has directed attention to their contribution to recovery boiler loads [131, 208, 209]. However, the carbonate formed in the effluent during oxygen delignification has received little attention to date.

It is known that acidic groups and other oxidative structures are formed in residual lignin and pulp carbohydrates during oxygen delignification [12, 105]. The

fragmentation of these acidic groups and the decarboxylation of some of these carboxylic acids when exposed to heat and alkaline environments inevitably lead to the formation of carbonate in aqueous alkali solutions. This filtrate is used for brown stock washing and then mixed with black liquor. Hence, the carbonate formed during oxygen delignification will contribute to the carbonate content in black liquor.

It is well understood that carbonate in black liquor is one of the major species responsible for fouling and scaling in kraft mill evaporators during chemical recovery [43]. The solubility of sodium carbonate is strongly dependent on the total solid content in the black liquor. It has been acknowledged that two types of carbonate salt precipitates are formed during black liquor evaporation. Burkeite, a double salt ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), is precipitated first, and then burkeite plus sodium carbonate is precipitated [43]. Therefore, the quantification of carbonate, its sources, and its solubility in black liquor is very important in controlling evaporator fouling, and thus, reducing mill downtime.

Chai et al [255] reported that the concentration of carbonate in the spent liquor of kraft pulping softwood (SW) was in a range of 1.6-1.8 g/L for production of a bleachable-grade kraft pulp, corresponding to ~18% of the total carbonate in black liquor. Murphy et al [256] studied the CO_2 evolution during H_2O_2 bleaching of lignin-containing pulps using dissolved pulps and milled wood lignin as models. The results indicated that the amount of carbon dioxide evolved was proportional to the lignin content of the pulp. The source of carbon dioxide was attributed to the decarboxylation of carboxylic groups formed in lignin fragments during alkaline hydrogen peroxide bleaching. Yuan et al [257] studied the formation of gaseous products and its relation to pulp bleaching during the peracetic acid treatment of kraft pulp. Their results demonstrated that although

oxygen was the dominant product of the wasteful reactions, carbon dioxide was also formed under these conditions. Studies by Chai et al [255] indicated that carbonate formation increased from 0.0 to 1.0 g/L while oxygen delignifying a loblolly pine kraft pulp with initial kappa number (K) of 20.9 for 0 - 120 min at 90 °C with 2.5% NaOH and 0.689 MPa of molecular oxygen. To date, no detailed work has been reported to quantify carbonate formation and its kinetic behavior during oxygen delignification.

This paper examines the dynamic change of carbonate formation in the effluent of a series of laboratory one-stage oxygen delignification treatments of a SW kraft pulp and its dependence on process conditions. An empirical dynamic model was developed to predict the amount of carbonate in the effluent and its application for pulp kappa number prediction. Based on the carbonate formation characteristics, a control strategy was suggested to achieve a pulp kappa number with desirable pulp viscosity and total fiber charge.

Experimental

Materials

A thoroughly washed commercial southern U.S.A. pine kraft pulp with a kappa number of 32.5 (% of mass lignin content = $0.13 \times$ pulp kappa number (K) [258]) and a viscosity of 24.6 mPa.s was used for the oxygen delignification study. The Ca, Mn and Mg concentration in the pulp were 1850, 44.7 and 473.9 ppm respectively. The deionized water had a Ca content of 4.41 ppm. All other chemicals and solvents were commercial reagent grade and used as received.

Oxygen delignification

All one-stage oxygen delignifications were conducted in a 2-liter inclined rotary stirred Parr reactor. Experimental conditions employed are summarized in Table M-1.

Table M-1.One-stage Oxygen Delignification Conditions

Parameter	Unit	Symbol	Conditions
NaOH	wt % on pulp	N	1.5, 2.5, 3.5
Temperature	°C	T	85, 100, 115
Oxygen	MPa	P	0.64, 0.80, 0.96
Time	min	t	0, 10, 20, 30, 45, 60

Note: 10% pulp consistency and the molar ratio of Mg:Mn = (31-33):1 [150]

In a typical experiment, never dried (30.00 g o.d.) unbleached SW kraft pulp was mixed with 1.00 N NaOH solution and MgSO₄ (see Table 1 for details), and pulp consistency was adjusted to 10% with deionized water. The reaction mixture was then added to the pre-heated reactor (70-90 °C), sealed, pressurized to the target pressure with molecular O₂, purged three times, sealed and then rapidly (~ 5 min) heated to the target temperature (see Table M-1). Upon the completion of the reaction, the vessel pressure was cooled, vented, and the oxidized pulp was filtered, washed with deionized water, and then stored at 2 °C for further analysis. The filtrate in post-O delignified pulp was pressed, immediately collected, and put in a vial without headspace, for further sodium carbonate determination. Control reactions without pulp were also conducted to obtain the carbonate content in the solution due to the absorption of CO₂ from the air.

Pulp carboxylic acid and filtrate carbonate content determination

Pulp sample preparation and procedures to determine carboxylic acid followed the method developed by Chai et al [201]. Sodium carbonate content in filtrate was measured using Headspace Gas Chromatography [259] .

Metal ion concentration

Metal ion concentration in pulp samples were analyzed using inductively coupled plasma emission spectroscopy following a literature method [200].

Pulp analysis

TAPPI Testing Methods [204] was used to measure pulp kappa number (T-236 om-99) and pulp viscosity (T-230 om-89).

Reproducibility and replicability analysis

Reproducibility and replicability of oxygen delignification and carboxyl group content determination were critical for this study. For this purpose, three oxygen delignification reactions under the same conditions (2.5% NaOH, 0.80 MPa O₂ and 100 °C for 30 min) were performed. The sample from each run was analyzed with three replicates for pulp kappa number, fiber carboxyl group content, and carbonate content in the corresponding effluent. The average values for pulp kappa number, fiber carboxyl group content, and filtrate carbonate content in each run and three replicates are shown in Table M-2. Their corresponding standard deviations for three replicates under the same conditions are less than 0.05, 1.40, and 0.03, respectively.

Table M-2. Pulp Properties Measured with Three Replicates at Three Different Treatments under the Same Conditions

Run	Test replicate	Pulp kappa number		Fiber carboxyl group (μmol/g)		Carbonate in the effluent (g/L, Na ₂ O)	
		Average	Stdev.	Average	Stdev.	Average	Stdev.
1	3	20.8	0.03	105.6	1.35	0.62	0.02
2	3	20.9	0.02	102.2	1.08	0.61	0.03
3	3	20.4	0.05	103.8	1.40	0.64	0.03

Results

Carbonate formation kinetics in the effluent of one-stage oxygen delignification

To quantify the amount of carbonate formed in the effluent of oxygen delignification and investigate carbonate formation kinetics, a series of one-stage of oxygen delignification experiments were conducted under the conditions described in Table 1. The experimental parameters examined included: reaction time, oxygen pressure, caustic charge, and temperature. The typical dynamic profiles for sodium carbonate formation in the filtrate of the oxygen delignified SW kraft pulps at different caustic charge are shown in Figure M.1.

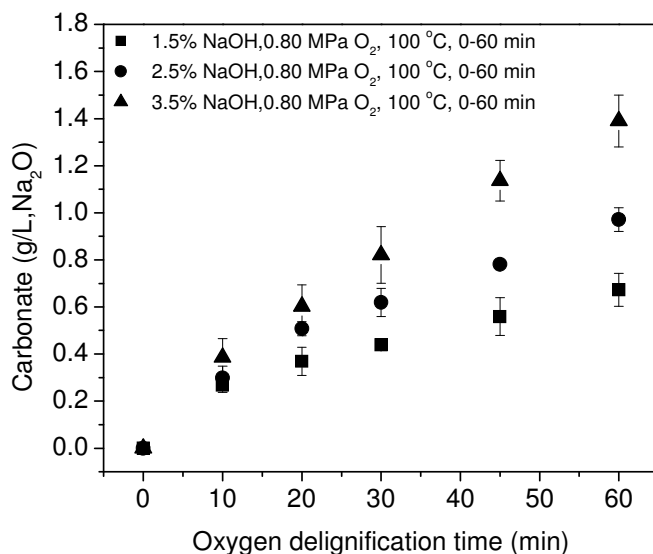


Figure M.1. Dynamic Change of Carbonate Content in the Effluent of One-Stage Oxygen Delignification of a SW Kraft Pulp

The Ca, Mn and Mg concentration in the initial pulp were 1850, 44.7 and 473.9 ppm respectively, as determined by ICP. The deionized water had a Ca content of 4.41

ppm. After 30 min oxygen delignification at 100 °C, 800 kPa O₂, and 1.5% NaOH, the concentration of Ca, Mn and Mg in the oxygen delignified pulps were 1780, 41.6 and 558 ppm respectively and 14.1, 0.27 and 13.7 ppm respectively in the corresponding filtrate. Hence, deionized water at most provides only a very small amount of calcium detected in the effluent (i.e. < 1.34%), regardless of counter anions.

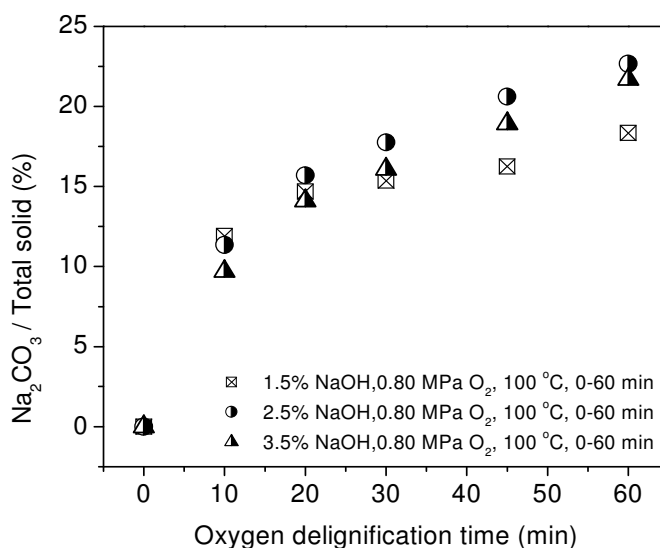


Figure M.2. Percentage of Carbonate on Total Solid Basis in the Effluent of Oxygen Delignified SW Kraft Pulps

The results in Figure M.1 indicate that filtrate carbonate formation increases steadily as oxygen delignification proceeds under conditions studied. When applied sodium hydroxide increases from 1.5% to 3.5%, the carbonate content in the filtrate increases over 100%, suggesting that the process parameters, such as caustic charge, have a significant impact on the carbonate formation. At the end of oxygen delignification

reactions, the carbonate concentration typically ranged from 0.60 g/L to 1.40 g/L in the effluent, corresponding to 16 - 23% of total solid in the effluent (Figure M.2). As reported by Chai et al [255], the typical carbonate content in the black liquor of SW kraft pulping is 1.6-1.8 g/L. Therefore, the amount of carbonate in the filtrate from oxygen delignification is an important contribution to the carbonate concentration of weak black liquor and needs to be taken into account when addressing the source of carbonate in the black liquor for pulp bleaching mills with an oxygen delignification stage.

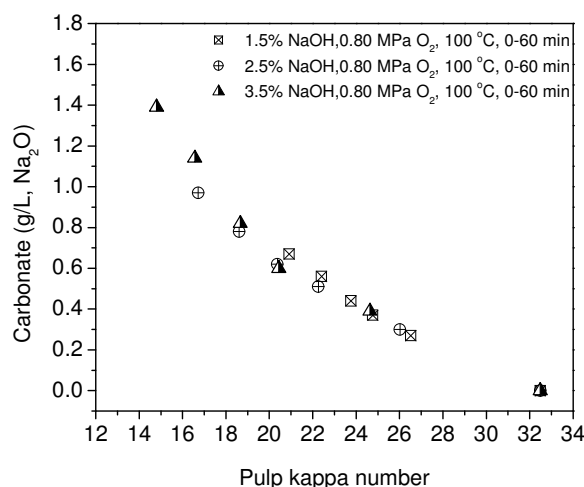


Figure M.3. Carbonate Formation with Kappa Number Reduction during Oxygen Delignification of a SW kraft Pulp

Kinetic Model Development

General analysis

As shown in Figure M.3, the initial increase of carbonate content in the filtrate correlated very well with the pulp kappa number, suggesting that carbonation formation in the initial oxygen delignification phase originates primarily from lignin degradation. However, when the rate of delignification decreases in the late stage of oxygen

delignification (Figure M.3), the carbonate formation accelerated, especially at higher alkali charge (3.5% NaOH). These results suggest that the degradation of carbohydrate, and/or further oxidation of degraded organic products, lead to additional carbonate formation.

It is known that 40-50% of residual lignin in kraft pulp can be readily removed by one-stage oxygen delignification processes [105]. The typical oxygen delignification process indicated by kappa number reduction with time is characterized by an initial fast phase followed by a slow second phase of delignification [153]. Study by Genco et al [260] on the kinetics of oxygen delignification of southern hardwoods demonstrated an apparent high rate order with respect to the kappa number was obtained in medium-consistency oxygen delignification experiments. The observed high rate order is actually a mathematical representation of the slow second phase of the delignification reaction, which is not due to lignin re-condensation reactions or mass-transfer limitations in the system studied but a large number of parallel first order reactions take place simultaneously during the delignification process due to the presence of different lignin moieties. In addition, some carbohydrates are attacked by active oxygen species, under alkaline conditions ($\text{pH} > 13.0$) at elevated temperature (75-115 °C), leading to degraded water soluble products. The oxidative components include: aliphatic acids (mono-, dicarboxylic acid, formic acid, acetic acid, etc.), carbohydrate, methanol, and carbon dioxide [261, 262]. However, the mechanism for carbon dioxide formation as a product from an O-stage has not been studied in detail during oxygen delignification. Possibly sources of CO_2 generation during oxygen delignification include oxidative degradation or decarboxylation of residual lignin and carbohydrate, or their oxidative products. The

conditions affecting the rate of lignin removal during oxygen delignification are primarily caustic charge, temperature, oxygen pressure, and the reaction time. The effect of caustic charge on carbonate formation in the oxygen delignification effluent is shown in Figure 1. Subsequently, it is reasonable to assume that carbonate formation should depend on the total carbon (lignin and carbohydrate fraction), oxygen pressure, hydroxide charge, reaction temperature, and reaction time.

Although carbon dioxide can be produced from pulp chemical components, mainly lignin and carbohydrate in the unbleached kraft pulps, considering the complexity and these reaction conditions, the following apparent kinetic mechanism for CO₂ and carbonate formations was proposed.

Carbon dioxide formation from alkaline oxidation of macromolecules of residual lignin and carbohydrate,



where C represents total carbon from residual lignin and carbohydrate; L* represent oxidatively degraded products; k₁ is rate constant.

During alkaline oxygen delignification, the final pH of the effluent is typically greater than 11. Therefore, any carbon dioxide produced from the oxidative reactions will instantly react with alkali in the liquid phase to form sodium carbonate as shown in Eq. 2, *i.e.* the rate of CO₂ consumption = the rate of CO₃²⁻ formation, k₂ >> k₁.



Chemical Kinetics

From Eqs. 1-2, the kinetic equation of carbonate formation can be derived as Eq. 3.

$$\frac{d[CO_3^{2-}]}{dt} = k_1 [C]^a P^b N^c \quad (3)$$

where k_1 is rate constant ($k_1 = f(1/T)$, g. L⁻¹.min⁻¹.MPa^{-b}), P is oxygen pressure (MPa); N is caustic charge (% on pulp); a , b , and c are the powers of each parameter.

During typical oxygen delignification, oxygen pressure and reaction temperature are kept constant. Therefore, Eq. 3 can be simplified as Eq.3a with Eq.4.

$$\frac{d[CO_3^{2-}]}{dt} = k_2' [C]^a \quad (3a)$$

$$k_2' = k^0 \cdot P^b \cdot N^c \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where k^0 is constant; E is activation energy (J/mol)

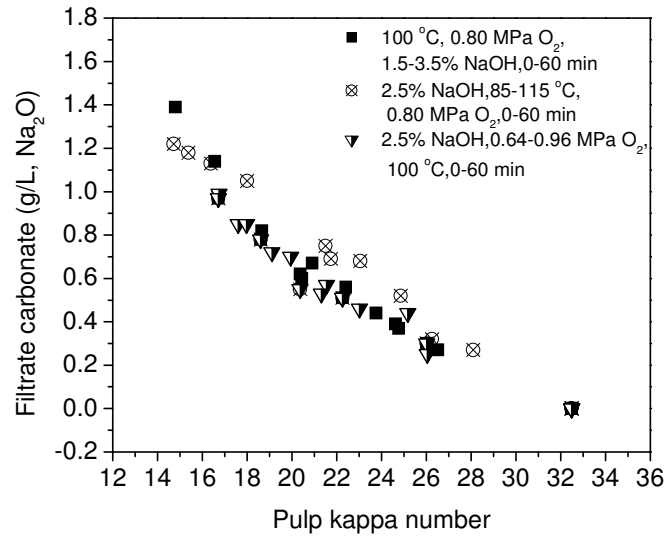


Figure M.4. A Relationship between Filtrate Carbonate Content and Pulp Kappa Number during Oxygen Delignification of a SW Kraft Pulp.

To integrate Eq. 3a, it must to define a relationship between carbonate concentration and initial total carbon concentration, which is not available. However, the experimental data in Figure M.4 demonstrates that there exist a relationship between filtrate carbonate concentration and pulp kappa number (K) in the form of Eq.5:

$$[\text{CO}_3^{2-}] = -A \ln (K) + B \quad (5)$$

where A and B are constants.

The estimates for A and B in Eq. 5 were estimated using SAS LIN procedure as shown in Table M-3.

Table M-3. The Estimate, Standard Error, and p-Value of the Parameters in Eq.5
($R^2 = 0.9586$)

Parameter	Estimate	Standard Error	p-value
A	-1.5201	0.04268	< 0.0001
B	5.2890	0.1323	< 0.0001

Since both carbonate formation and pulp kappa number reduction are the function of delignification time, for derivatives of both sides of Eq. 5 over time t, we obtained Eq. 6.

$$\frac{d[\text{CO}_3^{2-}]}{dt} = -\frac{A}{K} \frac{dK}{dt} \quad (6)$$

Using the relationship of lignin content (L) and pulp kappa number, *i.e.* $[L] = 0.13 * K$ [258], a derivative Eq. 7 was obtained.

$$\frac{dK}{dt} = \frac{1}{0.13} \frac{d[L]}{dt} \quad (7)$$

$$\text{Therefore, } \frac{d[CO_3^{2-}]}{dt} = -\frac{A}{K} \frac{dK}{dt} = -\frac{A}{0.13K} \frac{d[L]}{dt} = -\frac{A}{[L]} \frac{d[L]}{dt} \quad (8)$$

Typically, the rate of oxygen delignification can be expressed as Eq. 9 with $k_L = k_0 \exp(-\frac{E_L}{RT})$ [263].

$$\frac{d[L]}{dt} = -k_L \cdot P^m \cdot N^n [L]^q \quad (9)$$

Simplify Eq. 9 to obtain Eq. 10 with $k_L' = k_L^0 \cdot P^m \cdot N^n \cdot \exp(-\frac{E_L}{RT})$

$$\frac{d[L]}{dt} = -k_L' [L]^q \quad (10)$$

Since oxygen delignification is not first order reaction to lignin [260, 263], therefore $q \neq 1$ in Eq. 10. At $t = 0$ min, $[L] = [L]_0$, integrate Eq. 10 and applied the initial condition to get Eq. 11.

$$[L]^{q-1} = \frac{[L]_0^{q-1}}{(1 + (q-1)[L]_0^{q-1} k_L' t)} \quad (11)$$

Combine Eq. 8 and 10 to obtain Eq. 12.

$$\frac{d[CO_3^{2-}]}{dt} = \frac{A k_L'}{[L]} [L]^q = A k_L' [L]^{q-1} \quad (12)$$

Compared Eq. 12 with Eq. Eq.3a, both equations has the same format. Therefore, it is safe to define $[C]^a = f([L]^{q-1})$. And we can use Eq. 12 to develop the kinetic model for filtrate carbonate formation.

Substitute Eq. 11 into Eq. 12 to get Eq. 13.

$$\frac{d[CO_3^{2-}]}{dt} = \frac{Ak_L'[L]_0^{q-1}}{1 + (q-1)[L]_0^{q-1}k_L't} \quad (13)$$

$$\text{Integrate Eq. 13, } [CO_3^{2-}] = \frac{Ak_L'[L]_0^{q-1}}{(q-1)[L]_0^{q-1}k_L'} \ln(1 + (q-1)[L]_0^{q-1}k_L't) + c1$$

$$\text{Simplify, } [CO_3^{2-}] = \frac{A}{(q-1)} \ln(1 + (q-1)[L]_0^{q-1}k_L't) + c1 \quad (14)$$

Apply initial condition (t=0 min, $[CO_3^{2-}] = 0$) to Eq. 14, c1=0. Therefore, Eq. 14 ended up to Eq. 15 with Eq. 16.

$$[CO_3^{2-}] = \frac{A}{(q-1)} \ln(1 + (q-1)[L]_0^{q-1}k_L't) \quad (15)$$

$$k_L' = k_L^0 \cdot P^m \cdot N^n \exp\left(-\frac{E_L}{RT}\right) \quad (16)$$

Therefore, Eq. 15 with Eq. 16 is a general kinetic model developed for carbonate formation in the effluent of one stage oxygen delignification of a SW kraft pulp.

To use this model for filtrate carbonate prediction, the variables in Eqs. 15-16 need to be estimated. For a fixed $[L]_0$, $(q-1)[L]_0^{q-1}k_L^0$ is constant. Let's denote it as parameter β , and denote $\frac{A}{q-1}$ as α , then Eq. 15 is simplified as

$$[CO_3^{2-}] = \alpha \ln[1 + \beta \cdot P^m \cdot N^n \cdot \exp\left(-\frac{E_L}{RT}\right)t] \quad (17)$$

Using the experimental data and $[L]_0 = 0.13 \times 32.5$, the least square estimates of the parameters in Eq. 17 were estimated using SAS NLIN procedure as shown in Table M-4.

Table M-4. The Estimate, Standard Error, and p-Value of the Parameters in Eq. 17 ($R^2 = 0.9785$)

Parameter	Estimate	Standard Error	<i>p</i> -value
α	0.7977	0.0807	< 0.0001
β	4411.3	5596.2	0.4341
m	0.7986	0.2216	0.0007
n	1.4259	0.1260	< 0.0001
E_L/R	4736.929	443.8	< 0.0001

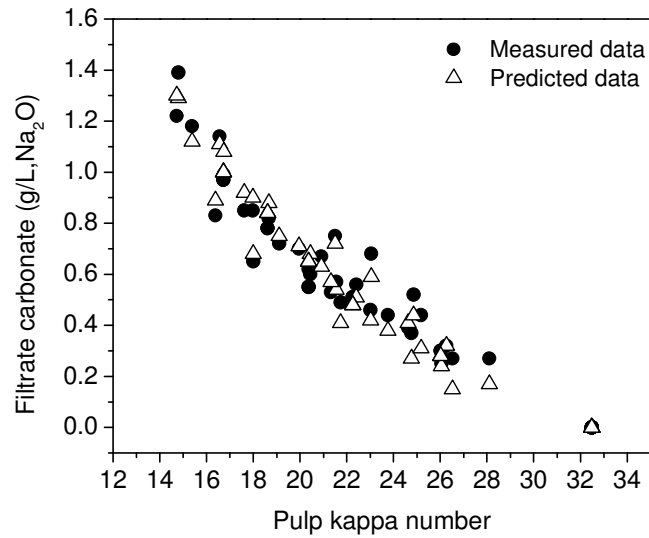


Figure M.5. Measured and Model Predicted Carbonate Content in the Effluent of One-Stage Oxygen Delignified SW Kraft Pulps

Figure M.5 shows the plots of both model predicted carbonate content and measured carbonate content in the effluent of one-stage oxygen delignified SW kraft pulps under the same reaction conditions studied. The predicted data fits the measured data very well (Figure M.5).

To test whether there is systematic error between the measured carbonate (y) and predicted carbonate (\hat{y}) from Eq.17, we can assume $\hat{y} = a + by$ and test the hypothesis that $a = 0$ and $b = 1$ using Statistic F . When $n = 54$, $\hat{y} = -0.0079 + 1.00219y$ with $R^2 = 0.9793$. $F = 0.3654$, its p-value = 0.6956, which is greater than 0.05, implying the predicted carbonate agrees closely with measured carbonate. Therefore, the developed model is valid and can be used for the prediction of carbonate concentration in the effluent of one-stage oxygen delignification of a SW kraft pulp under the experimental conditions studied.

It must point out that the coefficients and constants obtained in Table 4 were obtained from the experimental data for one stage oxygen delignification of a U.S. southern pine kraft pulp (kappa number of 32.5) at 10% pulp consistency. However, the model in Eq. 17 was derived in terms of the fundamental concepts with necessary assumptions, which can be used for other SW species. When it applies to a different species or different pulp consistency, the coefficients and constants in Eq.17 will change and need to be adjusted according to experimental data.

Model Applications: Pulp Kappa Number Prediction

During the oxygen delignification, the exposure of kraft pulp to caustic and oxygen at elevated temperature results in an oxidative depolymerization of lignin and the solubilization of oxidized lignin fragments. The rate of lignin removal varies as a function of process conditions, including: temperature, caustic charge, oxygen pressure, and reaction time. Meanwhile, the oxygen radical by-products, like hydroxyl radical, cause random cleavages of the cellulose chain, resulting in the degraded carbohydrate

products as side-reactions, which are also affected by the process conditions. The resultant effect of these process conditions can be represented by a lignin measurement parameter: pulp kappa number. Since hexenuronic acid in the pulp does not change during oxygen delignification [56, 264] and carbonate formation is a function of reaction parameters as shown in the developed model, a correlation between pulp kappa number and carbonate formation was anticipated. A relationship between pulp kappa number and filtrate carbonate concentration was readily developed from experimental data, as shown in Fig. M. 4 and Eq.5. Therefore, pulp kappa numbers, under different oxygen delignification conditions, can be predicted via the models described in Eq. 17 and Eq. 5. Table M-5 presented the predicted kappa numbers for oxygen delignified pulps at 45 and 60 min as 12.7 and 11.2, respectively when oxygen delignifying the kraft SW pulp under the conditions of 3.5% NaOH and 115 °C with 0.80 MPa oxygen applied. The predicted pulp kappa numbers are approximately equal to 12.6 and 11.5 respectively from experimental measurement.

Table M-5. Pulp Kappa Number Prediction for Oxygen Delignified Pulps

Time (min)	NaOH (%)	Oxygen (MPa)	Temperature (°C)	Filtrate carbonate (g/L, Na ₂ O)		Pulp kappa number	
				Measured	Predicted	Measured	Predicted
45	3.5	0.80	115	1.56	1.42	12.6	12.7
60	3.5	0.80	115	1.68	1.62	11.5	11.2

Model Applications- Process Control Strategy

From Figures M.4-5, a transition region was observed at the kappa number of 18.0-20.0, corresponding to carbonate content of 0.6-0.85 g/L in the effluent of one-stage of oxygen delignification. Beyond this region, lignin removal leads to enhance carbonate

formation, which significantly increases the inorganic compound load in the effluent. A similar transition region was also found for pulp viscosity and total fiber charge as a function of pulp kappa number (Figures M.6-7). After the transition region, both pulp viscosity and fiber charge decreased significantly.

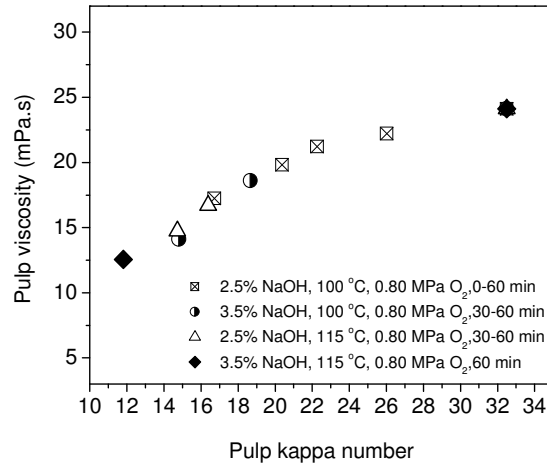


Figure M.6. The Relationship between Pulp Viscosity and Pulp Kappa Number for One-Stage Oxygen Delignified SW Kraft Pulps

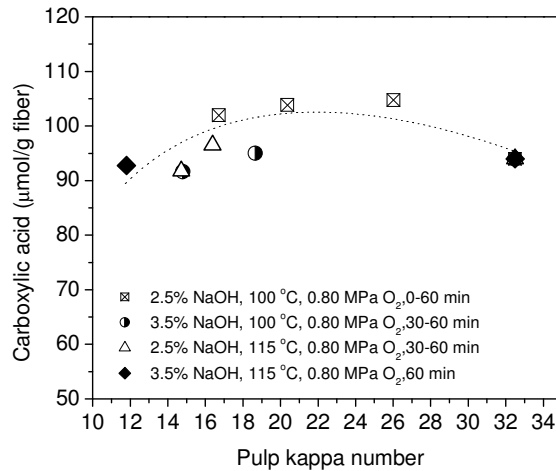


Figure M.7. The Relationship between Total Fiber Charge and Pulp Kappa Number for One-Stage Oxygen Delignified SW Kraft Pulps

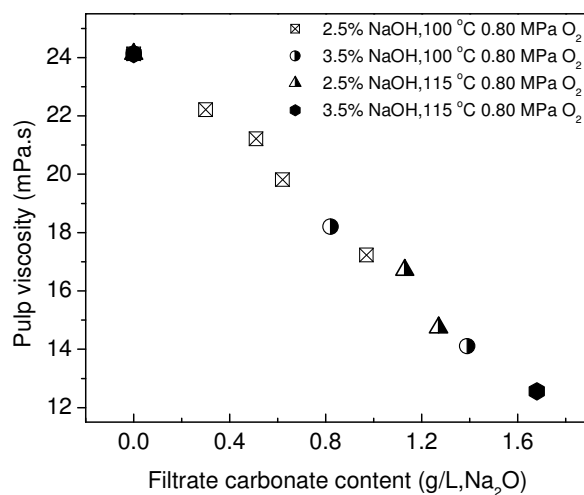


Figure M.8. The Relationship between Pulp Viscosity and Carbonate Content in the Effluent of One-Stage Oxygen Delignified SW Kraft Pulp

10% pulp consistency

When plotting pulp viscosity versus filtrate carbonate content, an inversely linear relationship was obtained for these two parameters (Figure M.8), suggesting that products of depolymerization are likely leading to the formation of carbonate.

Based on these results, to retain better pulp viscosity and total fiber charge with less carbonate formation, one-stage oxygen deignification treatment for a SW kraft pulp should not be delignified to a point of a pulp kappa number below 17.0 (48.0% delignification) for the pulp studied.

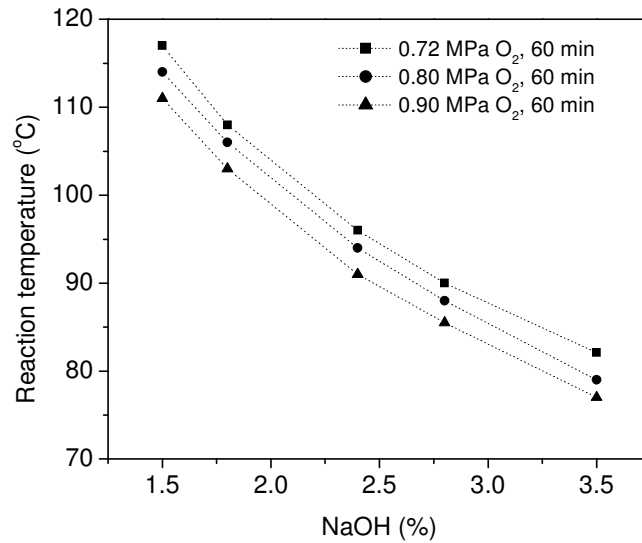


Figure M.9. Constant Kappa Number (18.5) Curves at Different Combinations of Reaction Temperature, Caustic Charge, and Oxygen Pressure

10% pulp consistency and 60 min delignification time

For control purposes, process parameters should be adjusted to achieve this target kappa number. Among oxygen delignification conditions, 60 min is usually chosen to allow enough time for better mixing and reaction. Medium pulp consistency (8.0-15.0%) is used for economic and operating consideration. For oxygen delignification reactions at 10% pulp consistency for 60 min, constant kappa number (18.5) at three different oxygen pressure levels (0.72, 0.80, and 0.90 MPa) were obtained from Eq. 5 and Eq. 17 by changing reaction temperature and caustic charge. These results are presented in Figure M.9. Any point on the curves represents a set of process parameter combination to achieve the same targeting pulp kappa number (18.5) at 10% pulp consistency for 60 min reaction.

Therefore, to select appropriate oxygen delignification conditions, the reaction temperature, oxygen pressure, and caustic charge can be adjusted to address specific operation requirements.

Conclusions and Significance

A new approach to quantitative modeling of carbonate formation in the effluent of one-stage oxygen delignification for a SW kraft pulp was developed and tested. The model was developed by assuming that the oxidation of carbon in the residual lignin and carbohydrate was the major pathways for carbon dioxide/carbonate formation.

This model predicts the dynamic change of carbonate content in the effluent of one-stage oxygen delignification from a SW kraft pulp and describes the kinetic characteristics of delignification when correlating with pulp kappa number, a parameter to represent pulp lignin content. The good linear correlation between the model predictions and 54 independent experimental results from statistic testing supports the essential validity of the modeling concepts and provided strong incentives for application. With this model, pulp kappa number in the solid phase (fiber) can be predicted from the behavior of liquid phase (carbonate formation in the effluent).

Furthermore, this model could be used to develop a process control parameter program to achieve the target delignification for a SW kraft pulp with desirable pulp viscosity and total fiber charge property.

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