

**The Investigation of Carboxyl Groups of Pulp Fibers during Kraft  
Pulping, Alkaline Peroxide Bleaching, and TEMPO-mediated Oxidation**

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Zheng Dang

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**The Investigation of Carboxyl Groups of Pulp Fibers during Kraft  
Pulping, Alkaline Peroxide Bleaching, and TEMPO-mediated Oxidation**

Approved by:

Dr. Arthur J. Ragauskas  
Advisor  
School of Chemistry and Biochemistry  
*Georgia Institute of Technology*

Dr. Jeffery S. Hsieh,  
Co-Advisor  
School of Chemical and Biomolecular  
Engineering  
*Georgia Institute of Technology*

Dr. Yulin Deng  
School of Chemical and Biomolecular  
Engineering  
*Georgia Institute of Technology*

Dr. John D. Muzzy  
School of Chemical and Biomolecular  
Engineering  
*Georgia Institute of Technology*

Dr. Preet M. Singh  
School of Materials Science and  
Engineering  
*Georgia Institute of Technology*

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## NOMENCLATURE

4OMeGlocA	4OMeGlocA=4- <i>O</i> -methylglucuronic acid
AFM	Atomic force microscopy
AmI	Amorphicity index
AQ	Anthraquinone
Ara	Arabinose
ca.	Circa: about, approximately
CCOA	Carbazole-9-carbonyloxyamine
CEL	Cellulolytic enzyme lignin
CK	Conventional cooking
CMC	Carboxymethyl cellulose
CrI	Crystallinity index
CSF	Canadian standard freeness
CTMP	Chemi-thermomechanical pulp
D	Chlorine dioxide
DP	Degree of polymerization
E	Alkaline extraction
E+O/Eo	Alkaline extraction reinforced with oxygen
EA	Effective alkali
ECF	Elementally chlorine-free
EMAL	Enzymatic mild acidolysis lignin
FQA	Fiber quality analyzer
Gal	Galactose
GalA	Galacturonic acid
GaTech	Georgia Institute of Technology
GCC	Ground calcium carbonate
GL	Green-liquor
GlcA	Glucuronic acid
Glu	Glucose

GWP	Ground wood pulp
HexA	Hexeneuronic acids
HPAEC-PAD	High performance anion-exchange chromatography with pulsed amperometric detection
HW	Hardwood
IPST	Institute of Paper Science and Technology
KP	Kraft pulp
LCC	Lower cooking circulation
Lo-Solids	Low solids
MALSI-MS	Matrix-assisted laser desorption ionization time-of-flight mass spectrometry
Man	Mannose
MeGlcA	4- <i>O</i> -methyl glucuronic acid
MeIdoA	4- <i>O</i> -methylduronic acid
MWL	Milled wood lignin
[ $\eta$ ]	Intrinsic viscosity
NMR	Nuclear magnetic resonance
NOBS	Nonanoyloxybenzene sulphonate
o.d.	Oven dried
P	Peroxide stage
PAE	polyamide-amine epichlorohydrin resin
PGW	Pressurized groundwood
PFI	Paper and Fibre Research Institute
PO	Hydrogen peroxide together with pressurized oxygen
PVSK	Potassium poly(vinyl sulfate)
Q	Chelation stage
SEC	Size exclusion chromatography
SEM-EDS	Scanning electron microscopy-energy dispersive spectrometry
SW	Softwood
TAED	Tetra-acetylenediamine
TAPPI/Tappi	Technical association of the pulp and paper industry



TCF	Totally chlorine-free
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy radical
TMP	Thermomechanical pulp
WC	Wash circulation
WRV	Water retention value
WSC	Water soluble carboiimide
Xyl	Xylose
Z	Ozone stage

## SUMMARY

Over the past 10 years, growing concerns over the modification of fibers have led researchers to focus on enriching the carboxyl group content of fibers by chemical oxidation and topochemical grafting. The current series of experiments continues this line of research by investigating the carboxyl group content of fibers during kraft pulping, alkaline peroxide bleaching, and 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO)-KBr-NaClO oxidation system.

The first experiment characterizes changes in the carboxyl group content of fibers for two sets of kraft pulps: 1) conventional laboratory cooked loblolly pine kraft pulps, and 2) conventional pulping (CK) versus Lo-Solids pulping (LS) pulps. The results indicate that effective alkali (EA), temperature, and H-factor are the primary factors controlling fiber charge during kraft pulping. This result is supported by the following findings. When pulping to the same H-factor, low EA charge and low pulping temperature were favorable for increasing bulk carboxylic acid group content of fibers. Sulfidity did not have an obvious effect on bulk or surface carboxylic acid group content of fibers. Bulk fiber charge had a linear relationship with water retention value. Another set of kraft pulps distinguished by conventional pulping and Lo-Solids pulping were investigated to determine the effect of H-factor and pulping protocol on fiber charge. When bulk fiber charge was plotted against kappa number, pulps from Lo-Solids pulping had a higher slope value than the conventional pulping pulps. The charge on holocellulose fibers approaches a constant value as pulping advances for both types of pulping processes.

The second experiment examines the influence of alkaline peroxide treatment on elementally chlorine-free (ECF) bleached softwood kraft pulp. Alkaline peroxide treatment on fully bleached pulp was carried out because it is known that peroxide can increase fiber charge, but there's no detailed study explored on it. The results indicate that fiber charge increases with the increase of peroxide charge. These increases were demonstrated in the following way: a maximum fiber charge increment of 16.6% was obtained with 8.0% more peroxide charge on oven dried (o.d.) pulp at 60.0°C. Copper number decreased when peroxide charges were 0.5% and 1.0% at 60.0°C and 90.0°C treatments, respectively, and then increased with the increment of peroxide charge. Both fiber charge and copper number approached constant values when a 4.0% or higher peroxide charge was applied. Fiber charge and copper number were compared after the peroxide treatment of ECF bleached kraft pulp versus sodium borohydride reduced ECF bleached kraft pulp. The results indicate that carbonyl group content of fibers is favorable for improving fiber charge after peroxide treatment. The effect of increased fiber charge on refining, cationic starch adsorption, and hornification was examined. Two pulps were investigated: (1) an ECF bleached softwood kraft pulp served as control and (2) the control pulp treated with alkaline peroxide which had a higher fiber charge. It was shown that the increased fiber charge can improve the efficiency of the refining treatment as indicated by differences in tensile index when pulps were refined from 0 to 1000 revolutions. Upon the addition of 2% cationic starch to both pulps, the tensile index of the control pulp increased by 13.7% and that of high fiber charge pulp by 23.7%. Enhanced fiber charge was beneficial for reducing hornification when pulp was dried at 105°C.

The final experiment investigates the effect of TEMPO-mediated oxidation of an ECF bleached softwood kraft pulp on carboxyl group content, carbonyl group contents, degree of polymerization, and water retention value of fibers. The results show that TEMPO-mediated oxidation is useful in enriching the carboxyl and carbonyl groups to fibers, as well as enhancing the property of water adsorption of fibers. This result is supported by the findings that the carboxyl group content of the fibers was improved with increasing NaClO charge whereas, the carbonyl group content of fibers approached a maximum when a charge of 0.85 mmol NaClO/g o.d. fibers or higher was employed. The degree of polymerization of fibers drastically decreased from 2416 to 688 depending on the NaClO charge during the TEMPO-mediated oxidation. Oxidized fibers were shown to exhibit 62.9% higher water retention values (WRV) than the original fibers. Due to the enhanced carboxyl group content after oxidation, a measurement of the physical strength of the paper revealed that the tensile index of the oxidized fibers was 13.8% greater than that of the original fibers. The individual fiber strength of the oxidized fibers was lower than that of the original fibers as determined by a zero-span strength measurement showing a 17.0% decrease.

These findings suggest that: (1) kraft pulping process can be modified to obtain the target carboxyl group content, (2) terminal peroxide bleaching provides higher fiber charge which can save energy and chemical charge of subsequent refining and wet-end processes, respectively, as well as reduce hornification during drying, (3) TEMPO-mediated oxidation of fibers is capable of improving the properties of fibers, including fiber charge and water adsorption, and enhancing final paper strength.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

The chemical properties of fibers are of great importance to the behavior of fibers during pulping and papermaking processes, as well as for final paper products. Wood pulp fibers carry a charge when suspended in water due to the presence of acidic groups in cellulose, hemicelluloses, and lignin. The acidic functional groups associated with wood consist of (i) carboxylic acid groups with an approximate  $pK_a$  value of 4.5; (ii) phenolic hydroxyl groups with an approximate  $pK_a$  of 10.2; and (iii) weakly acidic hydroxyl groups present in polysaccharides with a  $pK_a$  of roughly 13.7.[1] With the exception of pulps that contain significant levels of sulfonate groups, carboxylic acid groups are the only functional groups that give rise to the generation of charged sites on the fibers under typical papermaking conditions.

Carboxyl groups of fibers can be controlled and introduced by the kraft pulping process and through bleaching processes, including oxygen delignification, ozone bleaching, and peroxide bleaching.

The fiber charge of the kraft pulp, which is generated by the dissociation of the carboxyl group of fibers, is an important parameter to be considered during papermaking because many of the interactions between soluble and particulate fractions of papermaking furnishes are charge induced.[2, 3] The carboxyl groups of pulp fibers are

reported to be the primary retention sites of various wet-end additives in pulp suspensions. Therefore, the performance of retention aids, sizes, wet and dry strength resins, fillers etc., are influenced by the charge of fibers.[2-5] Also, the fiber charge strongly influences the swelling of wet fibers, fiber flexibility, fiber–fiber bonding, and refinability.[6-10] In short, the fiber charge not only determines the consumption of cationic additives used in papermaking, but is also very important for both fiber swelling and the interaction between the fibers during consolidation of the fibers in the dryer of the paper machine.

The main objective in kraft pulping is liberation of wood fibers and delignification. Delignification in the kraft pulping process occurs mainly through fragmentation and creation of phenolates into the lignin fragments and the residual lignin. During the kraft pulping of wood, a significant proportion of the initial 4-O-methylglucuronic acid side groups (MeGlcA) of xylan are converted to hexeneuronic acids (HexA) which can contribute to the fiber charge of kraft brownstock.[11, 12] Pulping conditions and green liquor pretreatment, prior to pulping, strongly affect the formation and stability of HexA.[13-15] Alkaline pulping also results in the formation of new polysaccharide carboxyl groups, generated from the peeling reaction which is stopped by the formation of metasaccharinic acid or other alkali-stable carboxyl groups.[16] The residual lignin in kraft pulps is known to contain carboxylic acid groups.[17, 18]

The bleaching of kraft pulps is directed at lignin decolorization and the removal of residual lignin.[19] The oxidants commonly used for kraft pulp bleaching include chlorine, chlorine dioxide, oxygen, ozone, and hydrogen peroxide. Peroxides are important bleaching reagents for cellulosic products. In 1993, the consumption of

hydrogen peroxide in North America was 530 million pounds by the pulp and paper industry and 60 million pounds by the textiles industry.[20] Hydrogen peroxide in particular is a potent, relatively inexpensive oxidant that chemically degrades chromophoric components in pulps and textiles. It is known that  $H_2O_2$  bleaching can introduce carboxylic acid groups by oxidizing cellulose, hemicelluloses, and also residual lignin of fibers.[21, 22]

Recently, a novel method for the catalytic oxidation of polysaccharides by a water-soluble nitroxyl radical, 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), has been reported to be an effective reagent to convert C-6 primary hydroxyl groups to carboxylates via a reactive aldehyde-intermediate.[23-32]

## **1.2 Objectives**

In spite of the practical importance of carboxyl group formation of pulp fibers during kraft pulping, few studies[13-15] have fully explored the effects of pulping processes. In fact, no study compares conventional kraft pulping to modern kraft pulping in terms of the carboxyl groups present in kraft pulp. Many studies that examined the effects of peroxide bleaching on carboxyl groups of pulp fibers were focused on mechanical pulp; therefore, not enough information is known about the effects of the alkaline peroxide treatment on fully bleached pulp fibers. The purpose of fiber modifications by novel methods, e.g., TEMPO-mediated oxidation and periodate, is to enrich functional groups of fibers, including the carboxyl and carbonyl groups of fibers.

The first goal of this study is to determine how fiber charge is influenced by varying kraft pulping conditions and two kraft pulping protocols: conventional kraft pulping and Lo-Solids continuous kraft pulping. These two protocols are also compared in terms of their impact on fiber charge. The second goal of this research is to understand the formation of carboxyl groups and carbonyl groups during the alkaline peroxide treatment of fully bleached softwood kraft pulp. Also, the influences of the enhanced fiber charge on wet-end chemical retention, refining, and hornification are examined. The third goal is to characterize the TEMPO-mediated oxidation of fully bleached softwood kraft pulp.

This study could lead to:

- (1) A better understanding of kraft pulping process for optimization of the modern kraft pulping process,
- (2) A practical technology of terminal peroxide bleaching which can benefit the final paper making process, and
- (3) A promising method to increase the carboxyl group content of fibers by TEMPO-mediated oxidation, which can not only be applied to paper manufacturing, but also provide valuable information with regard to cellulose chemistry.

### **1.3 Dissertation structure**

Chapter 1 of this dissertation briefly introduces the study and its objectives. Chapter 2 summarizes the basic knowledge and literature related to this research. The



experimental methods are described in Chapter 3. Chapter 4 details the results of the influence of kraft pulping on the carboxyl group content of softwood (SW) kraft pulps. The physico-chemical properties of elementally chlorine-free (ECF) bleached softwood kraft pulps treated by alkaline peroxide are investigated in Chapter 5. A novel chemical modification, TEMPO-mediated oxidation, on ECF bleached SW kraft pulp is discussed in Chapter 6. Lastly, Chapter 7 outlines the overall conclusions of this research and recommendations for future work.

## CHAPTER 2

### BACKGROUND LITERATURE

#### 2.1 The composition of wood fibers

A wood fiber is a complex of natural substances including cellulose, hemicelluloses, lignin, and extractives. Generally, the first three components have high molecular weights and contribute a lot of mass (see Table 2.1), while the latter component is of small molecular size. These polymer substances are not uniformly distributed within the wood cell wall and their concentrations change from one morphological region to another.[33]

Table 2.1. Typical composition (wt., % of dry material) of softwoods, hardwoods, and wheat straw.[34]

Components	Softwoods	Hardwoods	Wheat straw
Cellulose	42±2	45±2	36±5
Hemicelluloses	27±2	30±5	27±3
Lignin	28±3	20±4	11±3
Extractives	3±2	5±3	26±5

##### 2.1.1 Cellulose

Cellulose is a carbohydrate, meaning that it is composed of carbon, hydrogen, and oxygen. Cellulose is a straight-chain, unbranched, hydrophilic polysaccharide composed of repeating  $\beta$ -D-glucopyranose monomer units which are linked together by (1-4)-

glycosidic bonds (Figure 2.1). Note that  $\beta$ -D-glucopyranose chain units are in chair conformation ( ${}^4C_1$ ) and substituents HO-2, HO-3, and CH<sub>2</sub>OH are oriented equatorially.[35] Every other chain unit is rotated 180° around the main axis of the chain, which shows that the actual repeating unit of cellulose is cellobiose.[35] The length of the cellobiose unit is 1.03 nm.[36]

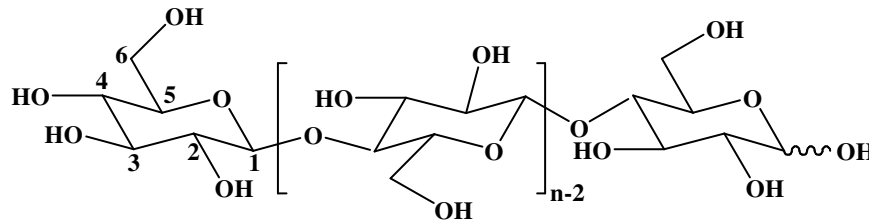


Figure 2.1. Structure of cellulose.[37]

The chemical formula for cellulose is  $(C_6H_{10}O_6)_n$ , where  $n$  is the number of repeating sugar units or the degree of polymerization (DP). The value of  $n$  varies with the different sources of cellulose and the treatment received.[38] The degree of polymerization (DP) is defined in Equation 2.1. The DP of cellulose in wood is approximately 10,000, while it is around 2,000 for commercial wood pulp.[39]

$$DP = \frac{\text{Molecular Weight of Cellulose}}{\text{Molecular Weight of One Glucose Unit}} \quad (2.1)$$

Table 2.2 outlines the DP of cellulose of various pulps.

Table 2.2. Degree of polymerization of cellulose of various pulps.

Pulp I.D.	DP of cellulose
Softwood[40]	
Semi-bleached kraft pulp	3600
Bleached kraft pulp	2900
Hardwood[40]	
Semi-bleached kraft pulp	3600
Bleached kraft pulp	2400
Commercial cellulose (acid-washed)[40]	1180
White spruce ( <i>Picea glauca</i> )[41]	
Kraft pulp (kappa # = 40)	2295
Sulfite pulp (kappa # = 40)	1677
Fully bleached kraft pulp from pine ( <i>Pinus taeda</i> )[42]	1597
Commercial bleached pulps[43]	
Hardwood kraft ECF	1208
Mixed hardwood kraft ECF	845
Birch kraft TCF	974
Eucalyptus kraft ECF	978
Pine kraft TCF	672
Birch kraft ECF	997
ECF* bleached SW (white spruce) kraft pulps[44]	1360
Kraft	1950
2% PS**	2000
5% PS	1900
10% PS	
O-ECF*** bleached SW kraft pulps	1250
Kraft	1630
2% PS	1420
5% PS	1500
10% PS	

\* D<sub>0</sub>EDD \*\* Polysulphide

\*\*\* OD<sub>0</sub>EDD

Cellulose has a strong tendency to form intra- and intermolecular hydrogen bonds, which stiffen the straight chain and promote aggregation, forming a crystalline structure.[36] Bundles of cellulose molecules are aggregated together in the form of microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions (See Figure 2.2).[35, 38] Microfibrils build up and form fibrils

which form cellulose fibers. As a consequence of its fibrous structure and strong hydrogen bonds cellulose has high tensile strength and is insoluble in most solvents.[38]

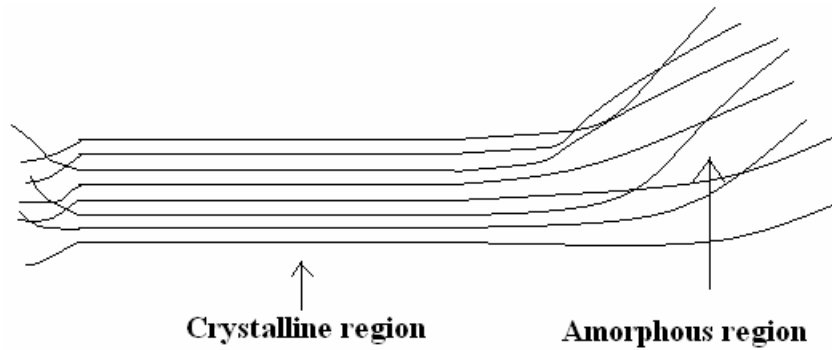


Figure 2.2. Schematic of molecular organization within a cellulose microfibril.[38]

The crystalline region of cellulose in wood and ECF bleached pulps accounts for 65%[45] and 40-50% of the biomass structure, respectively[46]. Lennholm and her co-workers[47] studied the crystallinity of cellulose materials by  $^{13}\text{C}$ -CP/MAS NMR. The results are shown in Table 2.3. It is evident that that the crystalline region in wood pulp can be increased by bleaching.

Table 2.3. The crystallinity index (CrI) and amorphicity index (AmI) values of cellulose in different cellulose materials.[47]

Lignocellulosic samples	CrI	AmI
Cotton	0.66	0.34
Oxygen delignified hardwood pulp	0.44	0.56
Fully bleached hardwood kraft pulp	0.43	0.57
Fully bleached softwood kraft pulp	0.52	0.48
Unbleached softwood kraft pulp	0.52	0.48
Aspen CTMP	0.47	0.53
Spruce CTMP	0.45	0.55
Unbleached GWP	0.44	0.56
Bleached GWP	0.45	0.55
TMP	0.49	0.51
Bleached spruce sulfite pulp	0.53	0.47

### 2.1.2 Hemicelluloses

Hemicelluloses differ substantially from cellulose, although both are polysaccharides of similar molecular chain structure. Cellulose is a homopolysaccharide, while hemicelluloses are heteropolysaccharides. The composition and structure of the hemicelluloses in softwoods differ in a characteristic way from those in the hardwoods. Hemicelluloses promote fiber's internal lubrication, leading to improved flexibility. During pulp drying, they tend to stiffen fiber.[48] Table 2.4 summarizes the DP and percentage of the major hemicelluloses in softwoods and hardwoods.

Table 2.4. The DP and percentage of the major hemicelluloses in softwoods and hardwoods.

Hemicellulose type		Degree of polymerization (DP)	Percentage in wood
Softwoods[45]	Galactoglucomannans	100	11-25%
	Arabinoglucuronoxylan	100	7-10%
Hardwoods[45]	Glucuronoxylan[49]	133	n/a
	Glucuronoxylan	200	15-30%
	Glucocomannan	200	2-5%
Hardwoods[50]	Glucuronoxylan		
<i>E.* globulus</i>		200	-
<i>E.* urograndis</i>		200	-
<i>Betula pendula</i>		160	-

\* *Eucalyptus*

Jacobs and Dahlman[51] developed a detailed database of the molar mass of hemicelluloses from wood and pulps using size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALSI-MS). The woods they investigated were birch, aspen, spruce, pine and larch wood all from Sweden. The results of the carbohydrate content of holocellulose from the woods are documented in Table 2.5. Jacobs and Dahlman[51] also reported the DP of hemicelluloses in woods, presented here in Table 2.6.

Table 2.5. The carbohydrate content of holocellulose from various woods and pulps by Jacobs and Dahlman.[51]

Samples	Relative carbohydrate composition (mass %)						
	Glu	Xyl	Ara	Man	Gal	4OMeGlocA	GlcA
Birch	57.6	34.1	0.3	3.1	0.5	4.4	-
Aspen	70.4	23.3	0.0	3.6	0.3	2.4	-
Spruce	75.9	9.1	1.4	9.1	1.7	2.7	0.1
Pine	75.5	9.3	2.0	9.3	1.3	2.4	0.1
Larch	80.0	6.3	1.1	10.4	0.6	1.4	0.2

Glu=Glucose; Xyl=Xylose; Ara=Arabinose; Man=Mannose; Gal=Galactose; 4OMeGlocA=4-*O*-methylglucuronic acid; GlcA=Glucuronic acid

Table 2.6. Degree of polymerization of hemicelluloses extracted from softwoods and hardwoods by Jacobs and Dahlman.[51]

Wood	Type of hemicellulose	DP of hemicellulose
Birch	Glucuronoxylan	101-122
Spruce	Arabinoglucuronoxylan	107-145
Pine		
Larch		
	Galactoglucomannans	118-132

#### 2.1.2.1 Softwood hemicelluloses

Figures 2.3 and 2.4 present the two main hemicelluloses in softwood, galactoglucomannans and arabinoglucuronoxylan, respectively.



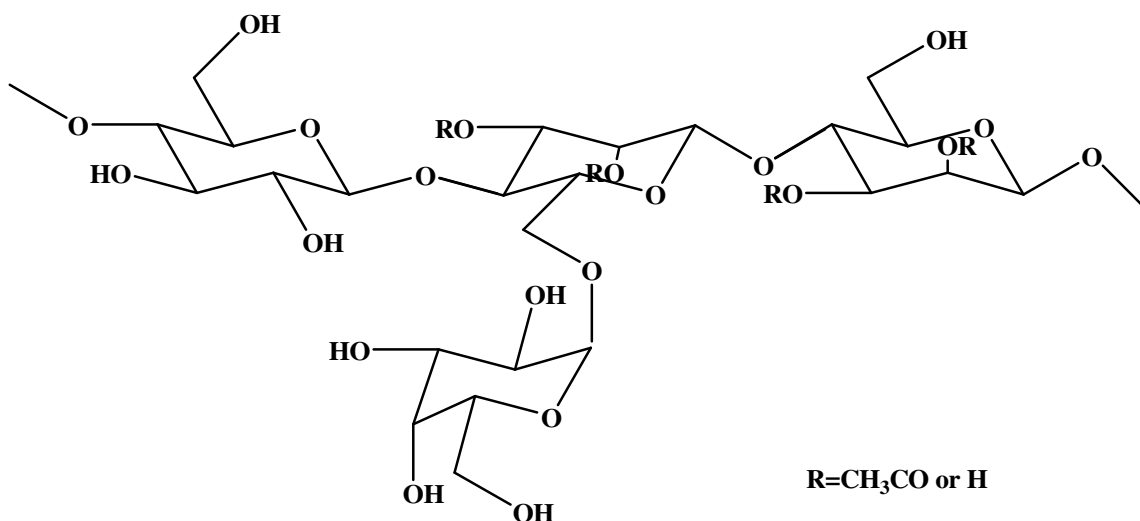


Figure 2.3. Principal structure of galactoglucomannans.[35]

Galactoglucomannans are the principal hemicelluloses in softwoods. Their backbone is a linear or possibly slightly branched chain which is built up of (1→4)-linked  $\beta$ -D-glucopyranose and  $\beta$ -D-mannopyranose units. The  $\alpha$ -D-galactopyranose residual is linked as a single-unit side chain to the framework by (1→6)-bonds.[35]

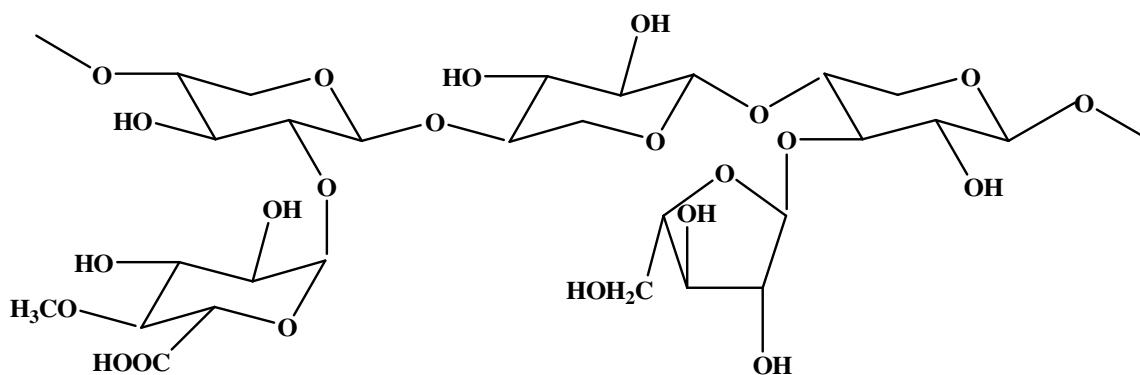


Figure 2.4. Principal structure of arabinoglucuronoxylan.[35]

Another major hemicellulose polymer in softwoods is an arabinoglucuronoxylan. It consists of a backbone of  $\beta$ -(1-4)-xylopyranose units with (1→2) branches of D-

glucopyranosyluronic acid and (1–3) branches of l-arabinofuranose.[52] Because of their furanosidic structure, the arabinose side chains are easily hydrolyzed by acids. Both the arabinose and uronic acid substituents stabilize the xylan chain against alkali-catalyzed degradation.[35]

#### 2.1.2.2 Hardwood hemicelluloses

The main hemicellulose in hardwood is glucuronoxylan. Xylans contain acidic groups, such as glucuronic acid, and have a molecular structure which is similar to that of cellulose when the xylans are stripped of their branches.[48]

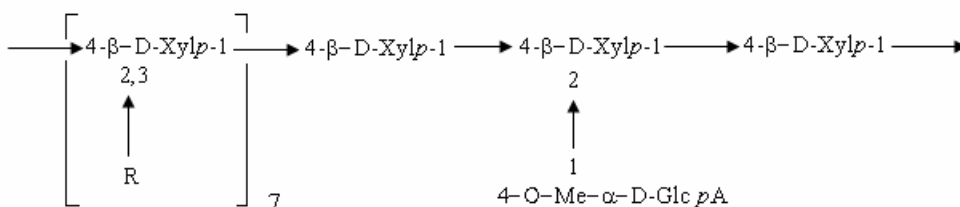


Figure 2.5. Abbreviated formula of glucuronoxylan.[35]

Xylp: xylopyranose; GlcpA: glucopyranosyluronic acid; R: Acetyl group (CH<sub>3</sub>CO).

The backbone which is linked by (1→4)-bonds consists of β-D-xylopyranose units (see Figure 2.5). Most of the xylose residues contain an O-acetyl group at C-2 or C-3 and there are about seven acetyl residues per ten xylose units. The xylose units in the xylan chain additionally carry (1→2)-linked 4-O-methyl-α-D- glucopyranosyluronic acid residues. Xylan chain consists of about one uronic per ten xylose residues.[35]

### **2.1.3 Distribution of the mono sugar content of woods and pulps**

Mono sugars found in woods and pulps include glucose, xylose, arabinose, mannose, and galactose. Currently, sugar content can be determined by high performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) analysis. Table 2.7 summarizes the sugar content of various woods and pulps. These samples include woods, mechanical pulp, unbleached kraft pulp, and bleached kraft pulp.

Table 2.7. The mono sugar content (on wood or pulp) of various woods and pulps.

Sample		Glucose (%)	Xylose (%)	Arabinose (%)	Mannose (%)	Galactose (%)
Wood	Pinewood ( <i>Pinus sylvestris</i> L.)[53]	49.1	5.7	1.2	12.9	1.7
	Loblolly pine ( <i>Pinus taeda</i> L.)[54]	43.1	7.6	1.6	11.2	1.8
	Top juvenile normal wood					
	Hardwoods[50]					
	<i>E. * globulus</i>	53.4	14.2	0.4	1.1	1.5
	<i>E. * urograndis</i>	52.1	11.4	0.4	0.7	1.2
	<i>Betula pendula</i>	44.5	23.6	0.7	2.1	0.8
Mechanical pulp	Yellow birch[55]	43.8	21.1	0.7	1.0	1.1
	Norway spruce ( <i>Picea abies</i> L.)[56]	46.9	4.4	1.2	10.4	5.3
Unbleached kraft pulp	Spruce PGW** pulp[57]	39.3	7.0	0.5	14.6	1.0
	Southern pine[58] (kappa # = 24.2)	84.9	7.1	0.5	7.2	0.3
	Hardwoods[50] (kappa # = 18.6)					
	<i>E. * globulus</i>	76.7	18.1	0.2	0.2	0.7
	<i>E. * urograndis</i>	82.0	13.9	0.2	0.2	0.2
Bleached kraft pulp	<i>Betula pendula</i>	73.1	23.4	0.2	0.6	0.0
	ECF*** SW[44]					
	Kraft	86.8	6.5	<0.5	6.3	<0.5
	2% PS****	84.9	5.9	<0.5	8.7	<0.5
	5% PS	82.2	4.6	<0.5	12.6	<0.5
	10% PS	80.1	5.6	<0.5	13.4	<0.5
	O-ECF***** SW					
	Kraft	87.1	5.9	<0.5	6.4	<0.5
	2% PS	85.3	5.6	<0.5	8.4	<0.5
	5% PS	83.6	4.2	<0.5	11.7	<0.5
	10% PS	82.2	4.5	<0.5	12.5	<0.5

\* *Eucalyptus*

\*\* Pressurized groundwood spruce pulp

\*\*\* D<sub>0</sub>EDD

\*\*\*\* Polysulphide

\*\*\*\*\* OD<sub>0</sub>EDD

#### 2.1.4 Lignin

Lignin is a complex aromatic polymer comprised of hydroxyphenylpropane units. It is an amorphous, crosslinked, three-dimensional phenolic polymer and is chemically bonded to the hemicelluloses. Lignin is much less hydrophilic than either cellulose or hemicellulose, almost to the point of being hydrophobic.[48]

Native lignin is a polymer comprised of coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol.[59] The general lignin precursors are shown in Figure 2.6.[19]

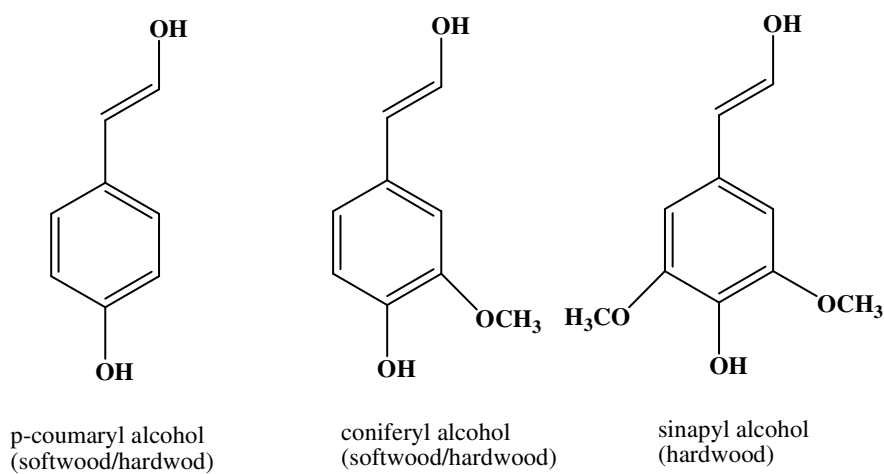


Figure 2.6. The structures of lignin precursors.[19]

The polymerization of these alcohols in the cell wall leads to a heterogeneous branched and cross-linked polymer in which the phenylpropane units are linked by C-C and C-O bonds. In addition, secondary reactions in the lignification process lead to the formation of benzyl alcohol and benzyl ether groups. Etherification of carbohydrates with benzyl alcohol groups leads to a cross-linking between lignin and polysaccharide chains. Figure 2.7 presents an example of a benzylic ether bond.[60]

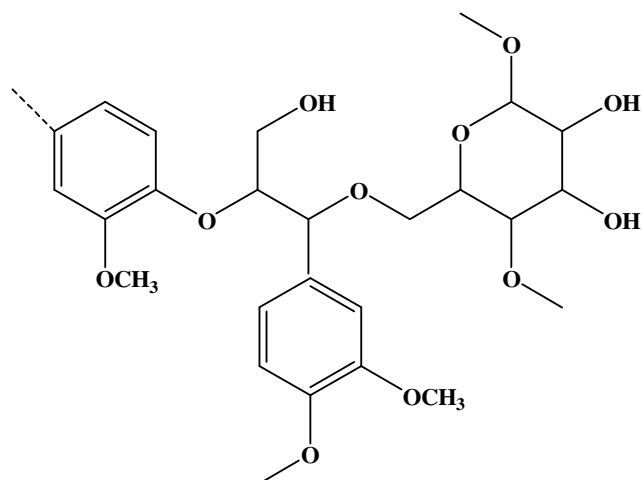


Figure 2.7. Chemical structure of a benzylic ether of the lignin-carbohydrate complex (LCC) type.[60]

The main linkages joining the phenylpropane units are depicted in Figure 2.8.[35]  
The exact structure of lignin is not clearly understood because of the random nature of linkages between the phenylpropane units.

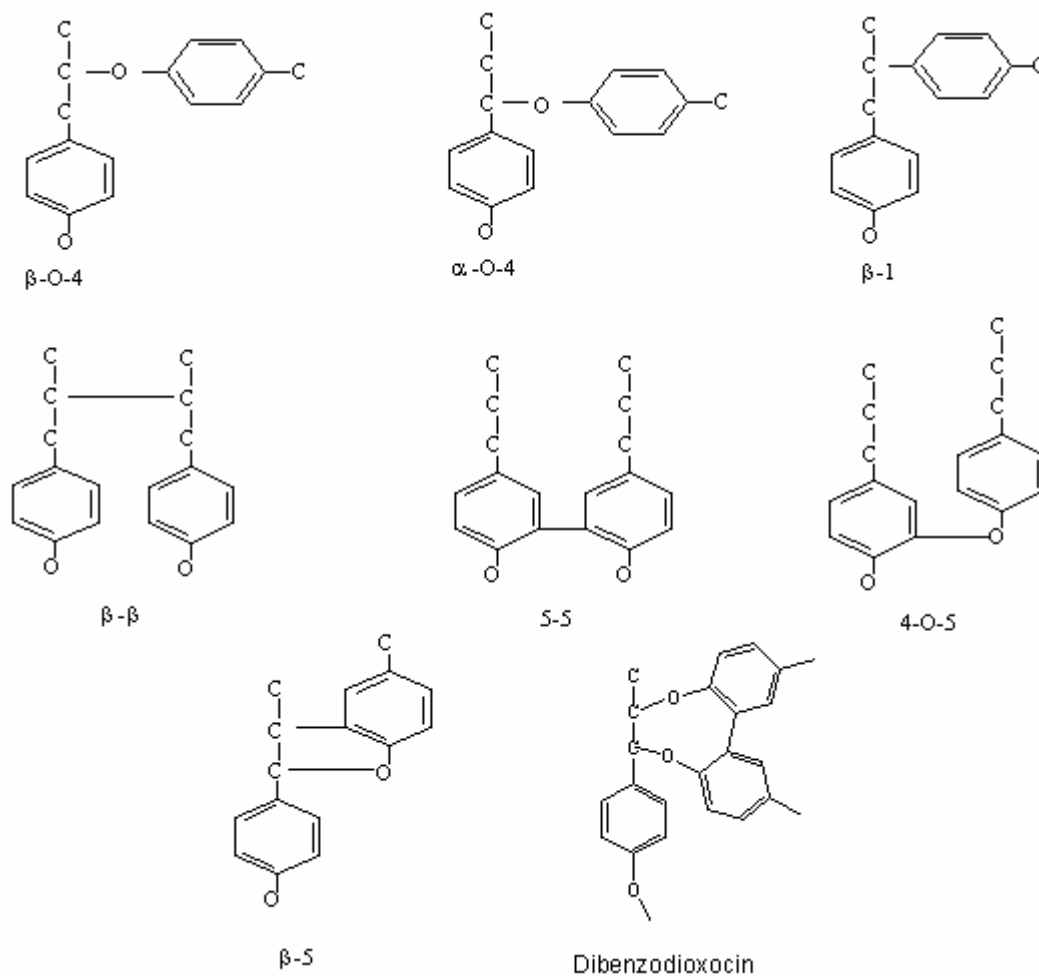


Figure 2.8. Inter-unit linkages in lignin.[35, 61, 62]

Lignin polymer in the wood is gradually degraded and dissolved during pulping and bleaching processes. Table 2.8 summarizes the functional groups in lignin from wood (native lignin), kraft pulp, and oxygen bleached kraft pulp of spruce.[63]

Table 2.8. Number of functional groups per 100 carbon atoms in lignin of wood, kraft pulp, and oxygen bleached kraft pulp of spruce.[63]

Type of carbon	Native lignin	Kraft pulp (kappa #=30.5)	Oxygen bleached pulp (kappa #=17.7)
Carbonyl	0.8	-	-
Carboxyl	-	2.1	3.5
Olefinic + aromatic Cq	39	54	52
Aliphatic CH <sub>x</sub> -OR	23.6	9.5	10.3
Methoxyl	11.2	9.1	8.2
Aliphatic CH <sub>x</sub>	4.9	10.4	10.4

The lignin content of the pulp after chemical pulping and bleaching usually is measured by a standardized reaction of potassium permanganate (KMnO<sub>4</sub>); this measure is referred to as a “kappa number”. The approximate lignin content in weight percent is calculated by multiplying the kappa number by 0.15.[19] Lignin can be isolated from wood and pulp through a number of methods including milling, solvent extraction, cellulolytic enzymatic treatments, acidic hydrolysis, and combinations.[64, 65]

Koda, Gaspar, Yu, and Argyropoulos studied the molecular weight of residual lignin in softwood (loblolly pine, i.e., *Pinus taeda* L.) kraft pulp.[66] The kappa numbers and lignin contents of various kraft pulps are shown in Table 2.9. A two-step enzymatic-acidolysis method[65] was applied in their study to isolate residual lignin. Figure 2.9 presents the molecular weight and polydispersity of residual lignin. It is clear from Figure 2.9-A that the weight average (M<sub>w</sub>) and the number average (M<sub>n</sub>) molecular weights of residual lignin decrease as of the degree of delignification increases, and that M<sub>w</sub> is more sensitive than M<sub>n</sub>. Polydispersity (Figure 2.9-B) is also observed to decrease during the process of delignification. These results suggest that the breadth of the molecular weight distribution becomes narrower as delignification proceeds.[66]



Table 2.9.<sup>i</sup> Kappa number and lignin content of kraft pulp from loblolly pine.[66]

	Wood meal	Kraft pulp				
Kappa number	-	104	89.3	70.7	38.4	27.4
Lignin content (%)	25.9	15.5	13.9	11.3	5.2	3.9
Acid insoluble (Klason) lignin (%)	25.0	14.5	13.0	10.5	3.9	2.2
Acid soluble lignin (%)	0.9	1.0	0.9	0.9	1.4	1.7
Degree of delignification (%)	0	39	46.4	56.4	80.0	85.0

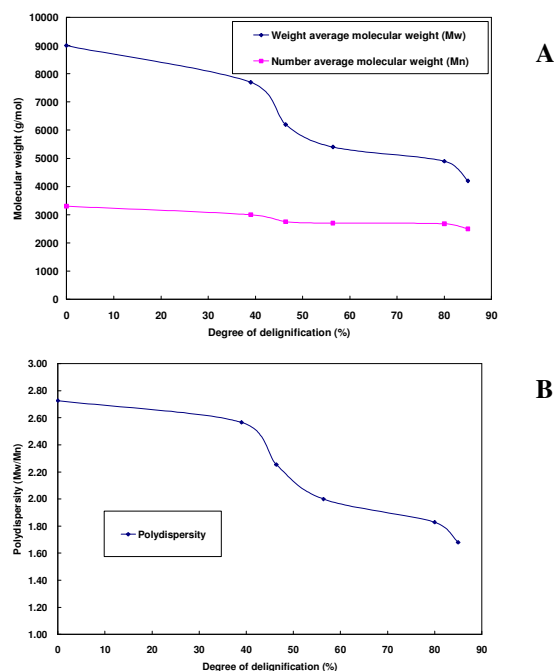


Figure 2.9.<sup>i</sup> The weight average and number average molecular weights of residual lignin in kraft pulp from loblolly pine compared to the degree of delignification.[66]

More recently, three lignin protocols for various wood species were examined by Guerra and co-workers[67]. The three isolated lignin are milled wood lignin (MWL),

<sup>i</sup> Table 2.9 and Figure 2.9 are reproduced with the kind permission from Appita Inc. The authors including Koda, Gaspar, Yu, and Argyropoulos of this manuscript are also appreciated for sharing their work.

cellulolytic enzyme lignin (CEL), and enzymatic mild acidolysis lignin (EMAL). The EMAL protocol was found to have much higher gravimetric lignin yields and molecular weights (MW) than those of the MWL and CEL (Table 2.10). The lignin yield was based on the Klason lignin content of extracted ground wood meal.

Table 2.10. Gravimetric yields and MWs of EMAL, MWL, and CEL from Douglas fir, redwood, white fir, and *Eucalyptus globulus*. [67]

Wood species	MWL		CEL		EMAL	
	Yield (%)	MW (g/mol)	Yield (%)	MW (g/mol)	Yield (%)	MW (g/mol)
Douglas fir	1.2	7400	7.0	21800	24.8	38000
Redwood	15.0	5900	13.0	23000	56.7	30100
White fir	11.0	8300	11.0	21700	42.9	52000
<i>Eucalyptus globulus</i>	34.0	6700	33.0	17200	63.7	32000

The functional group of the EMAL isolated from different wood species is listed in Table 2.11.

Table 2.11. Functional group contents of EMAL isolated from Douglas fir, redwood, white fir, and *Eucalyptus globulus*. [67]

Functional group*	Wood species			
	Douglas fir	Redwood	White fir	<i>Eucalyptus globulus</i>
Total $\beta$ -aryl ether	1600	1340	1490	2780
Syringyl OH	0.00	0.00	0.00	620
Guaiacyl OH	840	1060	930	350
<i>p</i> -hydroxyl OH	100	160	110	20
Uncondensed PhOH	940	1220	1040	Overlapped
Condensed PhOH	410	630	560	Overlapped
Total PhOH	1350	1850	1600	990
Carboxylic groups	130	160	190	150

\* It is determined by  $^{31}\text{P}$  NMR and values in  $\mu\text{mol/g}$ .

### 2.1.5 Extractives and inorganic materials

In addition to the major chemical components, wood contains small amounts of inorganic materials, and various extraneous, low molecular mass organic materials, normally referred to as "extractives". The extractives comprise an unusually large number of individual compounds of both lipophilic and hydrophilic types, including: terpenes, lignans, stilbenes flavonoids, and fats.[35] Wood extractives, for the most part, are dissolved in alkaline pulping liquor directly by soap formation or indirectly by micelle formation caused by the presence of ionized resin and fatty acids.[19] The inorganic materials are mostly transition metals.

## 2.2 The structure of wood fibers

Figure 2.10 shows the structure of a wood cell. It has a hollow center named a *lumen* and the sublayers of the *cell wall* include a primary wall and a secondary wall. The compound that connects the two adjacent primary walls is called the *middle lamella*. The primary wall is built of an open network of microfibrils embedded in an amorphous material. The crystalline cellulose accounts for approximately two-thirds of the cellulose. The hemicelluloses exist in the amorphous areas of cellulose microfibrils which bond them together.[33] Cellulose is the substance of the framework for the cell wall. In most wood species, cellulose is located predominantly in the secondary cell wall. Compared to the secondary wall, the primary wall has a lower amount of cellulose, but a higher

amount of lignin. The microfibrils have a parallel arrangement in the secondary wall. The difference between the three sublayers of the secondary wall is the angle of microfibrils in each layer.[33] The angle of microfibrils to the cell axis in S1 layer is  $50-70^{\circ}$ . It decreases to  $10-30^{\circ}$  in the S2 layer, and it changes to  $60-90^{\circ}$  in the S3 layer.[68] Lignin is biosynthesized by maturing cells and permeates the fiber walls and the intercellular regions (middle lamellae).[35] Typical softwood fibers are approximately 2.5 to 7.0 mm long and  $25-50\text{ }\mu\text{m}$  wide. Hardwood fibers are typically 0.8-1.6 mm long and  $14-40\text{ }\mu\text{m}$  wide. The thickness of the cell wall layers are shown in Table 2.12.

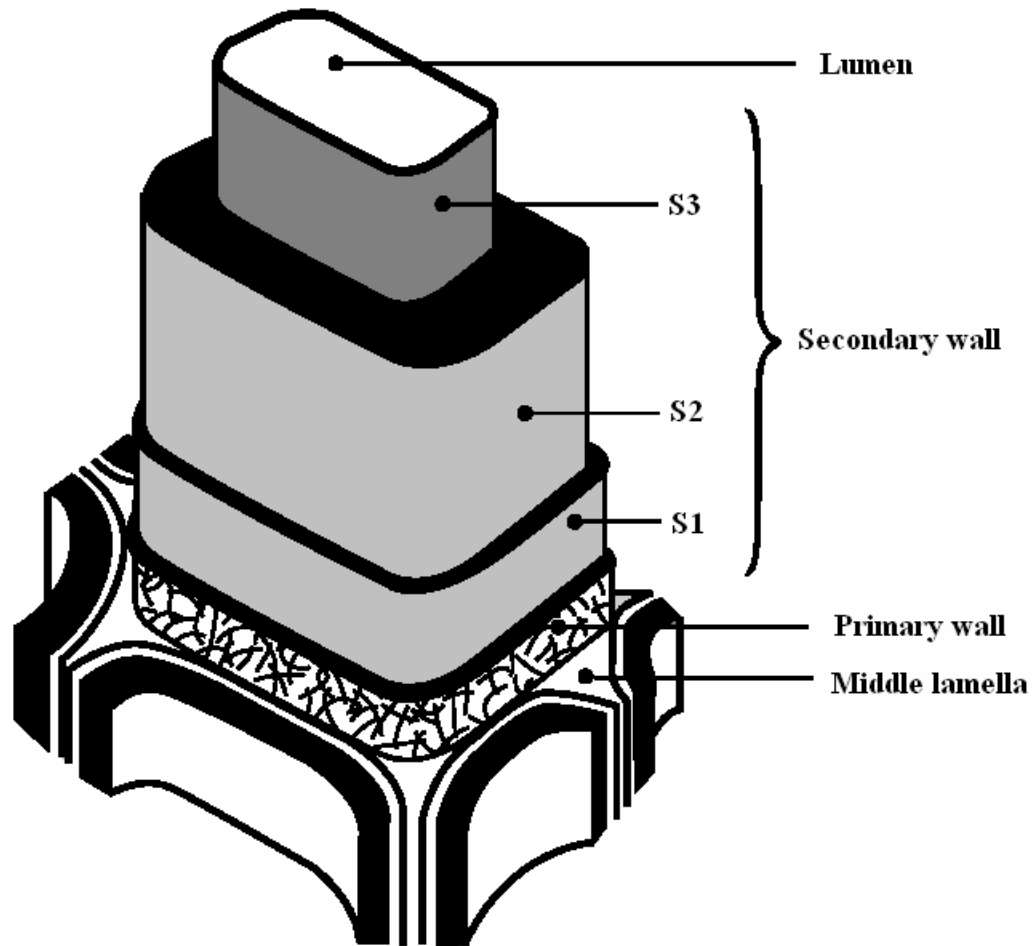


Figure 2.10.<sup>ii</sup> Schematic illustration of the cell wall structure of a softwood tracheid, P: primary wall, S: secondary wall.[68]

Table 2.12. The size of cell wall layers in a softwood tracheid.[69]

Cell wall layer	Size ( $\mu\text{m}$ )
Primary wall	<0.1
Secondary wall	
S1	0.1-0.2
S2	0.8-1.4
S3	0.1-0.2

<sup>ii</sup> This figure is reproduced with the kind permission from the University of Washington Press.

## 2.3 The effect of kraft pulping on fiber composition and properties

### 2.3.1 Kraft pulping conditions and chemistry

The dominant chemical pulping process in North America is the kraft process. The alkaline pulping liquor contains sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S). The pulping process is conducted at high temperatures (approx. 170 °C). Tables 2.13 and 2.14 summarize the pulping process parameters of Scots pine (*Pinus Silcestris*)[70] and loblolly pine[71], respectively.

Table 2.13. Industry batch cooking parameters of Scots pine (*Pinus Silcestris*).[70]

Wood	Scots pine ( <i>Pinus Silcestris</i> )
Yield from wood	47%
Moisture content of wood	45%
Chip temperature	10°C
Effective alkali charge (as NaOH)	18.5%
White liquor	
-effective alkali	115g/L
-active alkali	135g/L
-sulfidity	29.6%
-causticity	80.5%
Black liquor	
-temperature	70 °C
-dry solids content	15%
-density	1.05kg/m <sup>3</sup>
Liquor to wood ratio in batch cooking	4.5:1
Steam temperature	100 °C

Table 2.14. The kraft cooking conditions of loblolly pine.[71]

Wood	Loblolly pine
Yield from wood	44%~59%
Active alkali	15%~18%
Sulfidity	15%~30%
Liquor to wood ratio	4:1
Maximum cooking temperature	170°C
Cooking time	40~180 min
Kappa number	20~150

Degradation of lignin during kraft pulping firstly depends on the cleavage of ether linkages. The presence of hydrogen sulfite ions, compared to hydroxyl ions, greatly facilitates delignification because of their strong nucleophilicity. Hydrogen sulfite ions result in increased hydrophilicity of lignin because of the liberation of phenolic hydroxyl groups. Therefore, lignin can be degraded into water-soluble fragments in the pulping liquor as sodium phenolates.[35] Lignin can only be removed by approximately 90-95% through conventional kraft pulping technologies. It is well known that residual lignin contains carboxylic acid groups.[18]

Recently, Chakar and Ragauskas[59] reviewed, in detail, the softwood kraft lignin process chemistry. Lignin reactions that occur during kraft pulping are classified as degradation and condensation reactions. The former reactions result in the liberation of lignin fragments and enhance their dissolution, a desirable result. On the contrary, the latter reactions form alkali-stable linkages. The prevalent degradation reactions are the cleavage of  $\alpha$ -aryl ether and  $\beta$ -aryl ether bonds.[72] Figure 2.11 presents an example of an alkaline cleavage of an  $\alpha$ -aryl ether bond in a phenolic aryl-propane unit, and Figure

2.12 presents a competitive addition of external nucleophiles to quinone methide intermediate.

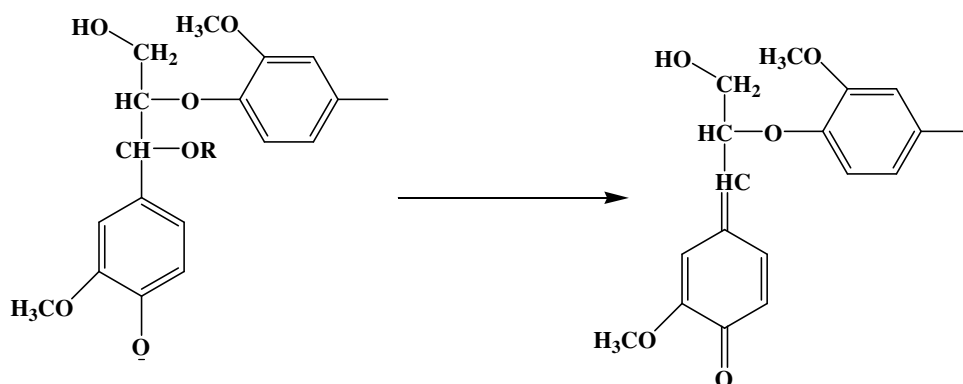


Figure 2.11. Alkaline cleavage of  $\alpha$ -aryl ether bond in phenolic aryl-propane unit.[72]

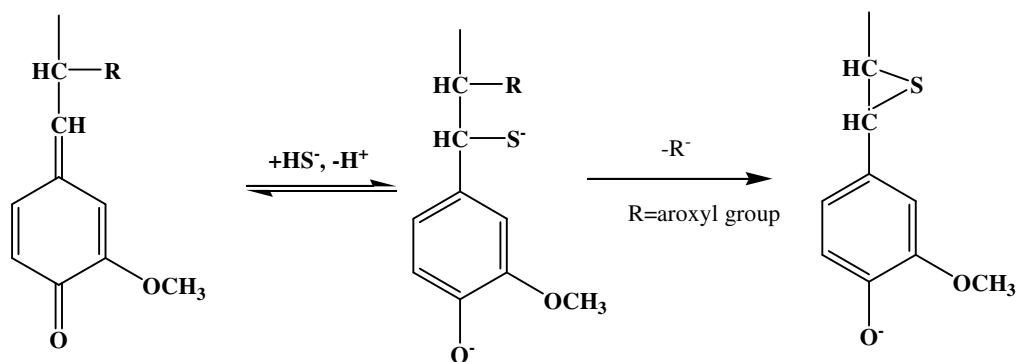


Figure 2.12. Competitive addition of external nucleophiles to quinone methide

intermediate: Oar, aroxyl group.[72]

The carboxylic acid group content of the residual lignin is affected by the kraft pulping process and its protocols. Froass, Ragauskas, and Jiang studied the carboxylic acid groups in residual lignin of conventional cooking (CK) and simulated extended modified continuous cooking (EMCC) pulps.[18] Their results are shown in Figure 2.13. It can be seen that the carboxylic acid group content of the lignin increases as



delignification proceeds, and both CK and EMCC lignins undergo similar increments in carboxylic acid group content.[18]

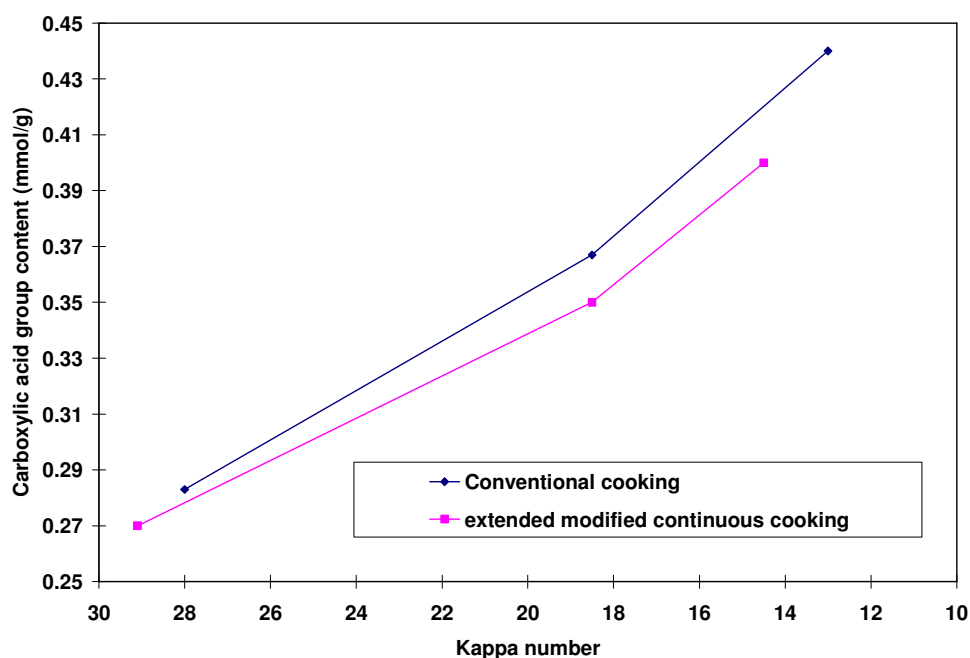


Figure 2.13. The carboxylic acid group contents of residual lignin isolated from CK and EMCC pulps.[18]

Jiang and Argyropoulos[73] also studied the functional groups of residual lignins in kraft pulps. In Table 2.15, it can be seen that kraft pulping can enhance carboxylic acid groups in residual lignin. This enrichment is accompanied by a decrease in the amount of aliphatic hydroxyl groups.

Table 2.15. The contents of functional groups of residual lignins isolated from wood and kraft pulps.[73]

Property of pulp and lignin	Spruce wood	Kraft pulps from spruce wood		
Kappa number	-	145	86.4	29.4
Hydroxyl units (mmol/g)				
Carboxylic acids	0.15	0.15	0.18	0.26
Aliphatic hydroxyls	4.27	3.09	2.78	2.76

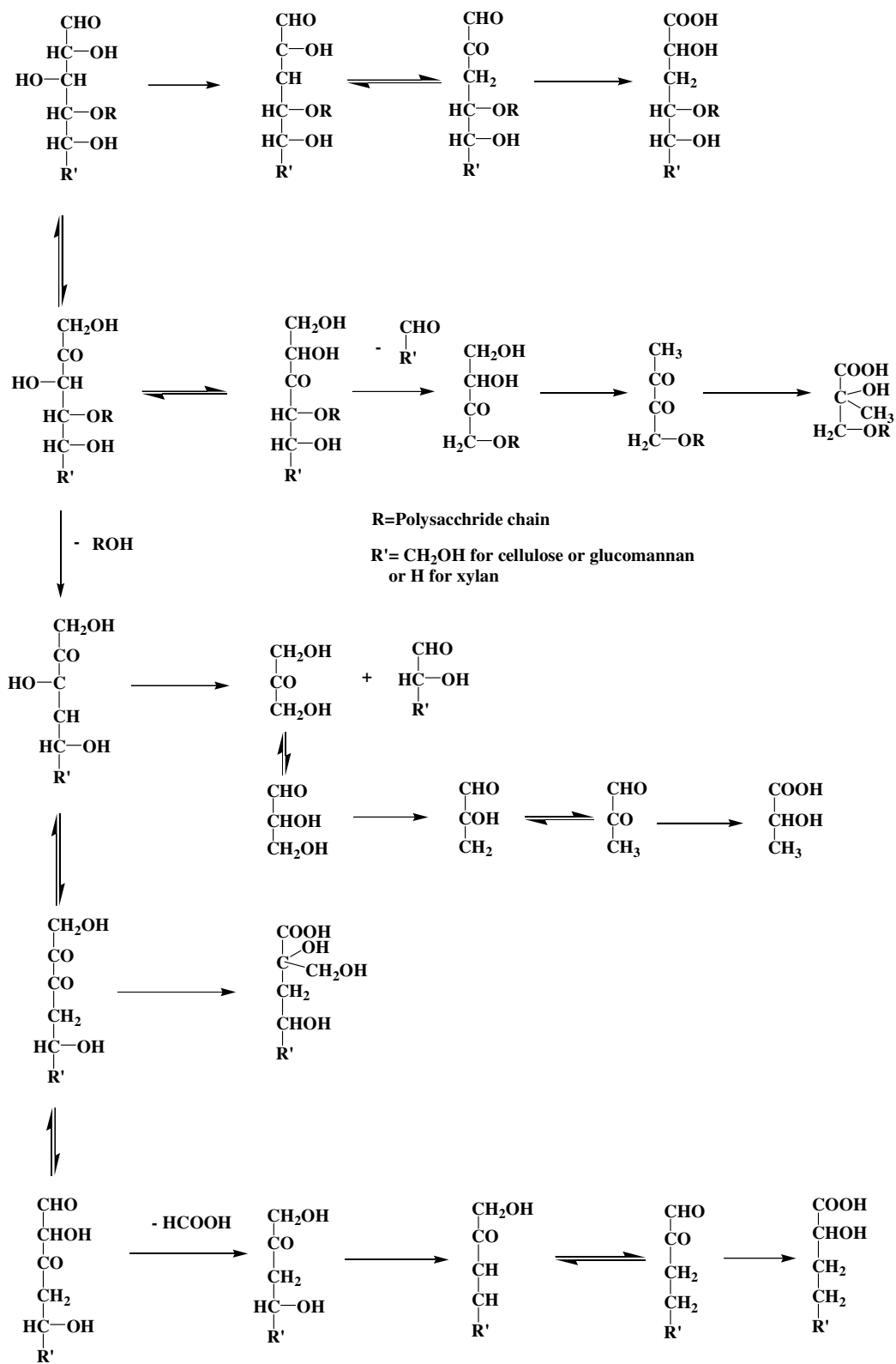


Figure 2.14. Peeling and stopping reaction of polysaccharides during kraft pulping.[74]

Polysaccharides, including cellulose and hemicelluloses, are degraded during the kraft process. As a result of the alkaline hydrolysis of glycosidic bonds, occurring at high temperature, new end groups are formed, giving rise to additional degradation. The peeling reaction is finally interrupted because the competing "stopping reaction" converts the reducing end group to a stable carboxylic acid group (see Figure 2.14).[35] At the end of kraft cooking, it can be assumed that virtually all carbohydrate end groups have been converted to carboxylic acids.

Lignin-carbohydrate complex (LCC) present in wood and pulps have been described in a number of studies.[60, 75-78] Lawoko, Henriksson, and Gellerstedt[76] reported carbohydrate and lignin analyses of spruce ball milled wood (BMW) and of various LCC fractions isolated from wood and pulps (Table 2.16).

Table 2.16. Carbohydrate and lignin analyses of spruce ball milled wood (BMW) and of various predominant LCC fractions isolated from wood and pulps.[76]

Fractions	Arabinan (%)	Xylan (%)	Mannan (%)	Galactan (%)	Glucan (%)	Klason lignin (%)
BMW	1.3	5.9	12.2	1.8	46.7	26.7
Kraft pulp (Kappa # = 35)	0.7	7.3	5.7	0.4	75	4.5
O-delig. Pulp (Kappa # = 10)	0.5	6.7	5.0	0.3	80	0.9
Wood						
LCC1	3.2	2.4	33.5	12.6	5.2	39
LCC2	1.0	0.9	2.5	0.2	85.2	7
Kraft pulp						
LCC3	0.5	3.5	4.0	0	88	2.4
LCC4	1.2	11.2	20.2	1.7	7.4	35
LCC5	4.4	56.8	6.3	0.4	7.7	23
O-delig. Pulp						
LCC6	0.9	7.6	41.6	2.8	13.3	19.6

LCC1=GalactoGlucoMannan-Lignin; LCC2=Glucan-Lignin; LCC3=Glucan-Lignin;  
LCC4=GlucoMannan-Lignin-Xylan; LCC5=Xylan-Lignin-GlucosMannan;  
LCC6=GlucosMannan-Lignin-Xylan

Table 2.17 summarizes the content of uncondensed  $\beta$ -O-4 structures and phenolic hydroxyl groups of LCC fractions present in wood and pulps. Among the various LCC fractions in wood, it was found that LCC1 (GalactoGlucoMannan-Lignin) has a higher content of  $\beta$ -O-4 structures than LCC2 (Glucan-Lignin). After cooking, the content of  $\beta$ -O-4 structures in the 3 LCCs (LCC3, LCC4, and LCC5) is much lower than that of the LCCs of wood; this difference is due to the degradation of galactoglucomannan during the initial phase of kraft cook. Since any cleavage of a  $\beta$ -O-4 structure in a lignin structure can lead to the formation of a new phenolic hydroxyl group, LCC3 appears to have high phenolic hydroxyl group content. LCC6 (GlucoMannan-Lignin-Xylan) is the predominant LCC isolated from oxygen delignified pulp, which contains 80% of the total pulp lignin. It still contains a considerable amount of  $\beta$ -O-4 structures. This result indicates the stability of the GlucoMannan-Lignin-Xylan complex during cooking and oxygen delignification, which is in agreement with a previous study by Lawoko et al.[79]

Table 2.17. Content of uncondensed  $\beta$ -O-4 structures and phenolic hydroxyl groups of LCC isolated from wood and pulps.[76]

Fractions	$\beta$ -O-4 structures $\mu\text{mol/g}$ lignin	Phenolic hydroxyl groups $\mu\text{mol/g}$ lignin
Wood		
LCC1	1169	Not analyzed
LCC2	658	1558
Kraft pulp		
LCC3	50	2129
LCC4	292	1450
LCC5	37	1230
O-delig. Pulp		
LCC6	90	680

LCC1=GalactoGlucoMannan-Lignin; LCC2=Glucan-Lignin; LCC3=Glucan-Lignin;  
LCC4=GlucoMannan-Lignin-Xylan; LCC5=Xylan-Lignin-GlucoMannan;  
LCC6=GlucoMannan-Lignin-Xylan

### 2.3.2 The fate of hexeneuronic acid groups during kraft pulping

Xylan in wood contains acidic groups, which are in the form of 4-O-methyl- $\alpha$ -D-glucuronic acid (see Figure 2.4 in Page 13). It has been reported that 4-O-methyl- $\alpha$ -D-glucuronic acid groups present in xylan are in part converted into a corresponding unsaturated acid, hexeneuronic acid (HexA), which is due to the loss of methanol during the alkaline pulping of wood (Figure 2.15).[12, 80]

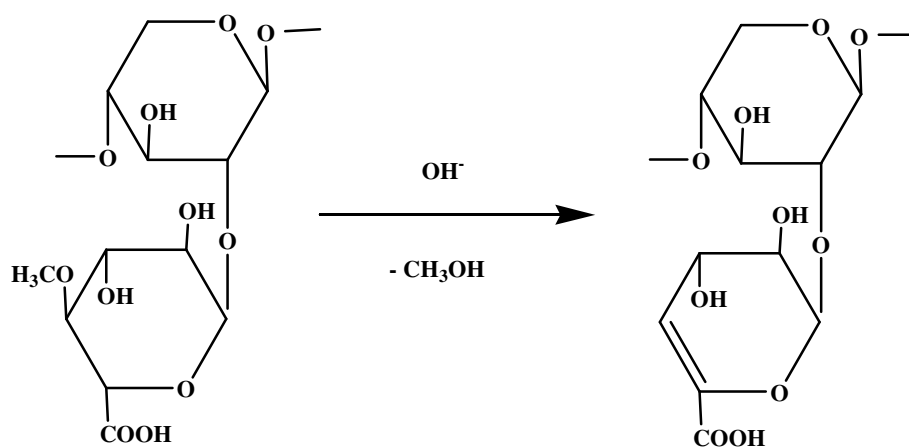


Figure 2.15. Formation of hexeneuronic acid groups in xylan during alkaline pulping.[12]

A study of HexA groups in terms of their pulping and bleaching chemistry was conducted by Jiang and co-workers.[80] HexA contains enol ether or unsaturated carboxylic acid groups, shown in Figure 2.16. HexA groups can react with electrophilic bleaching chemicals, such as chlorine dioxide and ozone.

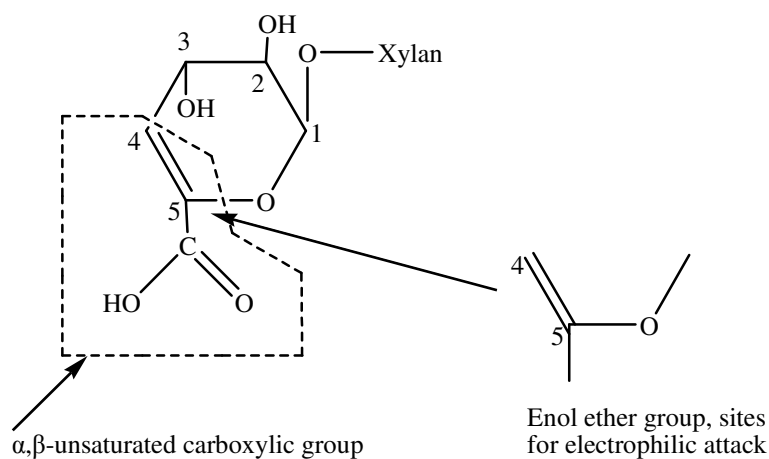


Figure 2.16. Functional groups of HexA attached to xylan.[80]

Figure 2.17 characterizes the amount of uronic acid groups present during the kraft pulping of pine. It can be seen that glucuronic acid content decreases as cooking time increases, while HexA content first increases and then decreases. Both groups eventually reach constant values.

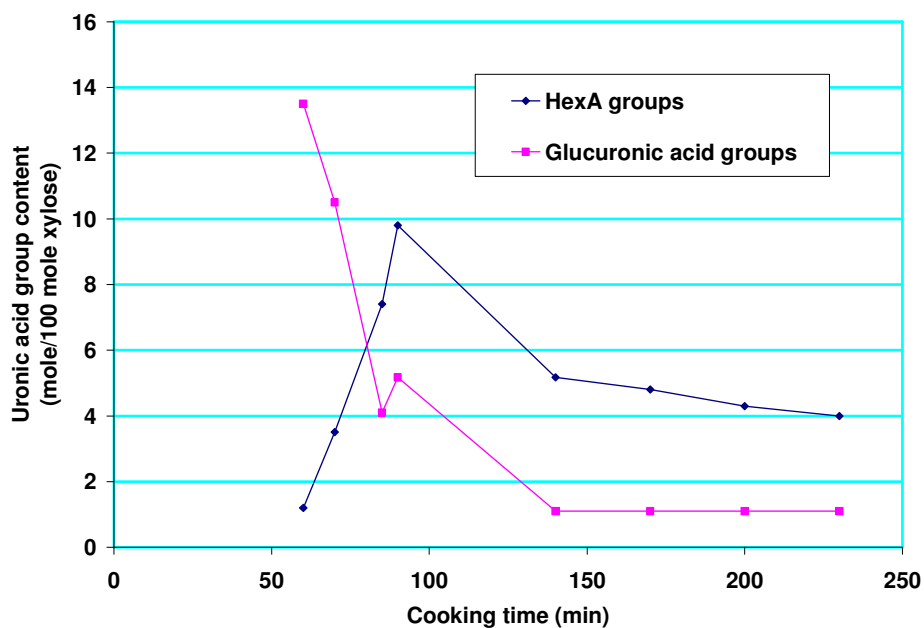


Figure 2.17. Profile of uronic acid content of xylose during kraft pulping of pine.[80]

A comparison between softwood and hardwood kraft pulps subjected to similar cooking conditions is also reported in the same study[80] (Table 2.18). Hardwood kraft pulps contain more HexA groups than do softwood kraft pulps, because hardwoods contain more 4-*O*-methylglucuronoxylan.

Table 2.18. The uronic acid content in conventional batch softwood and hardwood kraft pulps.[80]

	Hardwood (Birch)	Softwood (Pine)
Kappa number	18.2	25.9
Uronic acid content, $\mu\text{mol/g}$		
4- <i>O</i> -methylglucuronic acid	42	14
HexA	76	54
Total	118	68

Similar results for US hardwood kraft pulps were obtained by Chakar et al.[81] In Figure 2.18, it can be observed that the content of HexA groups in pulp increases as delignification is extended from a kappa number of 30 to 14. However, further depletion of HexA occurred as delignification was proceeded.



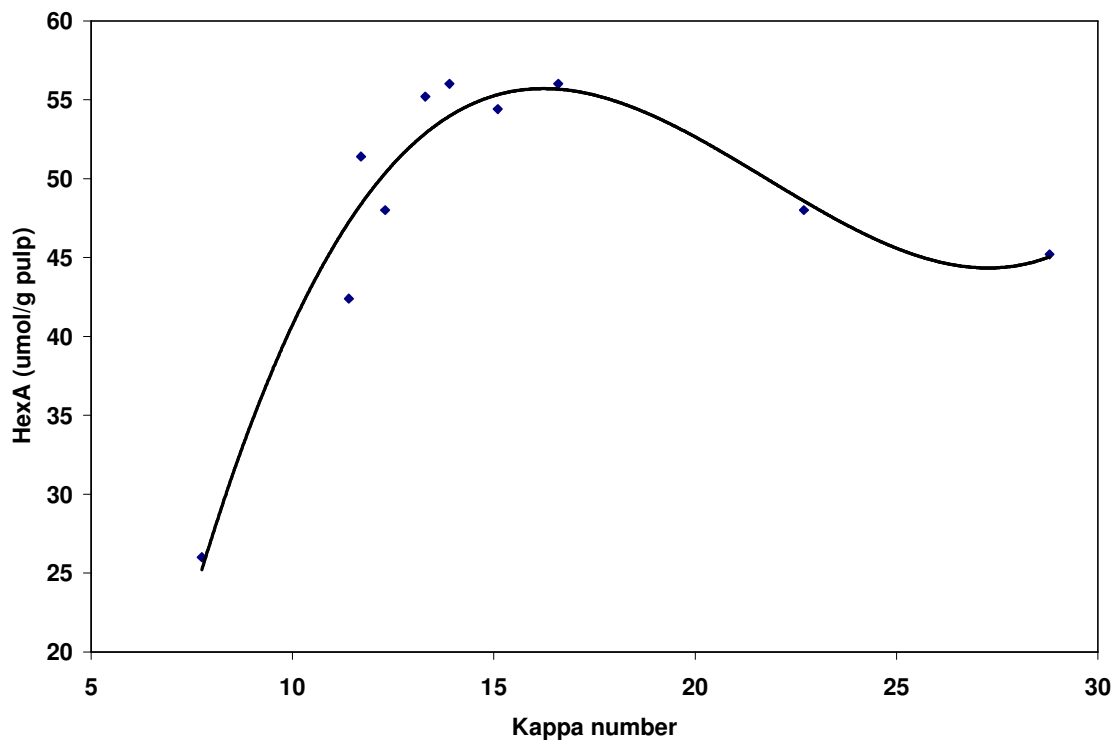


Figure 2.18. HexA group content of hardwood kraft pulp at different lignin content.[81]

Pulping protocols have also been found to affect the HexA group content of pulps.[82] Table 2.19 presents the HexA content of different pulps generated from conventional kraft pulping, Lo-Solids kraft pulping, soda pulping, soda AQ pulping, and polysulfide pulping. The wood used in this study was Scandinavian softwood.

Table 2.19. The HexA group content of pulps from different pulping protocols.[82]

Pulp sample	Kappa number	HexA content (mmol/kg)
Conventional pulping	25.5	22.7
Lo-Solids pulping	21.0	15.3
Soda	25.0	0.5
Soda AQ	21.0	3.7
Polysulfide	24.2	4.6

Gustavsson and Al-Dajani[83] developed an equation to determine HexA content during cooking (Equation 2.2).

$$HexA_t = HexA_0 \cdot \exp^{(-kt)}$$

$$k = 10^{-3} \cdot (-2.5 + 33.5[HO^-] + 6.8[HS^-] + 1.5[Na^+]) \cdot \exp^{(-\frac{123}{8.314} \cdot (\frac{1}{T} - \frac{1}{443.15}))}$$
(2.2)

HexA<sub>t</sub> and HexA<sub>0</sub> are the amounts of HexA at the cooking time t and the beginning of cook. According to the model, the rate increases incrementally in [HO<sup>-</sup>], [HS<sup>-</sup>], [Na<sup>+</sup>], and cooking temperature T. Moreover, the HexA content at a given kappa number can be reduced by applying a high [HO<sup>-</sup>], a high ionic strength, a low cooking temperature, and a low [HS<sup>-</sup>].

Similar to the study above, Chai et al.[71] proposed a mathematical model written as follows:

$$\frac{d[HexA]}{dt} = k \cdot \exp^{(-Ea/RT)} \times [(OCH3)_{-xylan}] [OH^-]$$
(2.3)

Based on this model, the effective alkali is the key factor controlling the formation of HexA for a given cooking temperature and wood species.

### **2.3.3 Effects of the kraft pulping process on the composition of pulps**

The conditions of kraft pulping influence the carbohydrate content of kraft pulps. Genco and co-workers[84] investigated the retention of hemicelluloses during kraft pulping. They studied the effects of wood chip thickness (2, 4, and 6mm), active alkali (AA) charge (20-28%), maximum temperature (160-180°C), and cooking time. When the

same kappa number of kraft pulp was generated, the pulping of the thinnest wood chip, 2mm, resulted in 2% and 3.5% greater hemicellulose content compared to that of the 4 and 6mm wood chips, respectively. At the fixed thickness of 4mm, it was found that the higher effective alkali (EA) of 23.8% resulted in a 1% lower hemicellulose content than the EA of 16.8%.[84]

Another factor that influences the chemical composition of kraft pulps is the use of pulping additives, such as anthraquinone (AQ) or polysulfide, which leads to increased pulp yields through greater retention of the hemicelluloses.[19] Typically, AQ added to the cooking digester are in the range of 0.05 to 0.1% in the mill. Zou and his co-workers[85, 86] cooked northeastern hardwood with the addition of AQ to the same kappa number (16~17). The results are summarized in Table 2.20.[86]

Table 2.20. The results of kraft pulping of northeastern hardwood by Zou et al.[86]

Pulp	Yield after pulping (%)	Cellulose content (%)		Hemicelluloses content (%)	
		Based upon pulp	Based upon wood	Based upon pulp	Based upon wood
Control	49.9	74.7	37.2	23.0	11.5
AQ 0.1%	52.1	72.9	38.0	24.8	12.9
AQ 1.0%	54.0	71.5	38.6	26.2	14.2
AQ 4.0%	54.8	71.0	38.9	26.7	14.6

Their conclusions are summarized as:

- AQ increases the pulp yield and shortens the cooking time.
- High pulp yield created by AQ-kraft cooking is caused by an increase in hemicellulose by approximately 70% and by the enhancement of cellulose by 30%.

- The selectivity during the followed oxygen delignification was improved for the high yield AQ-kraft pulp.[86]

Buchert et al.[87] examined the carbohydrate content of softwood (*Pinus sylvestris*) pulp after conventional cooking and after superbatches cooking. Superbatch cooking employs a warm black liquor impregnation process followed by a hot black liquor pre-treatment before cooking. The conditions of cooking and the results of carbohydrate content are shown in Table 2.21. The pulps generated from superbatches cooking had a higher carbohydrate content than the pulps generated from conventional cooking. Also, the carbohydrate content of the pulps increased during delignification.

Table 2.21. Carbohydrate content of kraft pulps from conventional cooking and superbatches cooking of softwood (*Pinus sylvestris*).[87, 88]

Pulping protocol	H-factor	Carbohydrate content* (%)			Lignin content (%)
		Glucose	Xylose	Mannose	
Conventional L:W=4:1 Active alkali=18.0-22.0% Sulfidity=34% Maximum temp.=170°C	204	58.1	6.2	5.9	17.9
	1007	69.6	6.9	6.0	6.5
	1500	69.8	7.4	6.0	4.8
	2001	72.0	7.3	6.0	3.5
	2517	72.5	7.5	5.6	4.4
Superbatch Active alkali=18-22% Sulfidity=38% Maximum temp.=170 °C	370	77.5	7.0	7.5	5.3
	830	83.8	7.0	7.1	2.5
	1820	84.6	6.1	6.8	1.5

\* The contents of arabinose and galactose did not present in the table, because only a trace amount of them in the pulp.

Danielsson et al.[89] used xylan as an additive for kraft pulping to modify the pulp fibers. The dissolution, degradation, and redeposition of xylan in kraft pulping were examined. Table 2.22 presents the conditions of this study. The pulps were generated

with a kappa number between 17 and 19. When birch xylan with a high molecular weight (12,200 g/mol) was added during the kraft pulping of spruce wood, the kraft pulp after 1000 revolutions PFI refining showed an increase of 10% on the tensile index compared to the kraft pulp without the xylan addition. When a low molecular weight (5,950 g/mol) xylan was applied, the tensile index only increased by 5%.[89]

Table 2.22. The conditions of two-stage kraft pulping of spruce wood with birch xylan as an additive.[89]

Parameters	Data
1 <sup>st</sup> stage cook	
Active alkali (%)	20
Sulfidity (%)	35
L:W	4:1
Maximum temperature (°C)	159
Cooking time (hr)	3
After 1 <sup>st</sup> cooking, half volume of black liquor is withdrawn and then same amount black liquor with birch xylan is added.	
2 <sup>nd</sup> stage cook	
Birch xylan charge (g/l)	7.85
Maximum temperature (°C)	159
Cooking time (hr)	1

#### 2.3.4 Modern continuous kraft pulping protocols

Over the last few decades, kraft pulping technology has significantly evolved to achieve extended delignification, enhanced yield, lower chemical use, reduced energy and increased production rates employing batch and continuous digesters.[90]

In Froass et al.'s study[18], an extended modified continuous cooking (EMCC) was compared with conventional cooking. They started by adding white liquor and

impregnating the chips for 30 min at 110 °C and 1000 kPa. The cocurrent cooking stage began after this impregnation stage by adding another charge of white liquor and raising the temperature to the maximum temperature. The conditions and results are given in Table 2.23. In table 2.23, it can be seen that EMCC obtains higher viscosity and a lower kappa number of kraft pulps compared to conventional cooking when the similar conditions were present.

Table 2.23. The conditions and results of EMCC and conventional cooking of softwood.[18]

Pulping protocol	Conventional cooking			EMCC		
White liquor % AA	27.4	27.4	27.4	27.4	27.4	27.4
Initial EA, % NaOH	19.7	19.7	22.0	12.0	12.0	12.0
Cocurrent EA %	-	-	-	5.0	5.0	5.0
Countercurrent EA %	-	-	-	4.0	4.2	5.0
Maximum temp. °C	170	170	170	158	161	169
H-factor	1715	2601	4238	1651	2229	4238
Kappa number	28.0	18.5	13.0	29.1	18.5	14.5
Viscosity, mPa·S	33.6	17.5	10.9	51.8	35.4	18.1
Screened yield, %	45.9	42.8	41.0	45.6	43.8	40.9

Low solids (Lo-Solids) pulping is an example of another modern continuous pulping technology. The main feature of the Lo-Solids pulping method is the extraction of dissolved organic substances before bulk delignification. These organic substances detrimentally impact pulp viscosity, brownstock brightness values, bleachability, final bleached pulp brightness ceilings, and pulp tear strength.[90, 91]

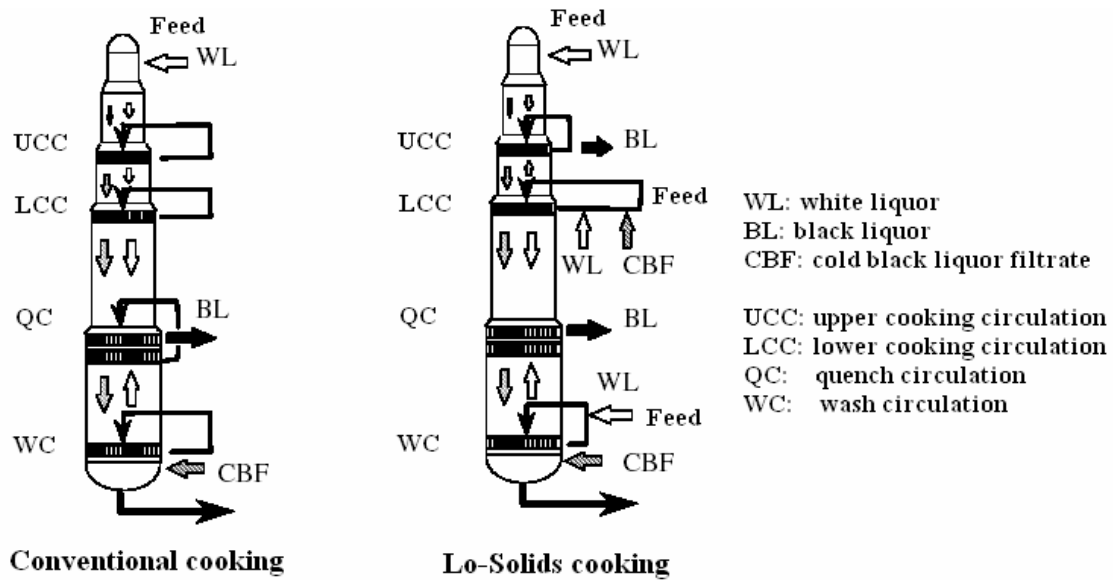


Figure 2.19. Conventional cooking and Lo-Solids cooking digesters.[92]

MiyanMiyanishi and Shimada[92] compared conventional kraft pulping against Lo-Solids kraft pulping. A diagram of the two digesters is illustrated in Figure 2.19. Table 2.24 presents the conditions of conventional cooking and Lo-Solids cooking. The white liquor is fed into the Lo-Solids digester at three points: at the top, at the lower cooking circulation (LCC), and at the wash circulation (WC). As for conventional cooking, the white liquor is fed only at the top of the digester. The results in Table 2.24 show a lower kappa number and a higher viscosity of the Lo-Solids cooking pulp compared to those of the conventional cooking pulp.

Table 2.24. The conditions and results of conventional cooking versus Lo-Solids cooking.[92]

Parameters	Conventional cooking	Lo-Solids cooking
AA charge (% on bone dry wood)	19	19
WL split ratio		
Feed from top (%)	100	54
LCC (%)	0	27
WC (%)	0	19
Kappa number	28~30	25
Viscosity (cP)	27	29

### 2.3.5 The influence of kraft pulping on carboxylic acid groups of fibers

Bhardwaj et al.[93] investigated the fiber charge of Lo-Solids kraft pulps with kappa numbers from 40 to 105. By conductometric titration, the fiber charge was found to vary from 6.2 to 11.4 mmol/100g o.d. pulp (Table 2.25).[93] This table indicates that carboxylic acid group content is positively proportional to the kappa number of kraft pulp.

Table 2.25. Carboxylic acid group content of Lo-Solids kraft pulp from *Pinus*

*Radiata*.[93]

Kappa number	Fiber charge (mmol/100g o.d. pulp)
39.6	6.2
60.8	8.4
79.9	10.4
94.7	11.0
105.0	11.4



Buchert et al.[87] studied the carboxylic acids of pulp fibers during kraft and superbatches pulping of *Pinus sylvestris*. Their results are shown in Table 2.26. The kraft pulps they generated through superbatches cooking had lower carboxyl group content than those that underwent conventional cooking. The reason the superbatches pulp had fewer carboxyl groups was due to the higher residual alkalinity in the superbatches pulping. It was concluded that the residual lignin of conventional kraft pulp with a kappa number of 24.2 accounted for 32% of the total acids; whereas, the residual lignin of the superbatches pulp with a kappa number of 11.8 accounted for approximately 45% of the total acids, which is due to the nearly complete degradation of HexA during the pulping process (see Table 2.26).[87]

Table 2.26. The results of carboxylic acid group and uronic acid group contents of softwood kraft pulps from conventional cooking and superbatches cooking.

Pulping protocol	Residual effective alkali, g/l	H-factor /Kappa number	Carboxyl group content (mmol/kg)	Uronic acid group content* (mmol/kg)
Conventional	19.3	204	186	75
L:W=4:1	9.5	1007	107	57
Active alkali=18.0-22.0%	7.8	1500	83	47
Sulfidity=34%	5.6	2001	77	43
Maximum temp.=170°C	4.7	2517**	77	40
Superbatch	25.0	370	71	43
Active alkali=18-22%	22.8	830	46	21
Sulfidity=38%	18.2	1820***	40	10
Maximum temp.=170 °C				

\* It is the sum of the amount of HexA, MeGlcA, MeIdoA, GalA, and GluA.

\*\* Kappa number = 24.2. Metasacchatinic acid content = 12 mmol/kg.  
Lignin bound acid content = 77-40-12=25 mmol/kg.

\*\*\* Kappa number = 11.8. Metasacchatinic acid content = 12 mmol/kg  
Lignin bound acid content = 40-10-12=18 mmol/kg

## **2.4 Pulp bleaching**

### **2.4.1 Bleaching chemistry**

Kraft pulp fibers are brown due to the formation of chromophoric groups during pulping.[19] The bleaching of kraft pulps is directed at removing residual lignin, hexeneuronic acids, and other chromophoric compounds, which leads to increased brightness.

Bleaching chemicals are used primarily as oxidants. They can break down residual lignin in pulp and increase its solubility in the bleaching liquor. Bleaching reactions can be categorized according to their principal mode of operation. According to the general concept developed by Gierer, bleaching reactions may be classified mechanistically as electrophilic or nucleophilic.[94] A mechanistic approach classifies them as electrophiles, nucleophiles, and radicals.

- Electrophilic reactions typically initiate lignin-degrading bleaching processes, which frequently take place in acidic conditions. They involve cations and radicals generated from the bleaching chemicals.
- Nucleophilic reactions typically occur in lignin-retaining bleaching. These reactions generally are in alkaline media. Anions and, to a much lesser extent, radicals are involved in the reactions.[70]

Table 2.27[19] presents a list of chemical species that participate in the bleaching process.

Table 2.27. The list of reactive bleaching chemical species.[19]

Reactant	Name	Type	E or N	Function initially	pH range
1. Present during bleaching with chlorine compounds					
$\text{Cl}^+$	Chloronium	Cation	E	Oxidant	Acidic
$\text{Cl}\cdot$	Chlorine radical	Radical	E	Oxidant	Acidic
$\text{OCl}^-$	Hypochlorite ion	anion	N	Reductant	Alkaline
$\text{ClO}_2$	Chlorine dioxide	radical	E	Oxidant	Acidic
2. Present during bleaching with oxygen, hydrogen peroxide, and ozone					
$\cdot\text{OO}\cdot$	Oxygen	Diradical	E	Oxidant	All
$\text{OO}\cdot^-$	Superoxide anion radical	Radical, anion	N	Oxidant	Alkaline/neutral
$\text{HOO}\cdot$	Hydroperoxide radical	Radical	E	Oxidant	Acidic
$\text{HOO}^-$	Hydroperoxide anion	Anion	N	Reductant	Alkaline
$\text{HO}\cdot$	Hydroxyl radical	Radical	E	Oxidant	Acidic
$\text{OH}^+$	Hydroxomium ion	Cation	E	Oxidant	Acidic
$+\text{OOO}-$	Ozone	Cation	E	Oxidant	Acidic
3. Present during alkaline treatments					
$\text{OH}^-$	Hydroxide ion	Anion	N	-	Alkaline

E= Eletrophile; N=Nucleophile

Oxygen, chlorine, and chlorine dioxide are commonly delignifying chemicals. Alkaline peroxide does very little delignification but reduce chromophores in lignin. Such chemicals may be called brighteners. Chlorine dioxide and hypochlorite are capable of doing both.[70]

#### 2.4.2 Modern ECF and TCF bleaching technologies

Generally, the oxidant chemicals used in pulp bleaching include chlorine (C), chlorine dioxide (D), hypochlorite (H), oxygen (O), peroxide (P), and ozone (Z). There are also other chemicals, such as enzymes (X), acid (A), sodium hydroxide (E), and chelants (Q), that are applied during the bleaching process and serve as either a pretreatment, an extraction, or as a single bleaching process.[38] The use of chlorine-

containing chemicals in pulp bleaching results in the formation of organochlorine compounds, i.e., absorbable organic halides (AOX).  $\text{ClO}_2$  bleaching produces much less AOX than  $\text{Cl}_2$  bleaching. Therefore, elementally chlorine-free (ECF) and totally chlorine-free (TCF) bleaching technologies are widely carried out in the paper industry due to environmental concerns. ECF substitutes  $\text{Cl}_2$  by chlorine dioxide, and commonly contains three to four stages including  $\text{ClO}_2$ ,  $\text{O}_2$ , ozone, and peroxide. TCF uses oxygen-derived compounds as the bleaching agents in all stages. These compounds consist of hydrogen peroxide, oxygen, or ozone. The total demand of bleaching chemicals in a bleaching sequence is often added up as total chlorine equivalent. The consumption mainly depends on the incoming kappa number, but also on the form of the residual lignin contained in the pulp.[70]

Chlorine dioxide reacts with residual lignin, which can dissolve lignin. Its reactions with carbohydrates are minimal. The consistency of  $\text{ClO}_2$  bleaching is conducted at 9% to 15%. Table 2.28 gives some typical bleaching sequences and their conditions for softwood kraft pulp.

Table 2.28. Typical ECF bleaching sequences conditions of softwood kraft pulp.[70]

Bleaching stages	DE <sub>0</sub> DED	ODE <sub>0</sub> DED	ODE <sub>0</sub> D
Initial kappa number	27	14	14
Delignification			
D <sub>0</sub> , ClO <sub>2</sub> , kg eq.Cl/tbdp	54	28	28
D <sub>0</sub> , pH	2	2.5	2.5
D <sub>0</sub> , temperature	60	60	60
Extraction			
E <sub>0</sub> , NaOH, kg/tbdp	33	17	20
E <sub>0</sub> , pH	10.5	10.5	10.5
E <sub>0</sub> , temperature	65	65	65
E, NaOH, kg/tbdp	10	8	-
E, pH	10	10	-
E, temperature	70	70	-
Bleaching			
D <sub>1</sub> , ClO <sub>2</sub> , kg eq.Cl/tbdp	30	25	35
D <sub>1</sub> , pH	4	4	4
D <sub>1</sub> , temperature	70	70	80
D <sub>2</sub> , ClO <sub>2</sub> , kg eq.Cl/tbdp	10	8	-
D <sub>2</sub> , pH	5	5	-
D <sub>2</sub> , temperature	75	75	-
Total equivalent chlorine kg/tbdp	94	61	63
Final brightness, % ISO	89	89	87

eq.Cl = equivalent chlorine; tbdp = tone bone dry pulp

Enzyme treatment is a relatively new bleaching technology. It usually uses xylanase to eliminate the xylans. Therefore, it breaks the link between the cellulose and lignin and leads to easier removing lignin in the subsequent bleaching stages.[95, 96] A mill trial was conducted by replacing (CD)(EO)D(EP)D with X(EOP)D(EP)D. The xylanase used in this mill was CartazymeHS. The conditions are shown in Table 2.29. The advantages of enzymatic bleaching from this mill trial are:

- Enzyme-treated brightness was 5-7 points than those of the pulp without enzyme bleaching.

- No negative effect of enzyme treatment on viscosity of pulp was found.
- Potentially, enzyme treatment can reduce the use of molecular chlorine.

Table 2.29. The conditions and results of an ECF bleaching sequence of X(EOP)D(EP)D of eucalyptus brownstock.[95]

Bleaching stages	Retention time (hr)	Temp. (°C)	Cons. (%)	Charge	Brightness (% ISO)
Enzyme (pH=3.5-5.0)	2.5	33-41	8	1.25*	-
EOP**	2.0	67	11	-	33.8
D <sub>1</sub> ***	2.0	65	12	-	65.7
EP	2.0	69	12	-	78.5
D <sub>2</sub>	3.0	68	12	-	88.2

\* The unit is AU/metric ton (1 AU=10<sup>6</sup> xylanase units)

\*\* The total charge of peroxide is 12.7 kg/o.d. metric ton pulp

\*\*\* The total ClO<sub>2</sub> charge is 13.8 kg/o.d. metric ton pulp

### 2.4.3 Reaction principles in peroxide bleaching and oxygen delignification

Hydrogen peroxide is a clear and colorless liquid. It is sold commercially in 30% to 70% solution concentrations. It is well-known that hydrogen peroxide brightens mechanical pulp, delignifies kraft pulp, and increases the brightness of bleached chemical pulp and secondary (recycled) fibers.[97-99] When used under relatively mild conditions (35-55°C), peroxide is an effective lignin-preserving bleaching agent. It can improve the brightness of groundwood and other highly delignified pulps without significant yield loss. Under more severe conditions (70-80°C), peroxide is used in the later stages of chemical pulp bleaching to provide increases in full bleach brightness and improve brightness stability.[38]

Traditionally, hydrogen peroxide has been classified as a lignin-preserving bleaching reagent. It preferentially removes chromophoric structures present in residual lignin, but is incapable of degrading the lignin network.[100]

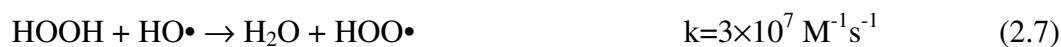
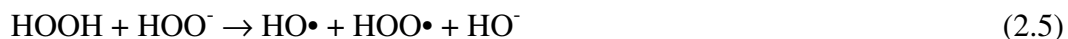
The action of alkaline peroxide as a bleaching agent can be explained through the reactions of the hydroperoxide anion,  $\text{HO}_2^-$ , formed in an alkaline medium according to the equilibrium:



Where  $\text{pK}_a = 11.6$  at  $25^\circ\text{C}$ .

The hydroperoxide anion,  $\text{HO}_2^-$ , is a mild oxidative species which attacks carbonyl groups present in lignin.[35]

A number of reactive free radical species are formed during the decomposition of aqueous hydrogen peroxide.[94, 101] In aqueous media, the kinetics and thermodynamics of the "active oxygen" species have been evaluated by pulse radiolysis.[102]



From the above information, reactions 2.5, 2.6, 2.7, and 2.9 appear to represent a viable mechanism for the base-introduced decomposition of hydrogen peroxide to oxygen

and water. In addition, as hydrogen peroxide is also produced in the alkaline hydrolysis of peroxy acids, the series of reactions outlined above will also occur [103].

It is generally accepted that the radicals of most concern during peroxide bleaching are the hydroxyl radicals, perhydroxyl radicals, and superoxide radicals in relation to the reaction with cellulose. The most critical of these is the hydroxyl radical due to its high reactivity with both lignin and carbohydrate.[94]

### Hydroxyl radicals

The hydroxyl radical ( $\text{HO}\bullet$ ) and its conjugate base, i.e., the oxy anion ( $-\text{O}\bullet$ ), are the most reactive of all the oxygen species. Hydroxyl radicals are extremely reactive molecules that are capable of several reactions: Hydrogen abstraction (Equation 2.11), electrophilic addition (Equation 2.12), radical coupling (Equation 2.13), and electron transfer reactions (Equation 2.14).[104]



The oxy anion is present under alkaline conditions. It performs similar chemistry to that of the hydroxyl radical and preferentially attacks aliphatic sidechains in aromatic structures instead of adding to the ring.[104]

### Superoxide anions



Superoxide anion ( $\text{O}_2^{\cdot-}$ ) is generated by reducing a molecular oxygen by one electron, and its conjugate acid is in the form of the hydroperoxyl radical ( $\text{HOO}^{\cdot}$ ). These anions are believed to be the principal active species involved in the elimination of chromophores in lignin structures, particularly conjugated carbonyl structures that are prone to react with the hydroperoxide anion.[105] Because of its specific and efficient action on carbonyl and conjugated carbonyl groups, the hydroperoxide anion can attack many of the chromophore groups present in pulp, including those created by the other reagents applied in previous bleaching stages. These stages including chlorine, chlorine dioxide, and oxygen are known to form quinone groups.[35, 106, 107]

#### 2.4.4 Reactions of hydrogen peroxide with lignin and carbohydrates

Residual lignins in kraft pulp are in the structure of  $\alpha$ -carbinol and  $\alpha$ -carbonyl groups.[108] In the presence of a free-phenolic hydroxyl compound  $\text{R}=\text{H}$ , the reaction proceeds by way of the Dakin-reaction (see Figure 2.20).[109]

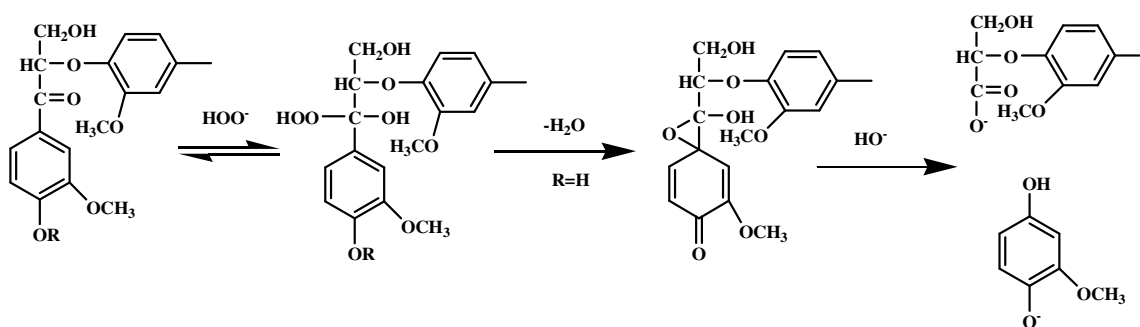


Figure 2.20. Dakin reaction of peroxide with lignin.[109]

Also, the peroxy anion attacks an o-quinone structure to form a carboxylic acid group (see Figure 2.21).[35] These quinoid-type chromophoric structures are rapidly degraded to mono/di functional carboxylic acids.[19, 109]

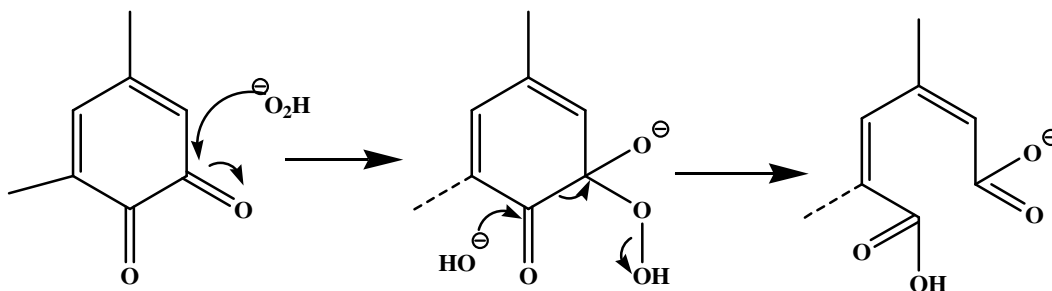


Figure 2.21. Attack of nucleophilic peroxy ion and alkaline quinoid-type chromophoric structures.[35]

The main oxidizing attack of bleaching agents occurs within the polysaccharide, but it can also be directed to the end groups. Figure 2.22 suggests a mechanism for how hydroxyl group degrades carbohydrate. The hydroxyl group first attacks the C2 or C3 position of the glucose unit to form a carbonyl group through hydrogen abstraction. A  $\beta$ -alkoxy elimination occurs at C4, which leads to the cleavage of the cellulose chain.

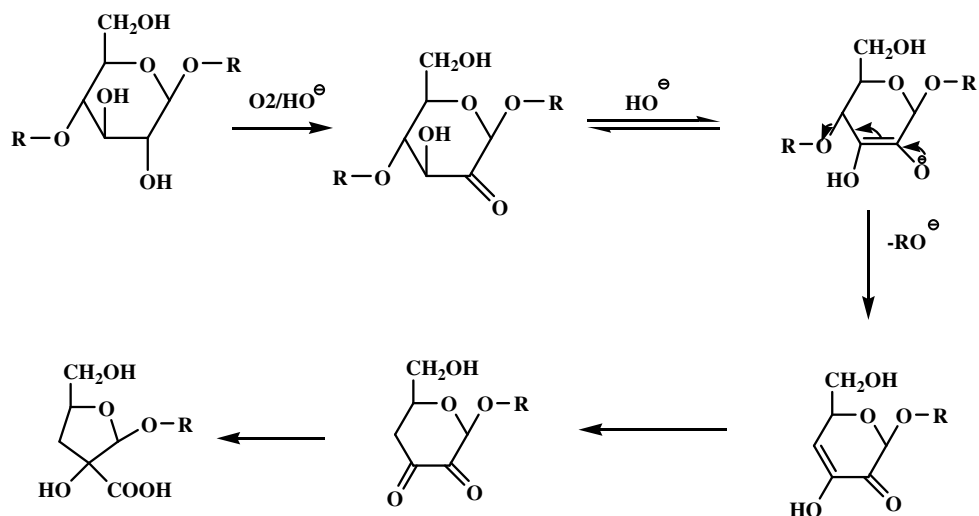


Figure 2.22. Cleavage of a glycosidic bond by alkaline oxygen/H<sub>2</sub>O<sub>2</sub> bleaching after formation of a carbonyl group.[35]

If the conditions are alkaline, the new reducing end groups generated as a result of the cleavage of glycosidic bonds will give rise to the peeling of the cellulose and hemicelluloses chains (see Figure 2.23).[35]

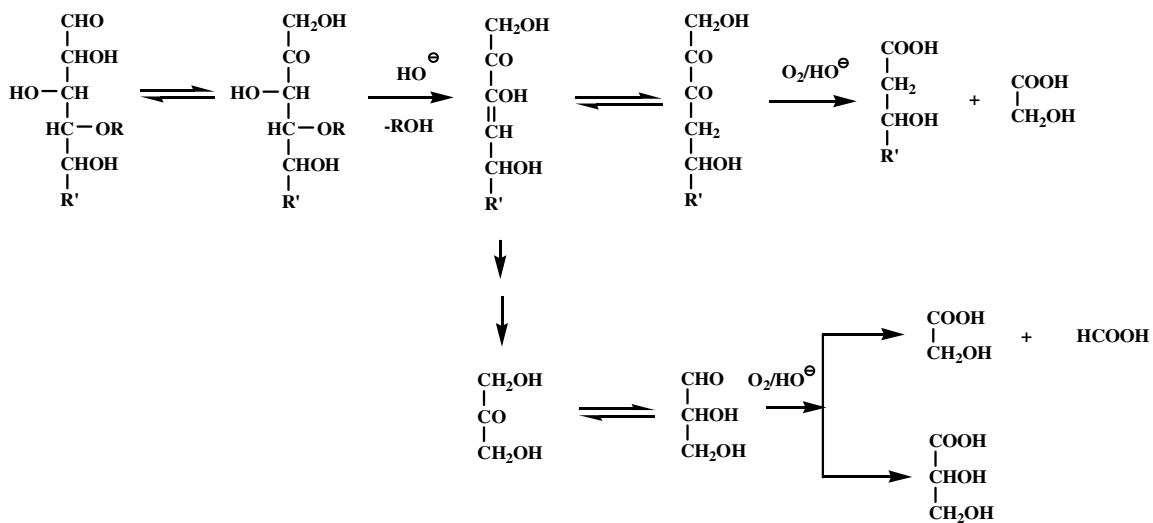


Figure 2.23. Peeling reaction of polysaccharides during oxygen/H<sub>2</sub>O<sub>2</sub> bleaching.[35]

Malinen and Sjöström studied the reactions of hydrocellulose during oxygen bleaching and found that the predominant end group is erythronic acid.[110] It has also been found that reactions of hydroxyl radicals at the C-5 and C-6 positions of D-glucose can produce aldehyde groups (Figure 2.23).[111] Superoxide radicals and H<sub>2</sub>O<sub>2</sub> can convert 2,3,4,6-tetra-o-methyl-D-glucose to 2,3,4,6-tetra-o-methyl-D-gluconic.[112] Isbell et al.[113] and Hebeish et al.[114] also reported that aldehyde groups of carbohydrate can be converted to carboxyl groups under an alkaline peroxide medium (Figure 2.24).

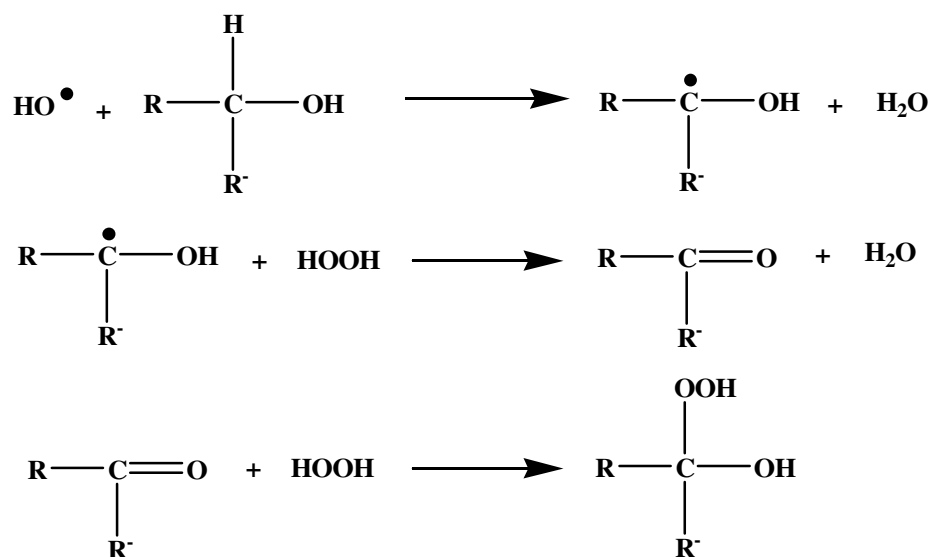


Figure 2.24. Reaction mechanism of alkaline peroxide with glucose forming a carboxyl group.[113, 114]

In summary, Figure 2.25 presents examples of carboxyl structures after polysaccharides are oxidized by hydrogen peroxide.[35]

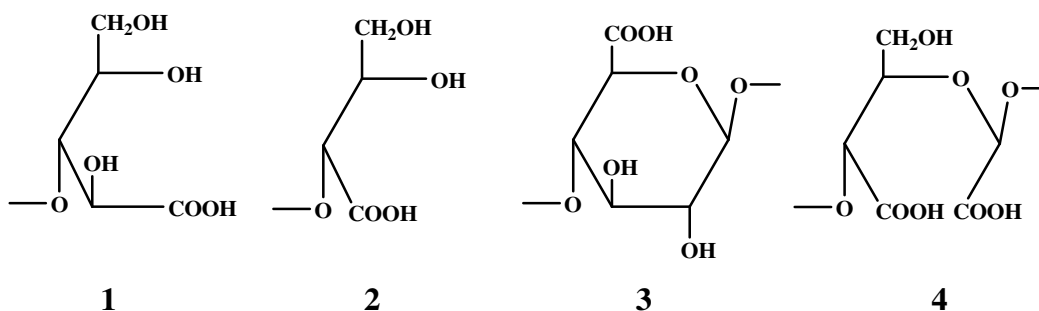


Figure 2.25. Examples of carboxyl structures formed in cellulose by oxidation action of bleaching agents. Types: arabinonic acid (1), erythronic acid (2), glucuronic acid (3), and dicarboxylic acid structure (4).[35]

By means oxygen delignification of model compounds, Guay[115] stated that a hydroxyl free radical ( $\text{OH}\bullet$ ) induced significant degradation to carbohydrate model compounds. He also found that molecular oxygen, superoxide anions, hydrogen peroxide, and hydroxyl anions did not show degradation to carbohydrate model compounds directly.[115]

Concerning the effect of bleaching on hemicelluloses, some researchers found that chemical pulps which had been subjected to totally chlorine free bleaching yielded xylans with degrees of polymerization similar to those of the corresponding xylans extracted from the unbleached pulps. This indicated that such bleaching does not cause any significant depolymerization of the hemicelluloses remaining in the pulp.[51]

#### **2.4.5 The influence of bleaching on HexA content**

Figure 2.26 describes the effect of bleaching sequences on HexA content of kraft pulps in a study by Buchert et al.[88] In Figure 2.26, it can be seen that HexA groups are

unreactive during alkaline oxygen delignification and peroxide bleaching, but that they can be significantly removed by ozone bleaching and chlorine dioxide bleaching.

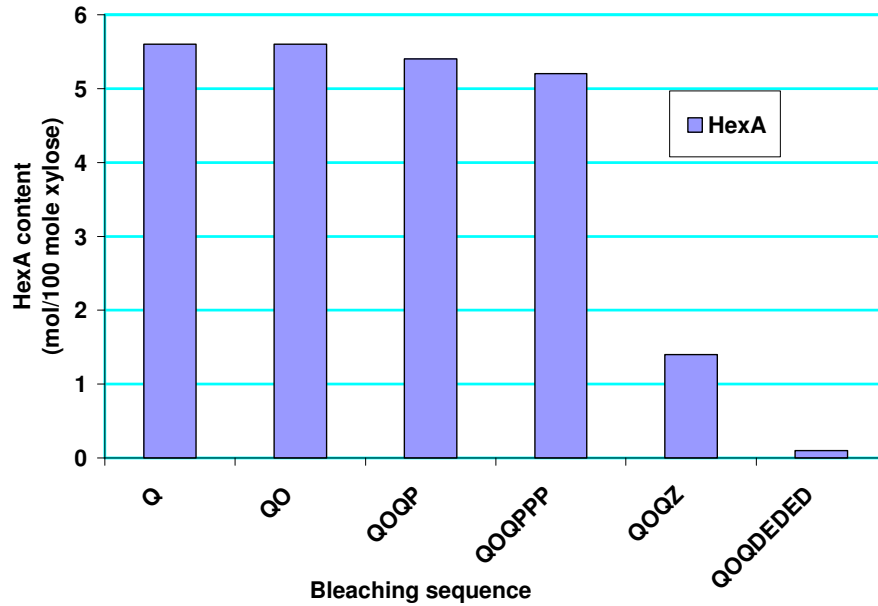


Figure 2.26. The effect of bleaching sequences on the HexA content of the kraft pulp of pine.[88]

A detailed study by Laine[116] was performed to understand the effects of ECF and TCF bleaching sequences on HexA. An unbleached softwood (*Pinus sylvestris*) kraft pulp with a kappa number 25.9 was subjected to a series bleaching sequences, including OZEP, OPZEP, ODEDED, and DEDED. The results of the HexA of pulps are reported in Table 2.30. The conclusions drawn from this study are:

- Oxygen delignification can increase HexA content by approximately 21%.
- Peroxide bleaching does not have an obvious effect on HexA.
- Chlorine dioxide bleaching and ozone bleaching significantly reduce HexA content.

Table 2.30. HexA group contents of softwood kraft pulps undertook various ECF and TCF bleaching sequences.[116]

Pulp after bleaching	Brightness (% ISO)	HexA content ( $\mu\text{mol/g}$ )
Kraft pulp	23.4	37.0
O	36.2	44.8
OZ	48.4	21.9
OZE	49.1	13.9
OZEP	74.1	12.1
OP	62.8	40.7
OPZ	74.2	10.4
OPZE	73.5	4.8
OPZEP	85.1	4.0
OD	55.1	17.4
ODE	59.8	13.9
ODED	79.0	4.6
ODEDE	77.4	3.9
ODEDED	86.8	2.3
D	38.4	17.0
DE	40.7	13.1
DED	68.7	7.1
DEDE	66.0	5.3
DEDED	81.9	3.2

Table 2.31 presents Allison et al.'s[117] data of the effect of oxygen delignification on HexA content of mill unbleached pulp and bleached pulps from radiata pine. In Table 2.31, it can be seen that oxygen delignification does not have an obvious effect on HexA, while the first chlorine dioxide bleaching removes 97% of HexA content of the original kraft pulp.

Table 2.31. The results of HexA content of softwood kraft pulps underwent a bleaching sequence of ODE<sub>0</sub>D.[117]

Pulp	Delignification (%)	HexA removal (%)
Kraft	0	0
O	-25	+4
OD	-94	-97
ODE <sub>0</sub>	-98	-97
ODE <sub>0</sub> D	-99	-97

#### 2.4.6 **Role of transition metals and activators during oxygen delignification and peroxide bleaching**

Transition metal ions are frequently present in wood and pulp. They are insoluble under alkaline conditions, and a heterogeneous surface-catalyzed reaction can be caused by colloidal transition metal ions. Table 2.32 lists the metal content of a southern pine kraft pulp and a fully bleached softwood kraft pulp with and without acid washing. After acid treatment, it can be observed that most of the metal ions can be removed except iron ions.



Table 2.32. Metal content of a southern pine kraft pulp and a fully bleached softwood kraft pulp with and without acid washing.[58, 118]

Metal (ppm)	Southern pine kraft pulp[58]	Fully bleached softwood kraft pulp[118]	
		No acid treatment	After acid treatment
Na	146	140	6
K	37	-	-
Ca	1620	50	20
Ba	3	-	-
Mg	288	20	6
Mn	34	4.3	0.3
Fe	20	37	31
Al	7	70	40

Earlier studies have shown that metal ions like manganese (Mn), copper (Cu), and iron (Fe) play an important role during the lignin oxidation process, and that metal ions can act as catalyzing agents during oxygen delignification.[119]

At high pH values, metal ions will catalyze hydrogen peroxide decomposition to generate hydroxyl radicals ( $\bullet\text{OH}$ ) and superoxide anion radicals ( $\text{O}_2\bullet^-$ ). Hydroxyl radicals initiate reactions which lead to both lignin and carbohydrate degradation.[120] Hall and co-workers found that Nickel (Ni) was the one metal that when present during oxygen delignification enhanced the selectivity of oxygen delignification, brought about by increasing delignification while suppressing carbohydrate degradation.[120]

To minimize the effects of these transition-metals-induced decomposition reactions, many techniques have been employed. The most widely used techniques in industry are acid washing and chelation. These methods deactivate or remove the metals, diminishing the decomposition of peroxide.[121]

Lapierre et al.[118] looked at the effect of magnesium ions on peroxide bleaching. After acid treatment of the fully bleached softwood kraft pulp (Table 2.32), the contents of Na, Ca, Mg, Mn, and Al obviously decrease. However, Fe seems resistant to the acid treatment.

Some approaches aim at activating peroxide, which can promote the oxidation potential of hydrogen peroxide. Kubelka et al.[122] employed 500 ppm of sodium molybdate under acidic conditions (pH=5) and a 2% peroxide charge, the kappa number reduced by 10 units. However, the kappa number only decreased by 3 units in the absence of molybdate. The disadvantage is that the viscosity was seriously destroyed with pronounced delignification.

Suchy and Argyropoulos[123] applied a vanadium peroxo complex, i.e., ammonium triperoxophenanthroline vanadate, as the activator of alkaline peroxide delignification. The conditions and results are summarized in Table 2.33. It is observed that the activated peroxide delignification obtained higher brightness and a higher degree of delignification. Finally, they reported the optimum conditions as: 0.5% activator, 80°C, 2 hour retention time, 3% for both peroxide and alkali charges.

Table 2.33. The conditions and results of alkaline peroxide delignification activated by ammonium triperoxophenanthroline vanadate of a oxygen-delignified hemlock pulp.[123]

H <sub>2</sub> O <sub>2</sub> Charge (%)	Alkali charge (%)	Brightness (% ISO)		Kappa number	
		Control	Activated	Control	Activated
1	1.6	45.3	45.6	12.9	11.8
2	2.0	50.1	54.8	11.3	8.8
3	2.6	53.0	59.5	10.2	7.1
4	3.0	57.8	66.2	9.6	5.8
5	3.0	58.0	66.8	9.4	5.5
Initial kappa number = 17.5 Initial brightness = 30.3 Peroxide treatment time = 2 hours Temperature during peroxide treatment = 80°C MgSO <sub>4</sub> charge, % = 0.05 DTPA charge, % = 0.2 Activator charge = 2%					

Some bleach activators for peroxide have been reported to be effective for whitening textiles. Among them, a cationic bleach activator offers increased affinity for the negatively charged surface, which results in minimizing hydrolysis in the bleach solution and maximizing oxidation at the relevant sites on the substrate.[124] A novel cationic bleach activator, *N*-[4-triethylammoniomethyl) benzoyl] caprolactam chloride (3) (Figure 2.27), was reported recently by Lim et al.[124] The process was optimized and the optimal conditions are given in Table 2.34. By comparing the results for the conventional conditions and the optimal conditions (Table 2.34), it can be seen that the bleach activator system can obtain a similar level of whiteness at a lower temperature and in a reduced time. Also, this system results in less damage of fiber based on the DP data

than the conventional conditions do. Unfortunately, their study did not measure the carboxyl group content after the treatments.

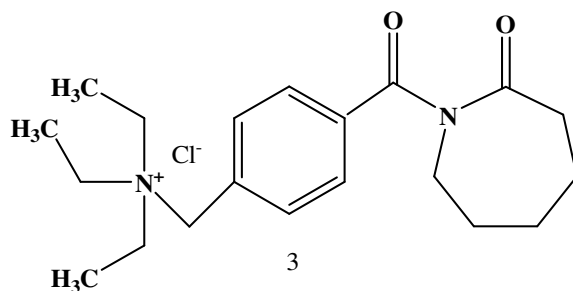


Figure 2.27. The structure of *N*-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride (3).[124]

Table 2.34. The conditions and results of conventional and cationic bleach activator added peroxide treatments.[124]

System	Conditions			Results	
	H <sub>2</sub> O <sub>2</sub> (g/200 ml)	Temp. (°C)	Time (min)	Whiteness index	DP
Conventional	1.71	25.0	110.0	75.91	2779
Bleach activator (0.6 g/200 ml)	1.71	18.3	102.5	75.56	2984

## 2.5 Carboxyl groups of pulp fibers

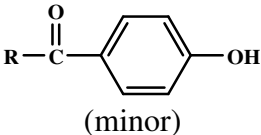
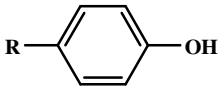
### 2.5.1 The origin and the determination of carboxyl groups of fibers

Table 2.35 summarizes the acidic functional groups associated with a solid wood matrix. Based on the results following from the pK<sub>a</sub> values of these acidic functions, all acidic groups remain unionized if wood material is brought to equilibrium with an aqueous solution at a low pH. However, raising the pH of the equilibrating solution to the

range of 6.0 to 8.5 only converts all carboxylic functions to carboxylate groups. The alcoholic hydroxyl groups are such weak acids that they are ionized only in the presence of strong alkali.[125] Therefore, the fiber charge of pulps is largely due to the dissociation of carboxyl groups of kraft pulp in the papermaking process which is under neutral or weakly acidic conditions.

Carboxylic acid groups of fibers can be distinguished as surface charge or bulk fiber charge depending on the location of acidic groups on the fiber.[4] Surface charge is the acidic groups which are located on the fiber's surface, on which it is believed that bond strength appears to be more dependent. Bulk fiber charge is the acidic groups located within the bulk of the fiber. The method of conductometric titration[126] is widely used to determine the bulk fiber charges. The surface charge of fibers can be evaluated by cationic polymer adsorption, which was first applied by Wågberg et al.[127] They used different polymers with different molecular masses to detect the bulk fiber charge and surface charge.[127]

Table 2.35. Type of acidic groups in wood.[125]

Acidic group	Structure	pK <sub>a</sub> (25°C)	Degree of ionization at pH 7, %
Carboxylic	R-CO <sub>2</sub> H (minor)	4-5	99-99.9
	R-CH(OR')CO <sub>2</sub> H	3-4	99.9-99.99
Phenolic	 (minor)	7-8	10-50
		9.5-10.5	0.03-0.3
Alcoholic	R-CH(OH)-R'	15-17	10 <sup>-8</sup> -10 <sup>-6</sup>
	R-CH(OR')CH(OH)-R''	13.5-15	10 <sup>-6</sup> -3×10 <sup>-5</sup>

R, R', and R'' = H, alkyl, or aryl

### 2.5.2 The effect of the bleaching process on carboxyl group content of fibers

Zhang et al.[128] summarized the carboxylic acid group content of several pulp samples (Table 2.36). The methodology utilized in their study was conductometric titration. It can be seen that peroxide treatment can increase the carboxyl group content of the TMP and CTMP.

Table 2.36. Carboxylic acid group content of various pulp determined by conductometric titration.[128]

Pulp sample	Carboxylic acid group content (mmol/100 g o.d. pulp)
Unbleached TMP	8.0-11.0
Bleached TMP (H <sub>2</sub> O <sub>2</sub> )	15.0-22.0
Unbleached CTMP	8.0-11.0
Bleached CTMP (H <sub>2</sub> O <sub>2</sub> )	15.0-25.0
Unbleached sulfate (kappa number <32)	6.0-8.0
Unbleached sulphite (kappa number <32)	5.0-6.0
Bleached sulphate	1.0-2.5

Laine[116] summarized the total fiber charge of softwood kraft pulp during ECF and TCF bleaching (Table 2.37). As seen in Table 2.37, oxygen delignification can increase the fiber charge by 5%.

Table 2.37. Total acid group content of softwood kraft pulps undertook various ECF and TCF bleaching sequences.[116]

Pulp after bleaching	Total acid content ( $\mu\text{eq/g}$ )
Kraft pulp	9.7
O	10.2
OZ	6.0
OZE	5.4
OZEP	5.4
OD	6.1
ODE	5.6
ODED	5.4
ODEDE	5.4
ODEDED	4.6

Oxygen delignification becomes one of the dominant bleaching process technologies. The principal advantages of adopting the oxygen delignification process are (1) improving bleaching process efficiency, (2) spent liquor is free of chlorine ions, (3) effluent can be handled by the kraft recovery system, and (4) decreased consumption of bleaching chemicals used in subsequent stages.[129] Gellerstedt and Lindfors[130] observed that there is an increase in the number of carboxylic acid groups when kraft pulp is bleached with oxygen, an additional advantage.

Toven[21] studied the effect of bleaching on the fiber charge of softwood kraft pulp. In his study, bleaching sequences including O (oxygen delignification), D (chlorine dioxide bleaching), Eo (alkaline extraction reinforced with oxygen), Z (ozone bleaching, and PO (peroxide bleaching together with pressurized oxygen were conducted. The data are shown in Table 2.38.

Table 2.38. Development of charged groups in softwood kraft pulp in bleaching by Toven.[21]

Pulp	Fiber charge	Hexeneuronic acid	Carboxylic groups in lignin
	(mmol/100 g o.d. pulp)		
Unbleached	12.3	1.69	2.5
O	11.3	1.78	2.0
ODEo	8.6	0.97	0.7
O(DZ)Eo	7.4	0.79	-
OZEo	7.6	0.67	1.0
ODEoD <sub>1</sub> ED <sub>2</sub>	5.1	0.03	-
O(DZ)EoD <sub>1</sub> ED <sub>2</sub>	4.9	0.03	-
ODEoQ(PO)	7.3	1.03	-
O(DZ)EoQ(PO)	6.8	0.70	-

The lowest fiber charge (4.9) of the fully bleached pulp was obtained by the bleaching process O(DZ)EoD<sub>1</sub>ED<sub>2</sub>. When the last bleaching sequences D<sub>1</sub>ED<sub>2</sub> was replaced by the Q(PO) stage, the fiber charge of the pulp was 6.8, 38.8% higher. Similar to the comparison above of ODEoD<sub>1</sub>ED<sub>2</sub> against ODEoQ(PO), the fiber charge increased by 43.1% by applying the (PO) stage as the final bleaching sequence. It can safely be concluded that the (PO) stage, i.e., hydrogen peroxide together with pressurized oxygen, leads to enhanced fiber charge. Also, if the two sets of the bleaching sequences are compared with regard to the difference of the chlorine and ozone bleaching stage (DZ), the resulting fiber charge suggests that the DZ stage reduces the fiber charge.

A study of the influence of oxygen delignification of softwood kraft pulp (SW-KP) was performed by a member of our research group, Zhang.[131] By dynamically profiling the carboxyl group content variation during the one-stage oxygen delignification of SW-KP with a kappa number of 32.5, the following results emerged:



- Fiber charge exhibited an initial 4-13% increase in the first 10-30 minutes followed by a steady or slight decrease (2-7%).
- The maximum of carboxyl group content of the pulp is found at kappa numbers from 20-24 (26-38% kappa number reduction).
- The optimal conditions for obtaining higher fiber carboxylic acid content for one-stage oxygen delignification are found at 1.5-2.5% NaOH, 800 kPa O<sub>2</sub> at 100°C.

Zhang also conducted a study of carboxylic acid group content of softwood kraft pulps after different various bleaching sequences (Table 2.39).[132] It was observed that the total pulp fiber charge of SW kraft pulps underwent the bleaching sequences of DEDED, D(EPO)DED, and OQPZP was 18.0-21.0% higher than those bleached with (D+C)EDED, (D+C)(EO)DED, and OD(EPO)DD. Also, hydrogen peroxide could increase fiber charge by 20.0%, when peroxide was applied as the terminal bleaching step instead of D in the bleaching sequence of OD(EPO)DP.

Table 2.39. The properties of softwood kraft pulps after different bleaching sequences.[132]

Bleaching sequence	Brightness (%)	Carboxylic acid content (μmol/g)
DEDED	87.8	41.1
D(EPO)DED	88.0	38.5
(D+C)EDED	87.4	35.9
(D+C)(EO)DED	88.2	32.9
OD(EPO)DD	87.1	32.3
OD(EPO)DP	88.1	39.2
OQPZP	87.1	41.2

### **2.5.3 The ionization of acid groups of pulp fibers – the Donnan theory**

Carboxylic acid groups of pulp fibers can become ionized during the papermaking process. These anionic groups can result in fiber swelling. The Donnan equilibrium theory[133] illustrates the ionized groups on one side of a membrane with the unequal distribution of free ions between that side of the membrane and the external solution. The Donnan theory has been applied to various systems since then. In Farrar and Neale's study of the cationic and anionic distribution ratio between cellulose and water for various salts, the Donnan theory was applied to cellulosic membrane for the first time.[134] Towers and Scallan[135] studied the mathematical model between fiber walls and the surrounding solution. Figure 2.28 represents the swelling of pulp fibers due to ionized acidic groups on the surface of pulps. In the case of cellulose fibers, the fiber wall acts as a membrane. The unequal distribution of ions across the fiber wall results in an osmotic pressure differential. This pressure differential then causes the fibers to swell.

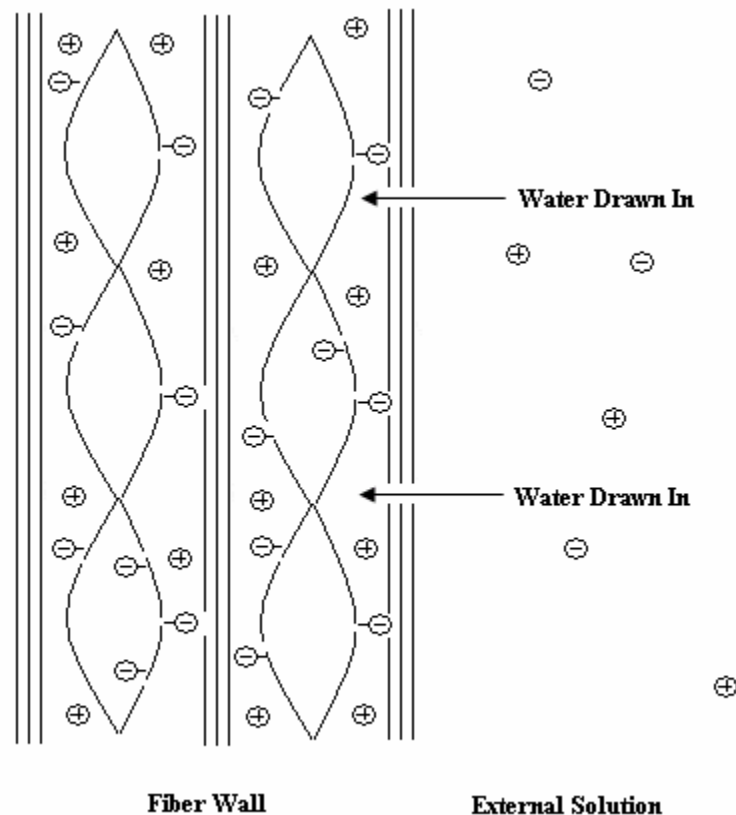
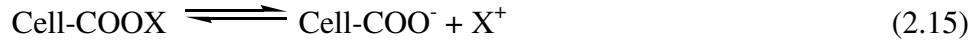


Figure 2.28. Representation of the swelling of pulp fibers due to ionized acidic groups on the surface of pulps.[135]

#### 2.5.4 The effect of acidic groups on the properties of fibers

Since acidic groups in pulps can become ionized, it is necessary to understand the role of cations as they act as counter-ions to these acidic groups. From a practical standpoint, industrial pulping takes place using tap water that contains numerous ions that can then affect the physical properties of the pulp. Scallan and Grignon[136] studied the effect of various cations on the properties of several different pulps. When cations are removed from pulp and replaced by a single cation species, it is found that the fiber

saturation point increases in the order of  $\text{Al}^{3+} < \text{H}^+ < \text{Mg}^{++} < \text{Ca}^{++} < \text{Li}^+ < \text{Na}^+$ . According to Proctor and Wilson[137], Scallan and Grignon theorize that fibers act much like gels:



where  $\text{X}^+$  is a free ion. Scallan and Grignon's work showed that there is a higher degree of swelling when  $\text{Na}^+$  is the counter ion than when  $\text{H}^+$  is. This makes sense given the fact that  $\text{Na}^+$  dissociates more easily than  $\text{H}^+$  from carboxylate groups.[6]

In a Katz and co-workers' study, it was observed that there is a near linear correlation between fiber saturation point and acidic group content for stone groundwood and refiner pulp treated with caustic soda.[138] It is their belief that the increased swelling is due to the increased number of acidic groups. They also observed an increase in the strength as the amount of acidic groups was enhanced.[138] They conclude that the increased swelling caused by the enhancement of acidic groups led to increased bond strength.

In another study by the same research group on the effects of alkali, ozone, successive alkali-ozone, and successive ozone-alkali on mechanical pulp, it was reported that both alkali-ozone and ozone-alkali successive treatments show a maximum amount of acidic groups achieved while swelling continues to increase.[8] Katz and Scallan[8] also explained that the swelling was partially due to the breaking of bonds within the wall of the fiber. It was verified by esterifying the acidic groups so that they could not dissociate and contribute to increased swelling. The results in Figure 2.29 show that the fiber swelling increased with the increase of acidic groups after ozonation. When the fiber with the highest acidic group content was esterified to the initial level of acidic group, fiber swelling decreased but not to the initial level. This indicated that breaking of

cross-links within the cell wall caused irreversible damage to the cell wall, thus resulting in a fiber wall more elastic and, thus, more easily swelled.[136]

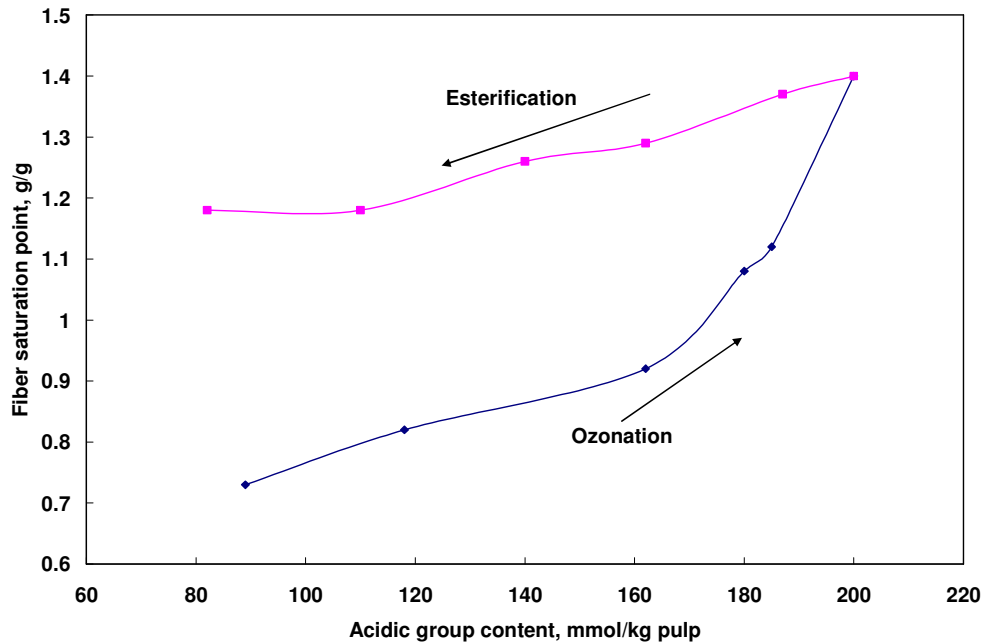


Figure 2.29. The effect of esterification on fiber swelling of a stone ground wood prepared from Douglas fir.[8]

It has also been stated that ionization of the acidic groups leading to increased swelling of the fibers is partly due to the electrostatic repulsion between the negatively charged carboxylate anions.[6, 136, 139]

A number of researchers have found a positive correlation between acid groups and bond strength of pulp fibers. Laine et al.[140] summarized the correlation between paper sheet tensile strength and the charge of the fibers. Firstly, the swelling and hence the flexibility of rewetted fibers can be enhanced with increasing charge. Secondly, the conformability of the fibers can be improved by increasing flexibility. Finally, it leads to higher tensile strength.[140]

Toven[21] studied the effect of bleaching processes of chemical pulp on fiber charge and reported that a (P+O) stage has a potential to increase fiber charge for D(E+O)Q and D/Z(E+O)Q kraft pulps (Table 2.40). It is also observed that the tensile index, water retention, density, and Scott bond strength of DEoQ(PO) pulp is greater than DEoD<sub>1</sub>ED<sub>2</sub> pulp. These results indicate that the increased fiber charge can improve the physical strength of paper and the water retention value to some extent.

Table 2.40. Paper properties of unbeaten ECF bleached softwood kraft pulps.[21]

Paper property	Bleached pulp		
	DEoD <sub>1</sub> ED <sub>2</sub>	DEoQ(PO)	(DZ)EoQ(PO)
Tensile index, Nm/g	25.9	26.8	27.8
Density, kg/m <sup>3</sup>	606	619	623
Scott bond, J/m <sup>2</sup>	100	109	109
Water retention value, g/g	1.14	1.22	1.21
Fiber charge, $\mu$ mol/g	51	73	68

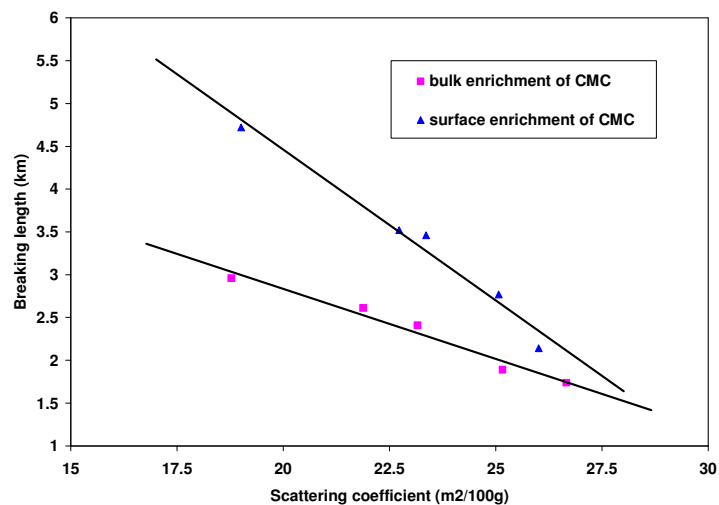
Zhang et al.[141] studied a peroxide stage on fully bleached pulps. The authors demonstrated that it is easy to enhance the final charge by 10-25%, which results in improved sheet tensile strength and stiffness properties.

## 2.6 Acidic group topochemistry of cellulose fibers

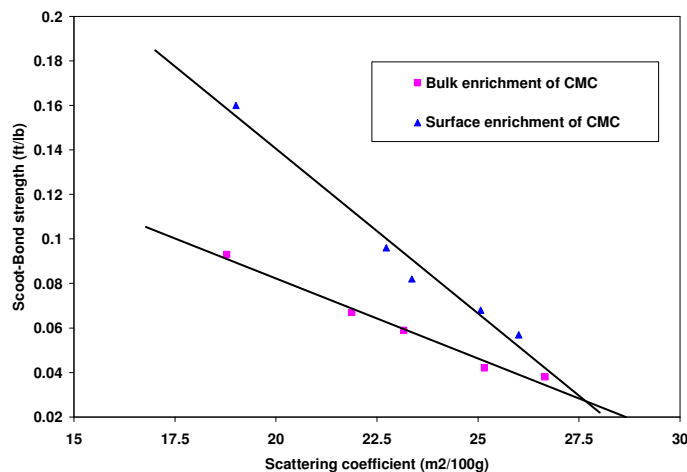
In addition to using oxidizing reagents to increase the number of acidic groups on pulp fibers, groups that contain acidic functionality can be graft polymerized onto fibers.

One of the popular approaches for introducing carboxylic acid groups into pulp fibers is the carboxymethylation of pulps using carboxymethyl cellulose (CMC). Barzyk et al.[9] is the first study that experimented with the topochemical modification of fibers

by carboxymethylation. The effectiveness of surface-substituted carboxylic acid groups compared to bulk-substituted (within the fiber) acidic groups was employed. The samples were prepared by enriching CMC to the bulk and surface of fibers, both holding 14.4 mmol/100 g o.d. pulp carboxyl group content. After this, the Tappi standard handsheets were prepared in the typical manner, with the exception that wet pressing pressures of 25-400 psi were conducted to form a serial of sheets having different scattering coefficients. Scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) confirmed the acid topochemistry of fibers. Surface-substituted carboxylic acid groups increased both breaking length and Scott-Bond strength to a greater extent than bulk-substituted acidic groups (see Figure 2.30).



A)



B)

Figure 2.30. The comparison of CMC enrichment on bulk and surface of fibers.

A) Scattering coefficient against breaking length and B) Scattering coefficient against Scott-Bond strength.[9]

More recently, Laine et al.[142] conducted a detailed study of CMC modified cellulosic fibers. Their study included the effects of temperature, pH, electrolyte concentration, and the degree of substitution of CMC on the attached CMC onto fibers



after washing (Table 2.41). The adsorption of CMC onto fibers was conducted in a 0.05M  $\text{CaCl}_2$  electrolyte solution. After treatment, if the pulp was washed by deionized water, the pulp was in its Ca-form. The pulp was also washed to its Na-form by using 0.001 M  $\text{NaHCO}_3$  whose pH value had been adjusted to 9.

Table 2.41. Conditions of CMC treatment of an unbeaten ECF bleached softwood kraft pulp.[142]

Parameters	Values
Temperature	80 and 120°C
pH value	3~13
Electrolyte concentration	Electrolyte free and $\text{CaCl}_2$ electrolyte solutions
Degree of substitution (D.S.) of CMC	0.39~0.80
CMC applied to the fibers	0~40 mg/g fibers

The conclusions are summarized as follows:[142]

- The treatment at an elevated temperature, i.e., 120°C, shows much higher attached CMC onto fibers. For example, attached CMC onto fibers after 120°C treatment is 28 mg/g, which is 2 times higher than that after 80°C treatment (13 mg/g).
- If the CMC treatment is subjected to electrolyte-free, no attachment takes place between pH 6 and pH 11. In the presence of electrolyte, CMC attachment decreases with the increase of pH value.
- Low D.S. CMC is more likely to attach to fibers than high D.S. CMC is.

Finally, a topochemical distribution of fiber charge was employed at two different molecular weights, i.e.,  $1 \cdot 10^6$  against  $2.8 \cdot 10^5$ , of CMC treatments. After treatment, the

surface charge of the two samples both increased by 26  $\mu\text{mol/g}$ . However, the high MW CMC treated fibers improved the total fiber charge by 27  $\mu\text{mol/g}$ , and the lower MW CMC by 44 $\mu\text{mol/g}$ . This result indicates that 96% of high MW CMC attached with fibers is attributed to the surface of fibers, but the lower MW CMC adsorbed onto the surface of fibers accounts for 59% of the total attached CMC. It suggests that CMC can be attached to cellulosic fiber surfaces with quantitative toposelectivity provided that the CMC has a sufficiently high MW.[142]

Beghelli and Lindström[143] studied the influence of carboxymethylation on the fiber flocculation process. The water retention value increased after CMC (DS=0.08) treatment, a 47% higher increase than the control. After the same treatment of CMC at 0.30% pulp consistency, the floc size decreased from 4.6 mm to 3.25 mm.

Lepoutre and co-workers[144] examined the water absorbance of pulp fibers that were modified by graft polymerization of polyacrylonitrile (PAN), followed by hydrolysis to create a polyacrylamide-sodium polyacrylate copolymer graft (Figure 2.31). They observed that the water retention value (WRV) increased by 30 times using this technique.

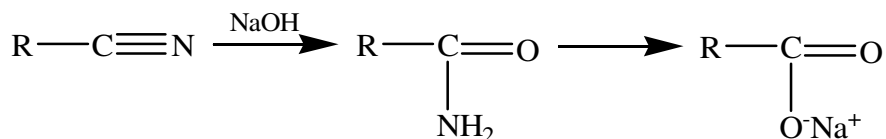


Figure 2.31. Hydrolysis of nitrile group to obtain carboxylate group.[144]

## 2.7 TEMPO-mediated oxidation of polysaccharides

Polysaccharides, including starch, cellulose, and wood fibers, etc., serve many commercial applications in the food, textile, energy, and paper industries.[145] In terms of the modification of cellulose and starch, the primary hydroxyl group (C-6) and the secondary hydroxyl groups (C-2 and C-3) are available for oxidation. Oxidation is capable of introducing carbonyl and carboxyl groups. Periodate[146] and hypochlorite[147] oxidation of starch can lead to 2,3-scission resulting in the formation of dialdehyde and dicarboxylic structures. During the last decade, a water-soluble nitroxyl radical, 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), has become one of the most promising agents to convert primary hydroxyl groups of polysaccharides into the corresponding aldehydes and/or carboxylic acid groups. Contrary to enzymatic or metal catalyzed oxidation, the TEMPO-oxidation process has many advantages[148]:

- It is highly effective in the conversion of the high molecular weight of polysaccharides;
- It has a high reaction rate and yield, and a high selectivity;
- There is a modest degradation of polysaccharides throughout the process.

The mechanism of TEMPO--NaClO-NaBr oxidation of polysaccharides is presented in Figure 2.32. The process can be illustrated as follows: (1) the generation of the TEMPO<sup>+</sup> ion, i.e., the nitrosonium ion, from the TEMPO radical. (2) TEMPO<sup>+</sup> converts the C-6 hydroxyl groups of cellulose to carboxylates, and becomes TEMPOH, i.e., hydroxylamine, which is the reduced form of TEMPO. The proton form of carboxylates of cellulose is converted to the sodium salt form in the presence of sodium

hydroxide. (3) The nitrosonium ion is regenerated by the reaction of hydroxylamine with hypobromide. (4) Hypobromide is generated by hypochlorite and bromide.[31]

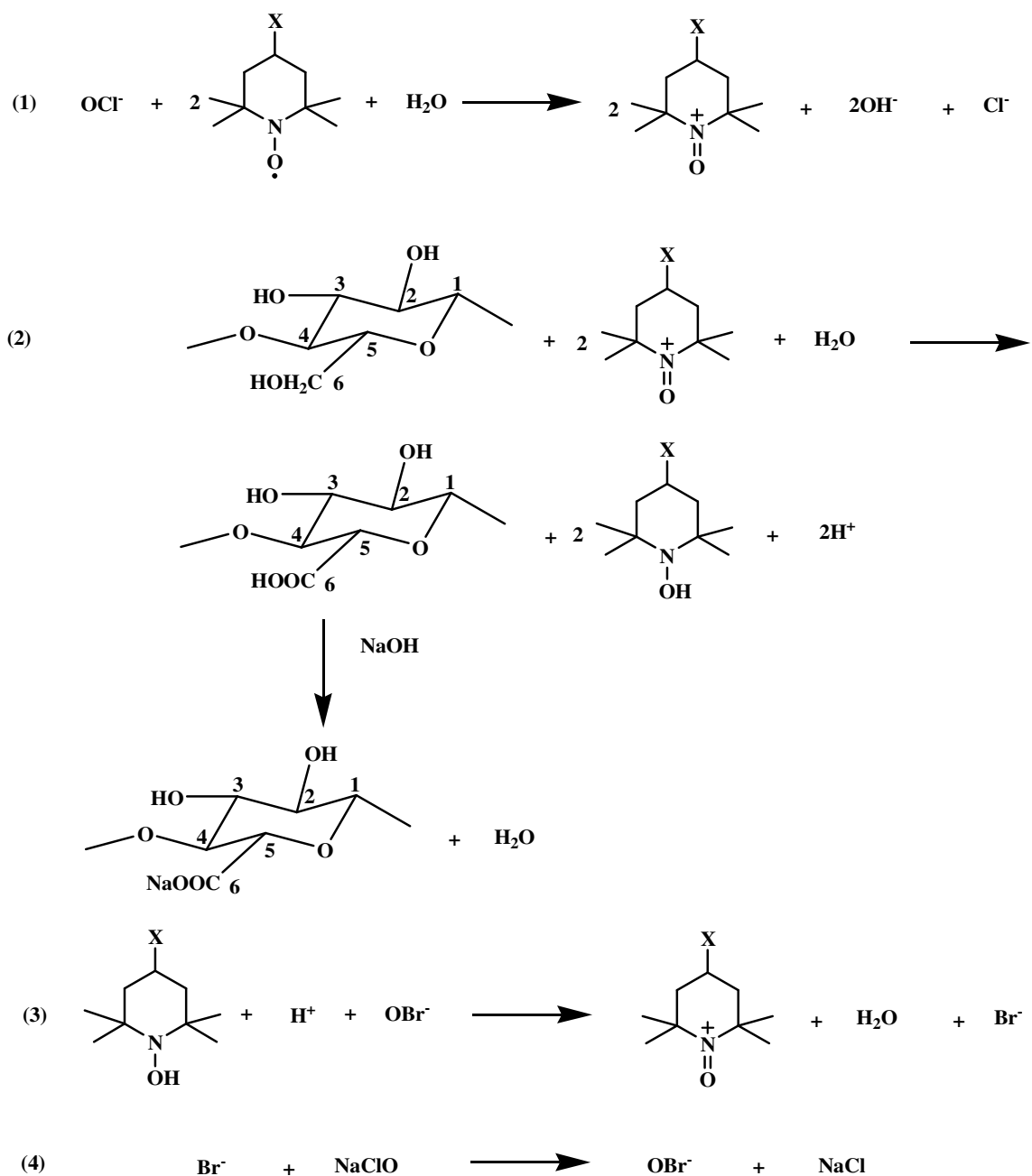


Figure 2.32. The mechanism of TEMPO-mediated oxidation of the C-6 hydroxyl group of cellulose.[31]

The TEMPO-mediated oxidation system was first applied to water-soluble polysaccharides by Nooy et al.[23] The optimum pH for this system of water-soluble glucans was found to be between 10 and 11, and corresponding polyuronic acids were obtained.[23] In a further study of pullulan[24], pullulan was oxidatively depolymerized and the minimum depolymerization was in the pH range of 9.2 to 9.7.

Isogai and Kato[25] applied TEMPO-NaBr-NaClO oxidation to generate polyuronic acid on a series of cellulosic samples (Table 2.42). In Table 2.42, it can be seen that native cellulose is not soluble in a TEMPO-mediated medium, while regenerated or mercerized cellulose is soluble.

Table 2.42. Solubility of cellulose samples in the TEMPO-mediated oxidation medium at room temperature and pH value of 10-11.[25]

Cellulose sample	Solubility
Native cellulose	
Microcrystalline cellulose powder	No
Micro-®brillated cellulose prepared from bleached kraft pulp	No
Linter cellulose	No
Softwood bleached kraft pulp (SBKP)	No
Hardwood bleached kraft pulp (HBKP)	No
Bacterial cellulose	No
Regenerated or mercerized cellulose	
Amorphous cellulose	Yes
Regenerated cellulose	Yes
Rayon	Yes
Mercerized microcrystalline cellulose (never-dried)	Yes
Mercerized linter cellulose (never-dried)	Yes
Mercerized SBKP (never-dried)	Yes
Mercerized HBKP (never-dried)	Yes
Mercerized bacterial cellulose (never-dried)	Yes
Others	
Chitin	Yes
Chitosan	Yes

For regenerated, or mercerized cellulose, Isogai and Kato's[25] study showed that almost all C6 primary alcohol groups could be converted to carboxyl groups and that the charge of TEMPO, reaction time and temperature were the key factors controlling the depolymerization of cellulose. For softwood and hardwood bleached kraft pulps, bacterial cellulose, and microcrystalline cellulose powder, they demonstrated that TEMPO oxidation of these substrates was less efficient.[25]

The depolymerization of polysaccharides during TEMPO-mediated oxidation has been attributed to sodium hypochlorite oxidation of polysaccharides, which leads to a 2,3-scission of the glucose unit; resulting in the formation of dialdehyde and dicarboxylic structures.[147] The presence of carbonyl groups at C-2, C-3 in a glucose unit facilitates depolymerization of celluloses via  $\beta$ -alkoxy fragmentation in an alkaline medium.[149] The mechanism is shown in Figure 2.33.

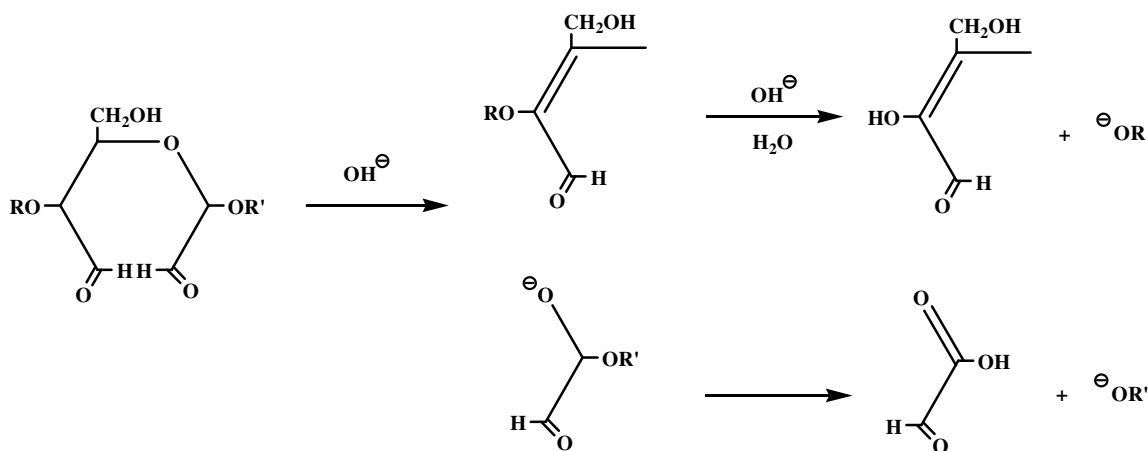


Figure 2.33. The mechanism of  $\beta$ -alkoxy fragmentation of cellulose with C-2 and C-3 aldehyde in alkaline medium.[149]

In addition, depolymerization can occur via  $\beta$ -elimination.[24-27] Interestingly, a bromide-free TEMPO-mediated oxidation of starch has been reported to proceed with high selectivity and limited depolymerization.[29]

The first study using TEMPO-oxidation to modify pulp fibers was conducted by Kitaoka et al.[26] A commercial bleached hardwood (HW) kraft pulp was investigated in this study. Table 2.43 summarizes the experimental conditions.

Table 2.43. The conditions of TEMPO-mediated oxidation of bleached HW kraft pulp fibers by Kitaoka et al.[26]

Parameters	Condition
CSF	470 ml
Pulp, o.d.	10 g
TEMPO	0.025 g
Sodium bromide	0.25 g
Sodium hypochlorite solution (10.5% content of NaClO)	2.5-40 ml
pH value during reaction	~10.5
Temperature	20°C
Reaction time	2 hour
Total volume	750 ml

The response variables are carboxyl group content, degree of polymerization, and the physical properties of paper, including tear index, tensile index, density, and brightness, which are partially presented in Table 2.44. Carboxyl group content, tensile index, and brightness of the oxidized pulps increased as the NaClO charge increased. Tear index and density did not show any obvious change after TEMPO-oxidation at different levels of the NaClO charge; in fact, the changes in these two properties were very small, in the small range of  $8.0 \pm 0.2 \text{ mN} \cdot \text{m}^2/\text{g}$  and  $0.60 \pm 0.02 \text{ g/cm}^3$ , respectively.

Table 2.44. The results of TEMPO-mediated oxidation of bleached HW kraft pulp fibers  
by Kitaoka et al.[26]

NaClO charge (% on o.d. pulp)	Carboxyl group content (mmol/100 g o.d. pulp)	Degree of polymerization	Tensile index (N·m/g)	Brightness
0	6	910	36.7	76
5	19	270	37.0	77
10	28	250	37.5	77.5
20	47	220	37.6	80
40	47	200	37.6	80

Le Roux et al.[150] modified unbleached TMP using TEMPO-oxidation to improve filler retention. The conditions are presented in Table 2.45. The carboxyl group content of the original TMP was 20 mmol/100 g o.d. pulp; it increased to 100, 150, and 180 after 1, 4, and 7 hour treatments, respectively.

Table 2.45. The conditions of TEMPO-mediated oxidation of unbleached TMP by Le  
Roux et al.[150]

Parameters	Condition
Pulp, o.d.	30 g
TEMPO additive	400 mg
Sodium bromide	15 g
pH value during reaction	~10
Temperature	20°C
Reaction time	1, 4, and 7 hour

Subsequently, the oxidized pulp was employed by amidation, which converts the carboxyl groups to quaternary amine ( $\text{NH}_4^+$ ). Giard's reagent[3] and water soluble carboiimide (WSC) salt was applied in the conditions of 1% consistency, room temperature, pH value of 4.75, and a 5 hour treatment. The pulp was treated by adding a cationic retention aid (0.25 kg/ton on o.d. pulp) and a filler, ground calcium carbonate



(GCC) (20% on o.d. pulp). Finally, GCC retention was determined and the results are presented in Figure 2.34. This graph clearly shows that the GCC filler retention of the TMP mixture containing oxidized TMP is 12.5% lower than that of only TMP. On the contrary, the GCC filler retention containing oxidized TMP after amidation is 28% higher than that of only TMP. These results indicate that improved filler retention of TMP can be obtained with a higher carboxyl group content of fibers when the carboxyl groups are converted into cationic form.

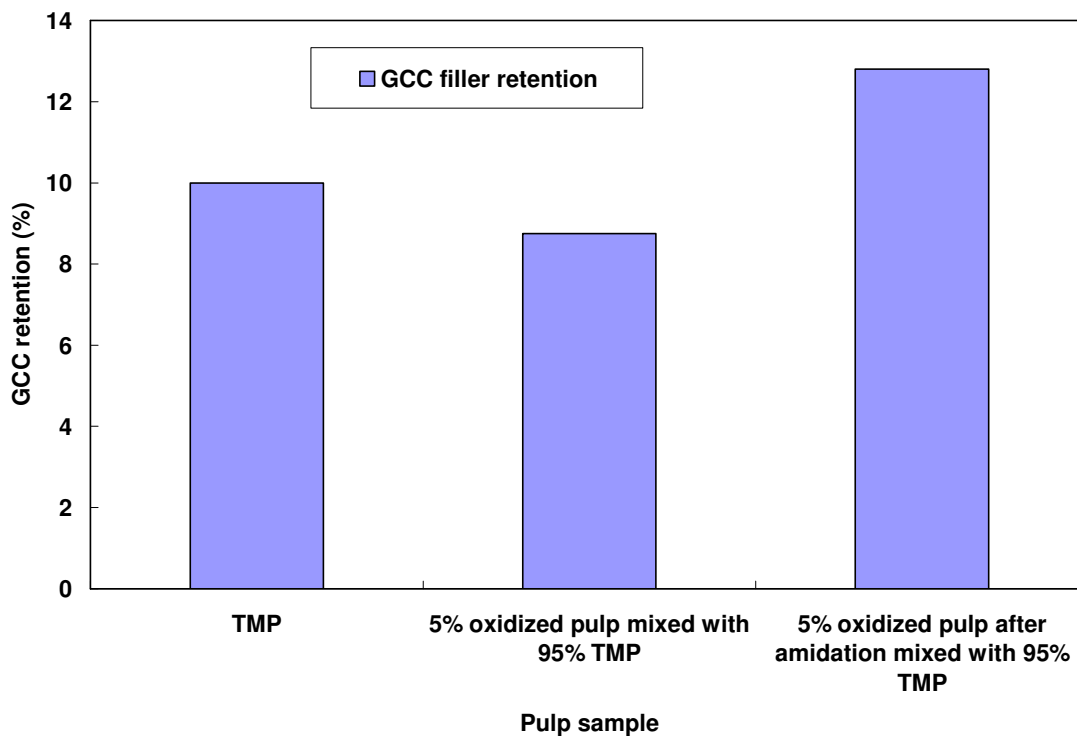


Figure 2.34. The results of GCC filler retention of various TMP with cationic retention aid treatment studied by Le Roux et al.[150]

## 2.8 Other enzymatic and chemical modification of fibers

Chandra et al.[151] modified the high lignin content softwood kraft pulp with Laccase to improve paper strength. The results are presented in Table 2.46. It is evident from the table that the wet tensile index of the pulp after Laccase treatment increased by 57% compared to the control.

Table 2.46. Carboxylic acid group content and wet tensile index of high lignin softwood kraft pulp treated with Laccase.[151]

Treatment	Carboxylic acid group content ( $\mu\text{mol/g}$ )	Tensile index (Nm/g)
Control	151	1.05
Laccase	162	1.65
Laccase + Gallic acid (276 $\mu\text{mol/g}$ pulp)	195	1.71

In a study by Gellerstedt et al.[152], the TCF bleached kraft pulp was subjected to succinylation for either 6 or 12 hours. Their objective was to increase fiber charge. The pulp was first disintegrated and then dried in a vacuum oven overnight at 50°C. Subsequently, it was treated by soxhlet extraction in acetone and further dried in the vacuum oven. The conditions of succinylation are described in Table 2.47. After succinylation, the fibers were washed thoroughly with ethanol and acetone to remove pyridine, then extracted by acetone and dried in the vacuum oven. Table 2.48 summarizes the results with regard to the fiber charge and surface charge of fibers after succinylation.

Table 2.47. The conditions of succinylation of TCF bleached kraft pulp.[152]

Parameters	Value
Succinic anhydride	4 g
Pyridine	250 ml
Fibers	5 g
Temperature	room temperature
Reaction time	0, 6, 12 hour

Table 2.48. Fiber charge and surface charge as a function of treatment time of succinylated TCF bleached kraft pulp.[152]

Treatment time (hr)	Fiber charge (mmol/100 g o.d. pulp)	Surface charge (mmol/100 g o.d. pulp) Using poly-DADMAC as the polyelectrolyte
0	8	0.4
6	31	4.1
12	68	10.0

In Table 2.48, it can be seen that fiber charge and surface charge increased as time increased. After determining the fibers perimeter change, it was found that fiber perimeter can increase 25% when the fiber charge is improved to 68 mmol/100 g o.d. pulp. This result indicates a positive effect of fiber charge on fiber swelling.[152]

## 2.9 Carbonyl groups of cellulose fibers

It is known that ketone and aldehyde groups in cellulose fibers are introduced during pulping and bleaching processes.[153] It has also been reported that in addition to ketone and aldehyde forms, carbonyl groups in fibers are present as hydrates and/or hemiacetals/hemiketals.[154] There are a few conventional approaches to determine the

amount of carbonyl groups in cellulose fibers. Copper number measurement is used to estimate the quantity of carbonyl groups in bleached pulp.[155] The reaction mechanism for this protocol is dependent on copper (II) salts that are reduced by reductive groups in fibers with the resulting Cu (I) determined titrimetrically. Table 2.49 outlines copper number values of various cellulosic samples. It is observed that ozone bleaching can introduce carbonyl groups into fibers.

Table 2.49. Copper number of various pulps by Röhring et al.[159]

Pulp	Copper number
Eucalyptus kraft pulp	0.25
Eucalyptus kraft pulp after ozone bleaching	1.51
Eucalyptus kraft pulp after ozone and peroxide stage	1.20
Beech sulfite pulp	1.25
Beech sulfite pulp after ozone bleaching	1.50
Beech sulfite pulp after ozone and peroxide stage	1.50

Measuring carbonyl groups is also possible by the oxime method [37], the hydrazine method[156], and the cyanohydrin method[157]. A new method is the determination of carbonyl groups in cellulose by fluorescence labeling.[158-160] This methodology is called CCOA to reference the marker carbazole-9-carbonyloxyamine. By comparing the results obtained by the methods CCOA and copper number, a linear relationship has been found between them.[159]

Carbonyl groups in pulps can be reduced with sodium borohydride ( $\text{NaBH}_4$ ) under caustic conditions.[161, 162] Carbonyl groups of fibers initiate the scission of the chains in an alkaline medium by a  $\beta$ -glucoxy elimination reaction.[100] Sodium

borohydride treatment for fibers has been frequently studied to improve the performance of peroxide bleaching and produce high brightness pulp[98, 163, 164]. It also can obtain better selectivity of the bleaching process, including oxygen bleaching and ozone bleaching[165, 166]. A sodium borohydride treatment of an ozonated softwood kraft pulp was conducted by Odermatt et al. (Table 2.50).[165] Table 2.50 describes the conditions of general sodium borohydride treatment on fibers, and the result indicates that sodium borohydride treatment can increase brightness by 3 units.

Table 2.50. The conditions of sodium borohydride treatment of an ozonated softwood kraft pulp.[165]

Sodium borohydride (%)	NaOH (%)	Brightness (% ISO)
0	0.4	80
0.03	0.4	80
0.06	0.4	81.2
0.09	0.4	82.2
0.12	0.4	82.5
0.15	0.5	82.9

\* The remaining conditions are: 70°C, 30 min, 10% consistency.

## 2.10 Fiber beating and drying

It has been well-established that mechanical treatment of fibers can modify their morphology and structure.[167-173] The objective of refining chemical pulps is an improvement in the properties of the end products.[174, 175] Bhardwaj et al.[176] determined the total fiber charge and surface charge of pulps after refining. It was found

that the total charge of unbleached and bleached softwood kraft pulp remained constant as refining increased, while the surface charge increased (Table 2.51). The increase in surface charge is due to the fact that refining increases both the outer and inner fibrillation; therefore, these actions enhance surface accessibility and facilitate greater interaction between the carboxyl groups and the cationic polymer.[176]

Table 2.51. Relation of ratio of surface charge to total fiber charge with pulp freeness of unbleached softwood kraft pulp.[176]

Freeness (ml)	Ratio of surface charge/total fiber charge
750	0.46
640	0.67
560	0.76
460	0.73
370	0.76

Drying or water removal of wood pulp fibers leads to shrinkage of the internal fiber volume.[177] This phenomenon is also termed “hornification”. Hornification causes less fiber bonding and a loss of swelling.[7, 178-180] Carboxyl groups can influence the hornification of kraft fibers. For example, Lindström and Carlsson[7] carboxymethylated fibers. The degree of hornification decreased if carboxyl groups were in their ionized form (instead of proton form) during drying. The degree of hornification can be quantified according to the change of the water retention value of fibers. Weise defined it as Equation 2.17.[181]

$$\text{Hornification, \%} = \frac{WRV_0 - WRV_1}{WRV_0} \times 100 \quad (2.17)$$

where,  $WRV_0$  and  $WRV_1$  are the water retention values of the never-dried fibers and dried fibers, respectively.

Rebuzzi and Evtuguin[182] studied the effect of glucuronoxylan (GX) on the hornification of *Eucalyptus globulus* bleached pulps. By extracting GX with KOH at different times, pulps with a different content of GX were obtained. The degree of hornification of these pulps was analyzed (Table 2.52). It is observed that the degree of hornification decreases with the increment of GX content of pulp fibers.

Table 2.52. The effect of glucuronoxylan on the hornification of *Eucalyptus globulus* bleached pulps.[182]

Xylan content in kraft pulp (%)	Hornification (%)
17.1	15
9.3	25
6.8	34
4.0	42

## CHAPTER 3

### EXPERIMENTAL MATERIALS AND METHODS

This chapter presents the materials, methods, and equipment utilized during this research. If not otherwise stated, the chemicals used in this study were purchased from Aldrich, JT Baker, and Fisher as analytical grade and were used as received.

#### 3.1 Material and preparation

##### 3.1.1 Experiment 1 (Chapter 4)

In this section, the materials pertinent to the first experiment, which is elaborated on Chapter 4, are presented. The first experiment undertaken in this research deals with the kraft pulping of loblolly pine (*Pinus taeda*).

##### 3.1.1.1 Kraft pulping of loblolly pine (*Pinus taeda*)

The air dried loblolly pine wood chips were obtained from T. J. Dyer[183]. The thickness of the wood chips ranged from 2 to 8 mm, and prior to use the chips were stored in a cold room at 4°C.

Two studies of kraft cooks were conducted in this experiment. The first study prepared a series of kraft pulps employing an M/K batch digester (Figure 3.1). The kraft pulping conditions, pulp kappa number and viscosity values are summarized in Table 3.1.



This first series of pulping was performed at the Institute of Paper Science and Technology (IPST) at the Georgia Institute of Technology (GaTech).

The second study within this experiment prepared a series of softwood kraft pulps using a conventional batch digester (CK) and laboratory simulation of Lo-Solids (LS) kraft pulping. It was conducted at Ahlstrom Machinery Corp., in Glens Falls, N.Y. using established procedures.[91] The conditions and results are presented in Table 3.2. Results are discussed in Chapter 4.



Figure 3.1. Photograph of the M/K digester for kraft pulping.

Table 3.1. Pulping parameters and the results of the laboratory kraft pulping of loblolly pine  
conducted in an M/K batch digester.

Parameters	Kraft pulping ID/Pulp abbreviation								
	M/K1	M/K2	M/K3	M/K4	M/K5	M/K6	M/K7	M/K8	M/K9
% EA	12	16	20	24	12	16	20	24	12
% Sulfidity	30	30	30	30	50	50	50	50	50
H-factor	1000	1000	1000	1000	1000	1000	1000	1000	1000
Maximum temp. (°C)	170	170	170	170	170	170	170	170	160
L/W	4	4	4	4	4	4	4	4	4
Kappa number	61.7	31.6	22.1	17.2	44.4	26.6	18.5	14.2	46.6
Intrinsic viscosity (ml/g)	1084	1024	858	684	1245	1029	835	686	1321

Table 3.2. Conventional and Lo-Solids pulping conditions of loblolly pine and pulp properties after pulping.

(L:W=3.5:1)

Parameters	Conventional cooking (CK)				Lo-Solids cooking (LS)				
	CK-1	CK-2	CK-3	CK-4	LS-1	LS-2	LS-3	LS-4	LS-5
EA charge									
Impregnation, % on wood NaOH	20.5	20.5	20.5	20.5	10.0	10.0	10.0	10.0	10.0
Displacement 1, g/l NaOH	NA	NA	NA	NA	89.6	92.9	92.9	92.8	92.8
Displacement 2, g/l NaOH	NA	NA	NA	NA	45.4	45.4	45.4	45.0	45.0
% White liquor sulfidity, %AA	30.0	29.8	29.8	30.0	29.8	29.8	29.8	30.0	30.0
Intrinsic viscosity (ml/g)	669	864	1068	1120	794	833	923	1140	1289
Maximum pulping temp. (°C)	171.0	170.0	168.0	166.0	170.0	169.0	166.3	166.6	166.3
H-factor	4000	1999	1201	995	4489	4126	3362	2442	2008
Kappa number	13.9	21.3	33.0	39.9	16.0	17.1	19.1	26.1	29.3

### 3.1.1.2 The preparation of holocellulose from softwood unbleached kraft pulp

Holocellulose pulps were prepared following the current method in the literature.[184] In brief, air dry softwood unbleached kraft pulp fibers equivalent to 1.500 g of oven-dry fibers were dispersed into 125.00 ml of deionized water in a 300 ml beaker, followed by the addition of glacial acetic acid (1.00 ml, 0.017 mol) and  $\text{NaClO}_2$  (1.00 g, 0.011 mol). The beaker was sealed using parafilm and placed on a hotplate. The slurry was heated to 70°C and stirred for 1 hour. Thereafter, a second addition of glacial acetic acid (1.00 ml, 0.017 mol) and  $\text{NaClO}_2$  (1.00 gr, 0.011 mol) was added, and the slurry was treated for an additional hour on the hotplate with stirring. The holocellulose pulp sample was then cooled to room temperature and stored overnight at 3°C. The sample was filtered and thoroughly washed with 2000 ml of deionized water. The pulp was air dried and the carboxyl group content was measured.

### 3.1.2 Experiment 2 (Chapter 5)

#### 3.1.2.1 Peroxide bleaching of ECF bleached softwood kraft pulp

The pulp used for the peroxide treatment was obtained from a pulp mill. It was an ECF bleached softwood kraft pulp which had undergone a D(E+O+P)D bleaching sequence. Basic pulp properties included a Tappi brightness of 84.5, a copper number of 0.43, an intrinsic viscosity of 672 ml/g, and a carboxyl group content of 3.98 mmol/100 g o.d. pulp. The pulp was thoroughly washed with distilled water until the effluent pH was neutral; it was then pressed to around 30.0% consistency, and stored at 2°C prior to use.

The pulp was bleached with alkali peroxide in a sealed plastic bag placed in a water bath. All bleaching studies were conducted with 10.0% pulp consistency, a bleaching time of 2.0 hour and a 2.0% charge of NaOH. The pulp mixture was vigorously mixed with a glass rod initially and then manually kneaded every 15 min during the reaction. The peroxide charge of 0.5%, 1.0%, 2.0%, 4.0%, and 8.0% were examined at bleaching temperatures of 60.0 and 90.0°C. Another set of peroxide treatments, which employed a 2.0% peroxide charge, were performed at a series of temperatures from 40.0 to 90.0°C. After the reaction, the pulps were thoroughly washed using Büchner funnel with suction. Carboxyl group contents, copper number, intrinsic viscosity, brightness, and the physical strength of paper were measured.

#### 3.1.2.2 Sodium borohydride ( $\text{NaBH}_4$ ) treatment of ECF bleached softwood kraft pulp

The ECF bleached kraft pulp was treated with sodium borohydride in a sealed plastic bag placed in a 60.0°C water bath for 2.0 hour. The caustic charge was 2.0% NaOH on o.d. pulp, and the sodium borohydride ( $\text{NaBH}_4$ ) was 0.5% on o.d. pulp. The slurry consistency was 10.0%, and the slurry was manually kneaded every 15 minutes. After 2 hours of treatment, the pulp was filtered and washed with 4 liters of distilled water in a Büchner funnel with suction. It was air dried in order to determine the carboxyl group content and copper number.

#### 3.1.2.3 Adsorption of cationic starch into ECF bleached softwood kraft pulp fibers

A cationic corn starch (CATO 31) with 0.35% quaternary nitrogen substitution was obtained from National Starch and Chemical Company. The solution was prepared according to the methodology outlined in Yan et al.[185] 1% starch solution was cooked at 95°C for 30 min. The pulp slurry was prepared to a consistency of 0.40%. Cationic starch was added in concentrations of 0.25%, 0.50%, 1.0%, and 2.0% to the pulp (based on o.d. fibers), and allowed to adsorb for 30 min. Subsequently, handsheets were prepared based on the Tappi standard method T 205.[186] Tensile strength and burst strength were measured.

#### 3.1.2.4 Drying and hornification of ECF bleached softwood kraft pulp

Six ECF bleached SW kraft pulp samples were prepared. Sample 1: Handsheets of the control pulp were air dried at 23°C (Tappi standard conditioning room temperature). Sample 2: Handsheets of the control pulp were dried at 105°C on a hot plate. A higher fiber charge pulp (HCP) was prepared by treating the control pulp at the conditions of 2% NaOH, 1% H<sub>2</sub>O<sub>2</sub>, 60°C, and 2 hour; HCP has a 12.8% higher fiber charge than control does. Samples 3 and 4: Handsheets of HCP were dried at 23°C and 105°C, respectively. Sample 5: Sample 2 was rewetted in water, which was then disintegrated, filtered, and alkaline peroxide treated. Handsheets were prepared and dried at 23°C. Sample 6: Protocol for Sample 5 was followed, but in this case, the handsheets were dried at 105°C. The drying at 105°C was performed on a hotplate with a constant temperature of 105°C. The drying time was set to 10 min. The intrinsic viscosity, carboxyl group content, tensile index, and burst index of each sample were measured.

### **3.1.3 Experiment 3 (Chapter 6)**

#### **3.1.3.1 TEMPO-mediated oxidation of ECF bleached softwood kraft pulp**

The same ECF bleached softwood kraft pulp discussed in Section 3.1.2.1 in page 94 was used to conduct this experiment. The sodium hypochlorite solution was purchased from Sigma-Aldrich. The solution contained 10% available chlorine and had a density of 1.206 g/ml, as labeled.

The oxidation procedure was based on current methodology in the literature.[26, 32] A diagram of the TEMPO-mediated oxidation technique used in this study is illustrated in Figure 3.2. The never-dried ECF bleached softwood kraft pulp (20.00 g oven-dried), TEMPO (0.050 g, 0.320 mmol), and KBr (0.500 g, 4.202 mmol) were mixed with deionized water (1840 ml) in a 2 liter beaker. Subsequently, a NaClO solution containing 10% available chlorine was added into the slurry. There were five levels of NaClO charge employed in this study, which were 1.70, 3.40, 8.50, 17.01, and 34.01 mmol, respectively. If the initial pH after adding NaClO was lower than 10.5, then the pH value was adjusted to 10.5 by adding 1.00 N NaOH. The TEMPO-oxidation reactions were performed at the room temperature (23 °C) for 2.0 h.

An additional series of TEMPO-oxidations were conducted at 4 to 80 °C, with a constant 0.85 mmol NaClO/g o.d. pulp. The effect of pH on oxidation was examined using the same conditions described above, except that the reaction pH was varied from 7.10 to 10.00. When the reaction started, pH values decreased due to the formation of carboxyl groups in fibers. Once the reaction pH value decreased to the targeted value, it

was kept constant by adding 1.00 N NaOH.

After reaction, the pulp was filtered and rinsed with 4 liters of distilled water in a Büchner funnel with suction. The carboxyl group content, copper number, viscosity, and physical testing of paper were then determined.

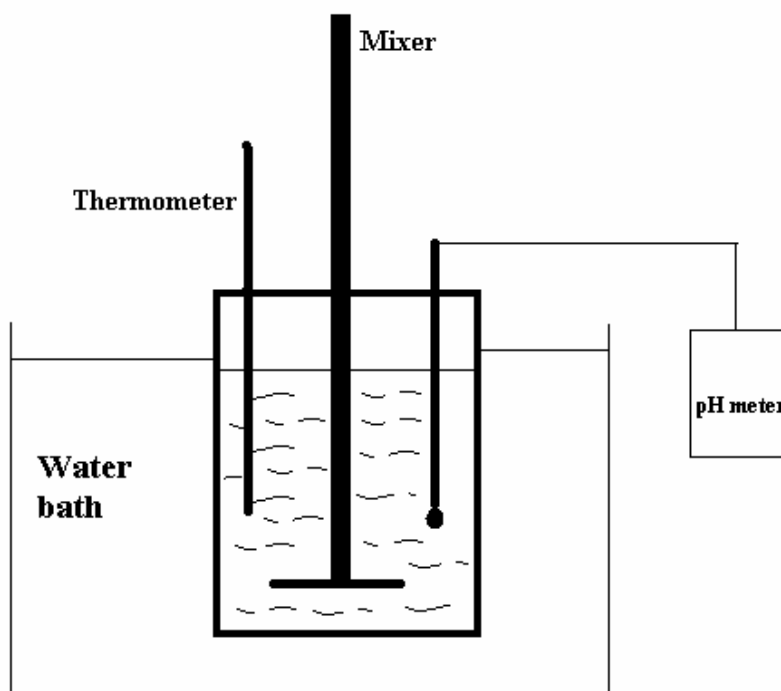


Figure 3.2. The diagram of TEMPO-mediated oxidation of ECF bleached SW kraft pulp.

#### 3.1.3.2 Preparation of cross-linked fibers

Polyethylene glycol (PEG) (1.00 g, MW 3,350 or 10,000) was dissolved in deionized water (99.00 ml) which had been acidified to pH 2.00 with 1.00 N hydrochloric acid. The solution was mixed until the dissolution of PEG was visually complete. ECF bleached softwood kraft pulp fibers (2.00 g oven-dried) were then added, mixed for 15 minutes and then filtered without washing. The fibers were heated at 105 °C for 30



minutes. The treated fibers were disintegrated and soaked in a pH 8.5 NaOH aqueous solution (300.00 g) for 1 hour. Subsequently, the water retention value of the treated pulp was measured.

#### **3.1.4 PFI refining of pulp fibers**

PFI refining is based on the Tappi standard method T 248.[187] In Chapter 4, the holocellulose samples were refined for 2000 revolutions (r) to obtain similar curl and kink. The curl and kink were measured by a fiber quality analyzer (FQA). In Chapter 5, the various beating degrees of the ECF bleached pulps were defined by the number of revolutions, namely: 500, 1000, 2000, 4000, and 8000 r.



Figure 3.3. Photograph of PFI refiner.

## 3.2 Methods and measurements

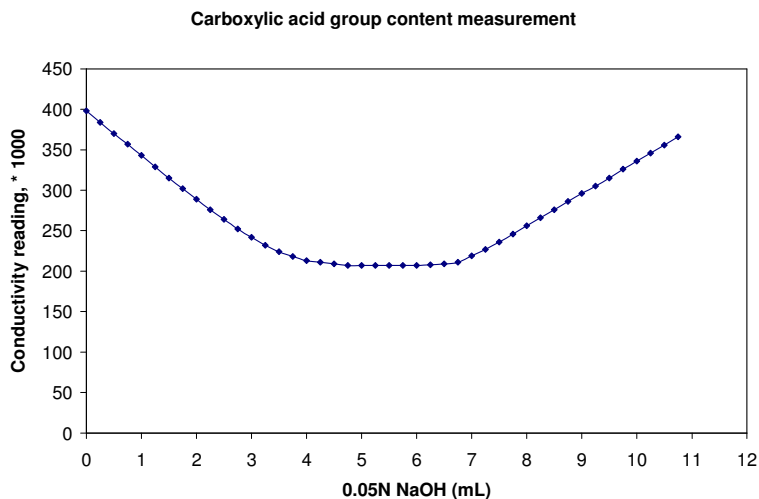
### 3.2.1 Carboxylic acid group content of fibers

Bulk carboxylic acid group content was measured by using conductometric titration methodology.[126] Air dry fibers equivalent to 1.500 g of oven dry fibers were added to 300.0 ml of 0.10 N HCl and stirred for one hour. The pulp was then filtered and washed with 2000 ml of deionized water until the effluent water conductivity was less than 5 mS cm<sup>-1</sup>. The washed pulp was treated with a 0.001 N NaCl (250.00 ml) and 0.10 N HCl solution (1.50 ml), stirred and conductrimetrically titrated with 0.05 N NaOH in an atmosphere of nitrogen. The conductivity (umhos \* 1000) was plotted against the volume of NaOH in Excel and the curve was parabolic in shape (Figure 3.4-I). Trend lines were added in Excel in order to draw lines through each linear region on the graph (Figure 3.4-II). A line across the “flat” portion of the curve was plotted too. The intersections of the left trendline and the right trendline with the flat line were obtained, and their X-axis values are represented by *A* and *B*. The carboxylic acid content of pulp fibers is obtained using equation 3.1.

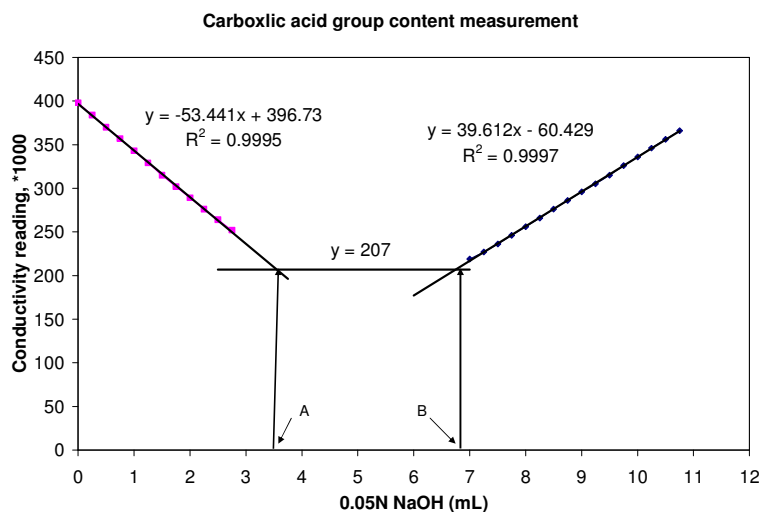
$$RCOOH \text{ content} = \frac{(B - A) \times 5}{w} \text{ mmol/100 g o.d. pulp} \quad (3.1)$$

where *w* is the o.d. weight of the pulp sample in grams.

The experiments were performed in duplicate and the results had an error less than ±3%. The detailed procedure is described in Appendix B.



A)



B)

Figure 3.4. Calculation of carboxyl group (RCOOH) content using conductivity method.

A) Original data and B) trend lines for calculating RCOOH content.

### 3.2.2 Copper number of pulp fibers

Copper number (Cu#) was measured following the Tappi standard method T 430.[188] Copper number is defined as the number of grams of metallic copper (as  $\text{Cu}_2\text{O}$ ) resulting from the reduction of  $\text{CuSO}_4$  by 100.00 g of pulp fibers. Four solutions were

prepared before any of the experiments began.

- Copper sulfate solution. 100g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in deionized water and diluted to 1000 ml.
- Carbonate-bicarbonate solution. 129 g anhydrous  $\text{Na}_2\text{CO}_3$  and 50 g  $\text{NaHCO}_3$  were dissolved and diluted to 1000 ml.
- Phosphomolybdic acid solution. 100 g  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  and 75 ml phosphoric acid (85%) were dissolved in a mixture of 275 ml concentrated  $\text{H}_2\text{SO}_4$  and 1750 ml  $\text{H}_2\text{O}$ .
- 5% Sodium carbonate solution. 50 g  $\text{Na}_2\text{CO}_3$  was dissolved by 950.00 g deionized water.

Air dry fibers equivalent to 1.500 g of oven dry fibers were disintegrated in a blender for 1 min and transferred to a 125 ml flask. 5 ml  $\text{CuSO}_4$  solution and 95 ml carbonate-bicarbonate solution were mixed and heated to a boil for 2 min. The mixture was poured into a flask and stirred well. The flask was placed in a water bath at  $100^\circ\text{C}$  and shaken every 15 minutes. After 3 hours of treatment, the flask was removed from the bath and filtered in the Büchner funnel with suction. The fibers were washed with 100 ml 5%  $\text{Na}_2\text{CO}_3$  solution and then flooded with 250 ml of hot water at  $95^\circ\text{C}$ . The fibers along with the filter paper were transferred to a 500 ml plastic beaker, and 25 ml of the phosphomolybdic acid solution was added. A glass rod was used to macerate the mixture well. The mixture was transferred to a clean Büchner funnel and washed thoroughly with water until the blue color of the fibers was removed. The filtrate was collected and diluted to approximately 700 ml. The solution was titrated with 0.05N  $\text{KMnO}_4$  to a faint pink end point. A blank test was also performed following the same procedures. The

copper number was calculated using equation 3.2.

$$\text{Copper number} = \frac{6.36 \times (V - B) \times N}{W} \quad (3.2)$$

Where:

$V$  = The volume of  $\text{KMnO}_4$  solution to titrate the filtrate from the specimen, ml.

$B$  = The volume of  $\text{KMnO}_4$  solution to titrate the blank filtrate, ml.

$N$  = Normality of  $\text{KMnO}_4$ , 0.05N.

$W$  = The o.d. weight of pulp fibers, g.

The copper number of each sample was measured in duplicate with an error of less than  $\pm 5\%$ . The copper number is an indication of aldehyde groups in fibers. It has been reported by Röhrling et al.[159] that there is a linear relationship between the carbonyl group content and copper number shown in equation 3.3.

$$\text{Carbonyl Group Content (mmol/100g o.d. pulp)} = (Cu^{\#} - 0.07)/0.6 \quad (3.3)$$

### 3.2.3 Surface charge of pulp fibers

Surface charge of fibers was measured using the polyelectrolyte adsorption method.[127, 128] Glycol chitosan was purchased from Sigma-Aldrich. The degree of polymerization of chitosan is greater than 400. This chitosan is used for colloidal titration. A solution of 0.001N potassium poly(vinyl sulfate) (PVSK) was purchased from ONDEO Nalco Company.

Prior to determining the surface charge of a given pulp sample, a series of control tests were conducted. Different volumes (12.50, 18.75, 25.00, and 31.25 ml) of the chitosan solution (1.00 g/l) were diluted with deionized water to a final solution weight of

300.00 g. After being mixed for 40 minutes, 25.00 ml of the diluted solutions were titrated with  $2.00 \times 10^{-4}$  N PVSK. This titration procedure was performed in triplicate, and analysis showed a linear relationship between the volume of chitosan and the amount of PVSK.

Subsequently, air dry pulp samples ( $4 \times 1.500$  g) were dispersed in 0.01 N HCl (300.00 ml) for 1 hour and then washed with deionized water (at least 2000 ml). The washed pulp samples were placed into a 0.005 N  $\text{NaHCO}_3$  (250.00 ml) solution. The pH value of the slurry was adjusted to 9.00 by addition of 0.05 N NaOH. After stirring for 20 minutes, the pulp slurry was filtered and washed with deionized water (at least 2000 ml). Different volumes (12.50, 18.75, 25.00, and 31.25 ml) of chitosan solution were added with the washed pulp samples separately, and diluted to 301.50 g with deionized water. After being mixed for 40 minutes, the slurries were filtered and the filtrates of unabsorbed chitosan were collected for titration. Each filtrate (25.00 ml) was pipetted into a flask and titrated with PVSK. Each titration was performed in triplicate. The amount of chitosan absorbed on the fibers was determined for each of the different volumes of chitosan solution added. By plotting the moles of chitosan adsorbed on fibers (surface acid, mmol/100 g o.d. pulp) versus the chitosan concentration added, the surface charge of fibers could be calculated. Figure 3.5 presents the calculation of the surface charge of fibers. The experimental error was within  $\pm 5\%$  of the average value.

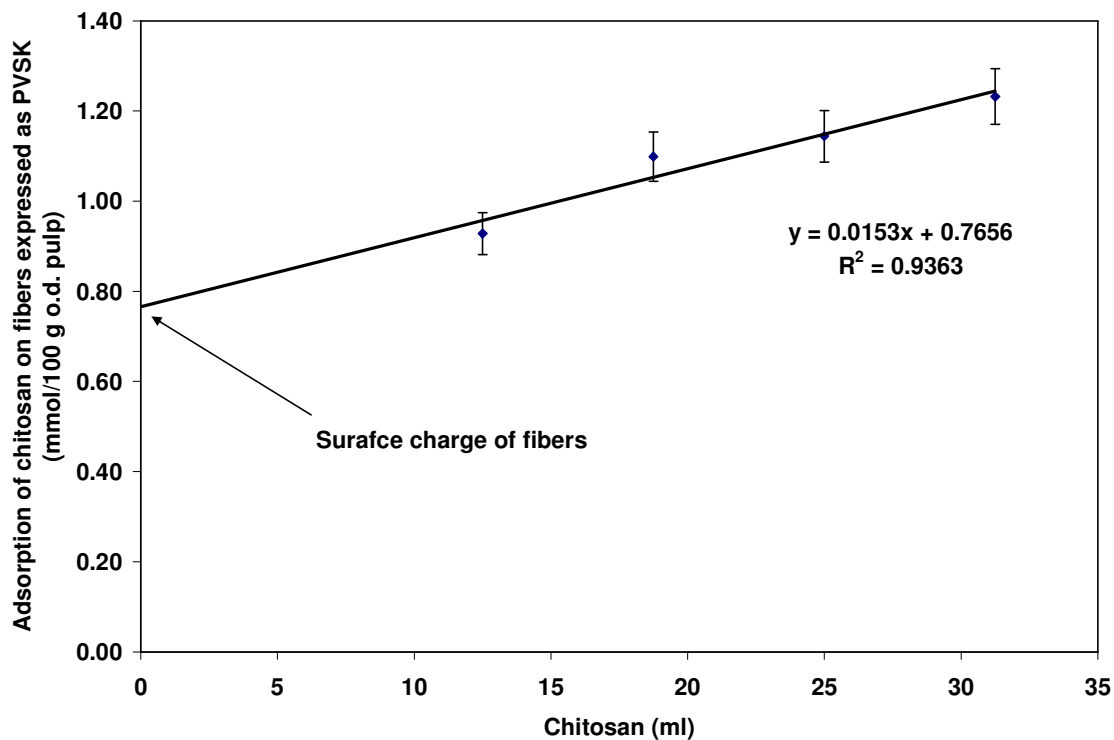


Figure 3.5. The calculation of surface charge of fibers by polyelectrolyte adsorption method.

#### 3.2.4 Carbohydrate analysis by high performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) of pulp fibers

The sample preparation of pulp and acid hydrolysis for carbohydrate analysis is based on method described in Tappi T-249.[189] The monomeric sugar content of the hydrolysed pulp was determined by HPAEC-PAD analysis (Figure 3.6).[190] Deionized water was used in all of the steps described here.

The air-dried pulp was ground to pass through a 40 mesh screen. 0.175g of each ground sample was weighed into a 50 ml tube. Standard sugars were also weighed in a 50 ml tube in order to put them through the same hydrolysis procedures as described for the pulp samples. The typical weights of standard sugars are presented in Table 3.3.



Figure 3.6. Photograph of high performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD).

Table 3.3. Typical weights of standard sugars for carbohydrate content analysis of pulp.

Standard sugar	Weight (g)
Glucose	0.1800
Xylose	0.0360
Arabinose	0.0100
Mannose	0.0200
Galactose	0.0100

1.5 ml of 72% sulfuric acid solution was added to each sample. The sample was stirred with a glass rod until wet. The glass rod was left in the sample and stirred occasionally throughout the primary hydrolysis process. The tube was placed into the



Digibloc set at 30°C. After 1 hour, the sample was diluted with 42 ml water. A watch glass was placed on the top of the tube and put into the autoclave for 1 hour on the 121°C setting. This was the secondary hydrolysis step. Until the pressure had dropped to zero, the sample could be taken out and cooled to room temperature. The solution was brought up to 50 ml with water and then filtered through glass filters. As for the pulp sample, 1 ml of the solution was pipetted and transferred to a 25 ml volumetric flask. Also, 1 ml of 1 mg/ml fucose was added and additional water was added to the mark of the volumetric flask. 5 standard solutions were prepared by the same procedure. Typical dilutions were composed of 1, 0.75, 0.50, 0.25, and 0.10 ml aliquots of stock each and 1 ml of 1 mg/ml fucose stock brought up to 25 ml. The diluted solution was transferred to a 0.5 ml vial and placed in the auto sampler for carbohydrate content analysis by HPAEC. The output screen of the carbohydrate content for a sample is shown in Figure 3.7. The results of sugar content ( $\mu\text{g/ml}$ ) could be obtained at the same time and for each sample, it was conducted in duplicate and the error was within  $\pm 2\%$  of the average value.

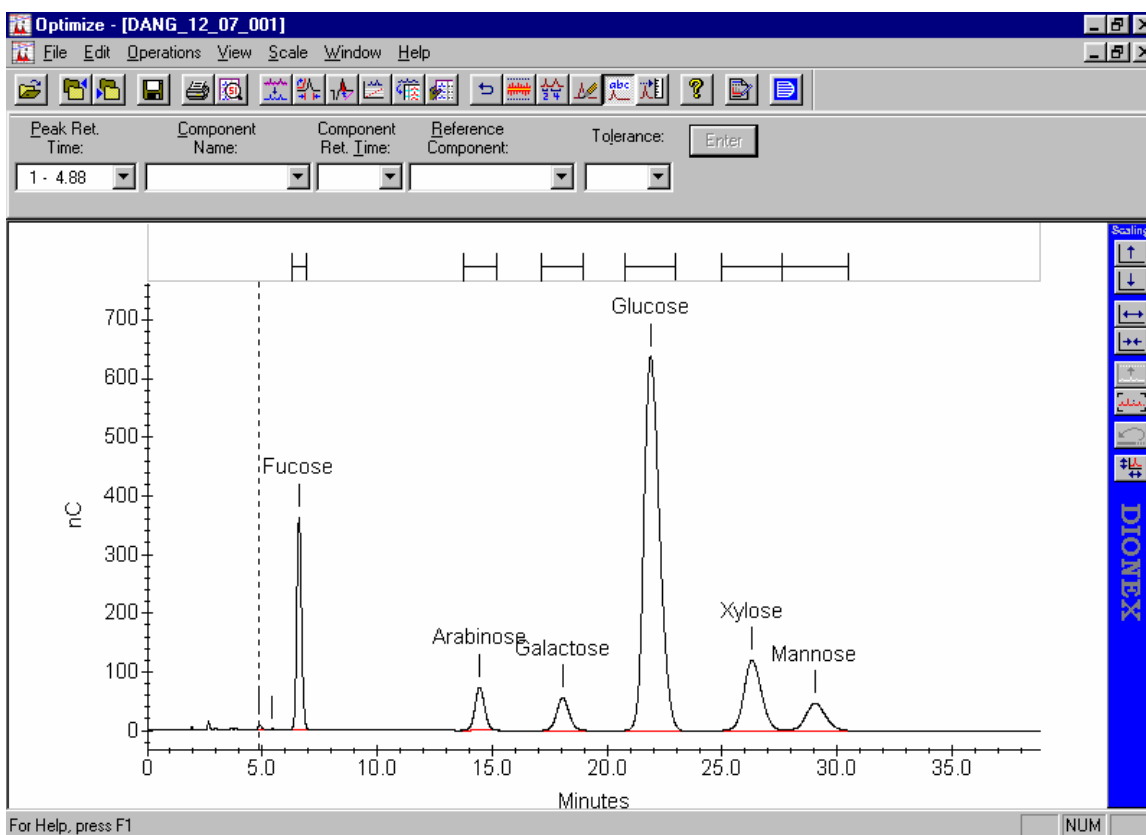


Figure 3.7. The output screen of HPAEC for carbohydrate content analysis of pulp.

### 3.2.5 Water retention value (WRV) of pulp fibers

Pulp water retention values were evaluated according to the Tappi Useful Method 256 Water Retention Value.[191] This methodology involves forming a pulp pad by draining a diluted pulp slurry on a fine mesh screen in a centrifuge cup. The pulp pad was prepared at a fixed basis weight of  $555 \pm 55 \text{ g/m}^2$ . The pulp pad was then centrifuged at 900 g for 30 min. The wet pad, after centrifuging, was weighed, dried at  $105^\circ\text{C}$ , and then reweighed. The WRV was calculated as the amount of water by weight retained in the pad after centrifuging per o.d. weight of fibers (equation 3.4).

$$WRV = \frac{W_w - W_d}{W_d} \times 100\% \quad (3.4)$$

$W_w$  is the weight of the wet sample after centrifuging, and  $W_d$  is that of the dry sample.

The tests were done in quadruplicate, and the typical error was  $\pm 5\%$  of the average value.

### 3.2.6 Fiber surface morphology by atomic force microscopy (AFM)

A silicon nitrile cantilever tip was used with a Digital Instruments 3100 Scanning Probe Microscope to evaluate the surface morphology of fibers. For each sample, height images were collected at 2 positions along each of 5 randomly chosen fibers. These values were averaged to provide roughness measurements in  $\text{nm}^2$  for each sample by using equation 3.5.[192]

$$R_{rms} = R(F \sum_{i=1}^N (Z_i - Z_{ave}), N) \quad (3.5)$$

where  $N$  is the number of points in the area examined,  $Z_i$  is the current height value, and  $Z_{ave}$  is the average height value.  $R_{rms}$  is the root-mean square of the standard deviation for the height (Z) data.

In Chapter 4, the standard deviation (S.D.) values of roughness determined by AFM are presented in Figure 4.7. Refined samples have standard deviation values between 29 and 48, and unrefined samples have standard deviation values between 24 to 34.

### **3.2.7 $^{13}\text{C}$ CP/MAS NMR and SEM analysis of oxidized bleached pulps**

Four samples in the last study, Chapter 6, were analyzed by solid-state NMR, which consisted of the untreated ECF bleached SW kraft pulp and oxidized pulps (see Table 6.1). The  $^{13}\text{C}$  CP/MAS NMR spectra were recorded at room temperature on an instrument Bruker Advance/DMX-400 operating at 100.06 MHz using an MAS 4 mm probe and  $\text{ZrO}_2$  rotors. The MAS spin rate was 5 kHz. Acquisition was performed with a CP pulse sequence using 4.5  $\mu\text{s}$  pulse, 2.0 ms contact pulse and 3.0 s delay between repetitions. 5000 scans were accumulated for each sample.

SEM images of the original ECF bleached SW kraft pulp and the fibers treated with a charge of 1.70 mmol  $\text{NaClO/g}$  o.d. pulp were acquired using a LEO 1530 thermally-assisted field emission (TFE) microscope at 10 kV. The coated quartz side and the smooth side of the paper test sheets were gold coated prior to analysis.

### **3.2.8 Kappa number and intrinsic viscosity of pulp fibers**

The kappa numbers of the pulps were measured according to the TAPPI standard method T 236.[193] The intrinsic viscosity  $[\eta]$  was measured according to ASTM standard D1795-62.[194] Both of these tests were performed in duplicate, and the typical errors were  $\pm 0.5$  for kappa number, and  $\pm 5 \text{ ml g}^{-1}$  for intrinsic viscosity of the average numbers, respectively.

### 3.2.9 Paper testing

Handsheets were prepared according to the Tappi test method T205[186] using standard sheet mold (Figure 3.8). The brightness of the paper was determined by the Tappi test method T452.[195] 15 spots of handsheets were chosen during testing, and the typical standard deviation was 0.15 units. All of physical testing of the paper was performed following the Tappi test methods T220[196] and T402[197]. The caliper was measured according to Tappi test method T411 with an error less than 5%.[198] Tensile strength[199], burst strength[200], and zero-span strength[201] were determined following the Tappi test methods T494, T403, and T231, respectively. The experimental error was generally less than 5% of the mean values.

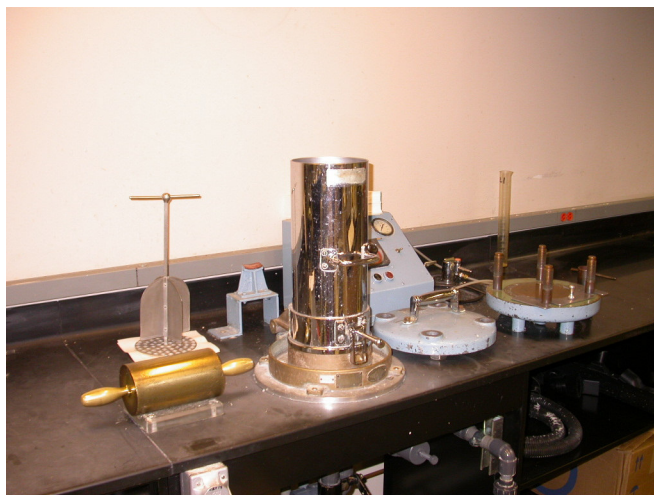


Figure 3.8. Laboratory sheet mold for making handsheets by the Tappi test method T205.

### 3.2.10 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) content

Peroxide solution (35% wt) was purchased from Sigma-Aldrich. 100 ml concentrated peroxide solution was diluted to 1000 ml and stored in a refrigerator prior to

use. 5 ml of the peroxide solution was pipetted into a flask. The sample was acidified by adding 10 ml 20%  $\text{H}_2\text{SO}_4$ . The mixture was then titrated with 0.1N potassium permanganate until a pink end point. The volume (V, ml) of 0.1N potassium permanganate added to the sample was recorded for calculating the peroxide content using equation 3.6.

$$\text{H}_2\text{O}_2 \text{ (g/l)} = 0.3402 \times V \quad (3.6)$$

### **3.2.11 Fiber quality analyzer (FQA) for pulp fibers**

The fiber quality analyzer (FQA) was used to optically characterize the curl and kink properties of the fiber. Figure 3.9 shows a photograph of the FQA. A diluted fiber suspension of approximately 0.0008% consistency was prepared and run through the FQA. Fiber length, curl, and kink were reported after 5000 fibers were counted by the program. The data and experimental error is presented in Table 4.2.



Figure 3.9. Photograph of fiber quality analyzer.

## CHAPTER 4

### INFLUENCE OF KRAFT PULPING ON CARBOXYLATE CONTENT OF SOFTWOOD KRAFT PULPS

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#### 4.1 Introduction and objective

This study is directed at determining how fiber charge is influenced by varying kraft pulping conditions, including effective alkali (EA), sulfidity and pulping temperatures for batch pulping.

The effect of kraft pulping conditions on fiber charge was investigated by preparing a series of laboratory prepared conventional loblolly pine kraft pulps. The experimental parameters varied included effective alkali, sulfidity, and pulping temperature. The pulp IDs for the samples described in Table 3.1 were assigned M/K1 to M/K9. The primary pulping factors investigated were effective alkali and sulfidity. A preliminary study for the effect of maximum pulping temperature on fiber charge was accomplished comparing kraft pulp M/K5 versus M/K9. M/K5 was prepared at 170°C

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<sup>iii</sup> This manuscript was initially published in Industrial and Engineering Chemistry Research, 2006, 45(13), 4509-4516. It is titled as "Influence of Kraft Pulping on Carboxylate Content of Softwood Kraft Pulps". The other two authors are Dr. Tom Elder from USDA Forest Service, Southern Research Station and Dr. Arthur J. Ragauskas from the School of Chemistry and Biochemistry at the Georgia Institute of Technology.

and M/K9 at 160°C. Basic fiber properties including kappa number and viscosity are summarized in Table 3.1. The results of intrinsic viscosity values shown in Table 3.1 indicate that the viscosity decreases with increasing effective alkali when kraft pulping is performed at same sulfidity, H-factor, and maximum pulping temperature. This result is in agreement with Dyer and Ragauskas' prior studies.[202]

The effect of the Lo-Solids continuous kraft pulping technology on fiber charge was also compared with conventional kraft pulping. The primary parameters examined in the latter study were H-factor and pulping protocol. The conditions and results are shown in Table 3.2.

## **4.2 Results and discussion**

### **4.2.1 The effect of effective alkali, sulfidity, and pulping temperature on carboxylic acid group content of bulk fibers and holocellulose fibers**

The results for bulk carboxylic acid group content for kraft pulps are presented in Figure 4.1. EA increases in the order M/K1 to 4 and in the order MK/5 to 8. The latter set of four samples has higher sulfidity. Condition M/K9 has lower maximum pulping temperature, but is otherwise similar to condition M/K5 as summarized in Table 3.1.

These results indicate that the higher the EA for a batch kraft cook, the lower the carboxylic acid content of the resulting pulp when pulping is accomplished at the same H-factor and pulping temperature (170°C). This result is in accordance with other researchers' studies. [15, 87, 203] It has been reported that a higher alkalinity in extended pulping serves to minimize the reprecipitation of lignin and under these conditions the



reprecipitation of the hemicellulose onto fibers surface is also decreased.[204] Hence, the results of this study which indicate that a lower effective alkali charge during pulping leads to kraft pulps with higher fiber charge is consistent with literature findings. In contrast, pulping sulfidity did not appear to have an obvious effect on carboxylic acid group content of bulk fibers, except under low EA (12%) conditions. Analysis of the results from M/K9 and M/K5 indicate that a lower temperature possibly favors the retention of carboxylic acid group content in the pulp.

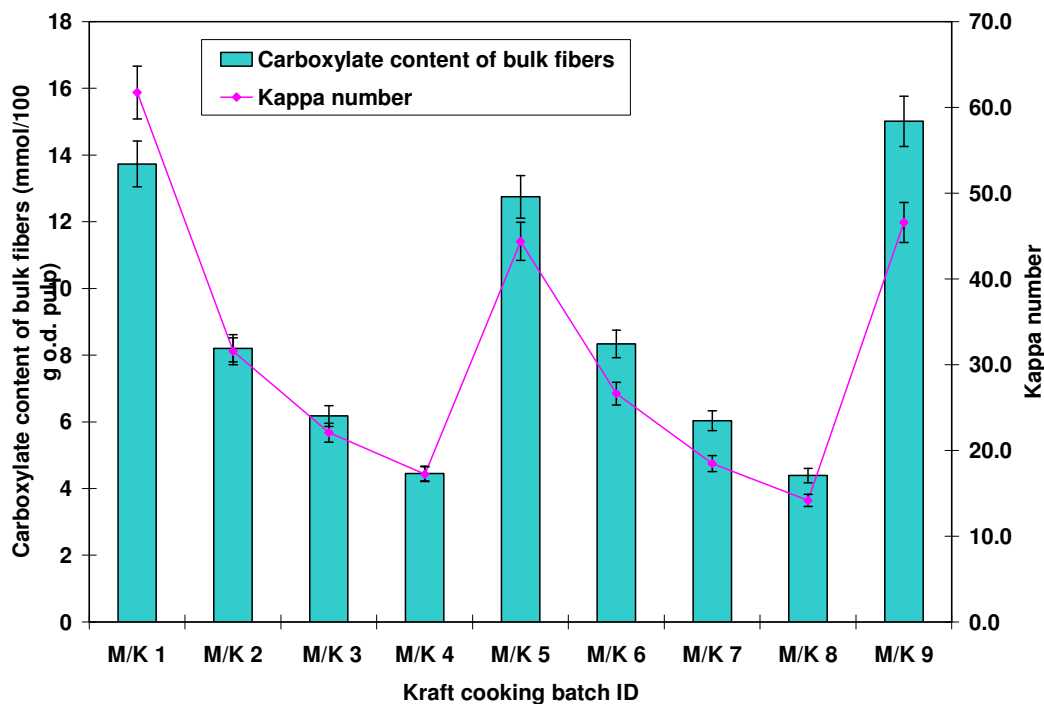


Figure 4.1. Carboxylate content of kraft pulps prepared with varying EA, S, and maximum pulping temperature employing M/K digester at constant H-factor of 1000 and Liquid:Wood of 4:1 of loblolly pine.

The differences in carboxylate content of kraft pulps reported in Figure 4.1 are due to differences in the carboxylate content of fiber polysaccharides and lignin. In ECF

bleached pulps, fiber charge originates primarily from carboxylate groups attached to saturated polysaccharides. It is now well established that most hexeneuronic acids in pulp are oxidatively removed during ECF bleaching.[116] In order to evaluate the content of fiber charge associated with bleached polysaccharides, the kraft pulps in Table 3.1 were holocellulose pulped. Figure 4.2 shows the carboxylate content of holocellulose pulps. The difference between carboxylate group content of bulk kraft pulp fibers and that of holocellulose pulps is attributed to the charge associated with lignin and hexeneuronic acid groups present in the kraft pulps. These results demonstrate that approximately 56-86% of the carboxylic acid groups of the kraft pulps can be attributed to saturated pulp carbohydrates. The key pulping parameters influencing fiber charge on saturated polysaccharides include effective alkali and pulping temperature. Although holocellulose pulping is not employed industrially, it is relevant to ECF bleaching protocols. The results in Figure 4.2 indicate that the kraft pulps with higher fiber charge maintain higher fiber charge after holocellulose bleaching when compared against kraft pulps having lower fiber charge.

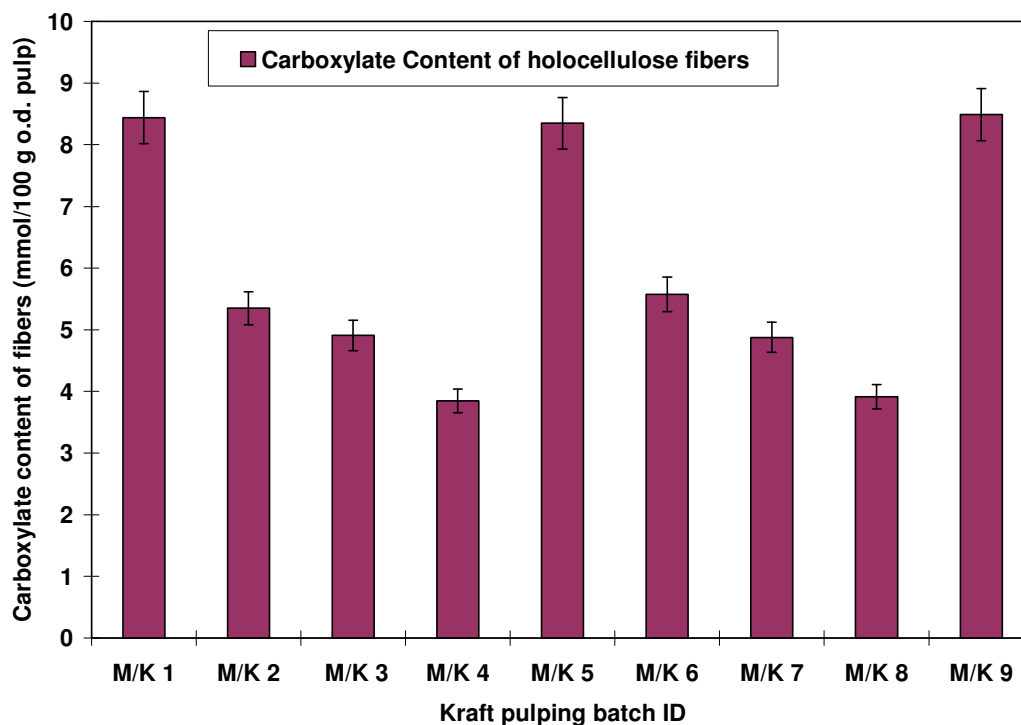


Figure 4.2. Carboxylate content of holocellulose fibers from kraft pulps prepared with varying EA, S, and maximum pulping temperature employing M/K digester at constant H-factor of 1000 and Liquid:Wood of 4:1 of loblolly pine.

#### 4.2.2 The effect of effective alkali, sulfidity, and pulping temperature on surface charge on fibers

Figure 4.3 summarizes the effect of EA profiles on surface charge. At the same H-factor and pulping temperature (170 °C), a high EA in the digester yields a low surface charge. In contrast, no significant difference in fiber surface charge was observed when 30% or 50% sulfidity was employed for pulping. The only exception to this observation was noted when the pulping conditions employed a low EA charge (12%), as previously

observed for bulk fiber charge. As for the pulping temperature effect, the M/K9 pulp prepared with a maximum pulping temperature of 160 °C resulted in a slightly higher (2%) surface charge compared to M/K5 pulp (i.e., same conditions except pulping temperature). These results suggested that a lower EA is favorable for increasing overall surface charge; while sulfidity is not a key parameter for controlling surface charge during kraft pulping. After comparing surface charge with bulk fiber charge, it suggests that surface charge accounts for approximately 4% to 7% of the bulk fiber charge.

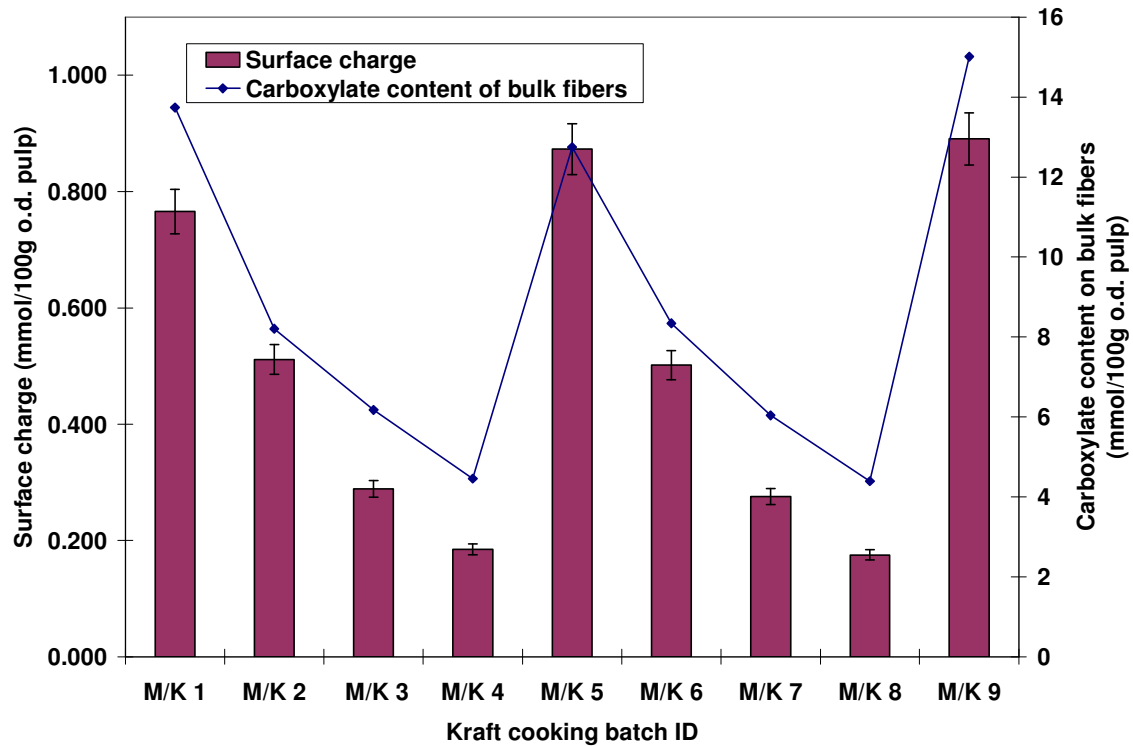


Figure 4.3. Surface charge of kraft pulps prepared with varying EA, S, and maximum pulping temperature employing M/K digester at constant H-factor of 1000 and Liquid:Wood of 4:1 of loblolly pine.

#### **4.2.3 The relationship between carboxylate content of bulk fibers and water retention value of pulps**

Water retention value (WRV) is useful for evaluating the performance of pulps in dewatering on a paper machine and for some paper applications.[205] It can also provide a relative indication of the swelling capability of the pulps. As fibers swell, they are more easily beaten and defibrillated thus, exposing greater surface area for bonding to occur. It is commonly acknowledged that enhanced fiber swelling relates to increased concentration of acid groups in the pulp.[6, 8, 138, 139] The swelling of fibers has been attributed to two effects. One is Donnan equilibrium theory[133] which was applied to cellulosic membrane[134, 135]. The other is the electrostatic repulsion between the negatively charged carboxylate anions of fibers.[6, 136] Figure 4.4 summarizes the relationship between bulk fiber charge and water retention value of pulps. It is shown that there is a linear relationship coefficient of determination,  $R^2$ , of 0.93.

Prior studies have demonstrated that WRVs clearly increase by introduction of carboxyl groups into pulps via carboxymethylation under alkaline conditions.[7, 9, 128, 206] Kitaoka et al. studied the chemical modification of pulp fibers by TEMPO-mediated oxidation; their results have shown that WRVs of pulps were roughly constant, even though these pulps had carboxyl contents from 0.06 to 0.47 mmol/g.[26]

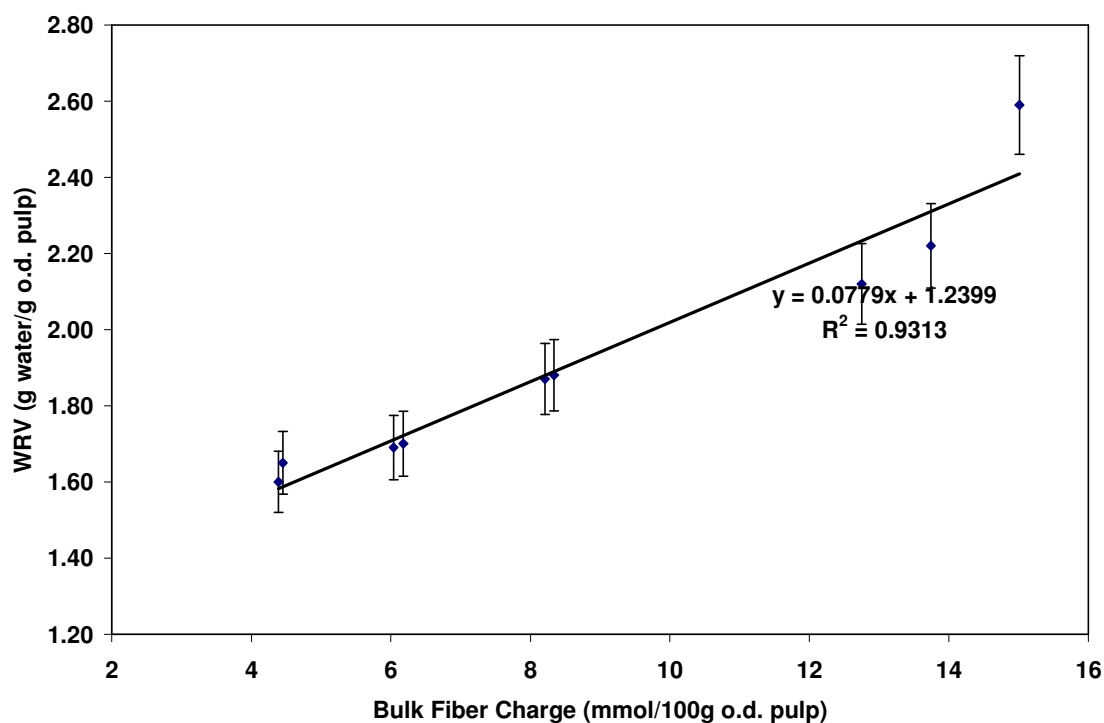


Figure 4.4. The relationship between bulk fiber charge and water retention value of original M/K1 – M/K9 kraft pulps.

#### 4.2.4 Carboxylate content of holocellulose fibers versus total carbohydrate content of pulp fibers

In order to determine carboxylic acid group content per unit carbohydrate, including cellulose and hemicellulose of fibers, monomeric sugar content was determined by HPAEC-PAD. The results are shown in Table 4.1.

Table 4.1. Fiber charge and mono saccharide content of kraft pulps underwent pulping condition M/K1 to M/K9.

Kraft Pulps ID	Fiber charge of holocellulose (mmol/100 g o.d. pulp)	Glucan (%)	Xylan (%)	Mannan (%)	Arabinan (%)	Galactan (%)	Total carbohydrate content <sup>*</sup> (%)	Fiber charge of holocellulose fibers vs. carbohydrate content
M/K 1	8.44	74.80	7.99	4.80	0.88	0.86	89.33	9.45
M/K 2	5.35	81.93	7.54	5.75	0.66	0.56	96.44	5.55
M/K 3	4.91	84.28	5.95	6.16	0.48	0.45	97.32	5.05
M/K 4	3.85	86.24	4.53	6.26	0.35	0.37	97.75	3.94
M/K 5	8.35	77.25	9.20	5.19	0.96	0.63	93.23	8.96
M/K 6	5.58	84.97	7.12	5.58	0.62	0.50	98.79	5.65
M/K 7	4.88	85.35	6.46	6.24	0.50	0.42	98.97	4.93
M/K 8	3.91	87.18	5.07	6.72	0.38	0.33	99.68	3.92
M/K 9	8.49	77.41	9.92	5.14	1.10	0.67	94.24	9.01

\* It is expressed by the summation of monomeric sugar content including glucan, xylan, mannan, galactan, and arabinan.

The results show that mannan was relatively resistant to removal by increasing EA charge, during kraft pulping. Total carbohydrate content expressed by sum of the monomeric sugar content increased with increasing EA charge. Based on Table 4.1, it is indicated that fiber charge of unit holocellulose appeared highest at the lowest EA charge. It can be concluded that EA charge is the most important factor controlling carboxylic acid group of holocellulose of kraft pulp fibers during kraft pulping.

#### **4.2.5 Paper physical testing and PFI refining of holocellulose pulps**

To further investigate the effect of acidic group on fully bleached paper physical strength, the strength properties of holocellulose pulped M/K1, M/K2, M/K5 and M/K6 were determined. Since it is well known that curl and kink detrimentally impact physical strength properties, the holocellulose pulps were PFI refined to obtain similar curl and kink values. Bulk fiber charge analysis of the pre- and postPFI refined pulps indicated that the refining process did not change bulk fiber charge when the fibers are refined at 2000 revolutions. This result is consistent with recent reports that beating does not alter total fiber charge.[176] Table 4.2 summarizes the results of paper physical strength and fiber quality of holocellulose fibers after PFI refining with 2000 rev. The results of fiber quality analysis (FQA) show that holocellulose fibers have similar curl and kink values after PFI treatment of 2000 revolutions. From Table 4.2, it can be seen that higher fiber charge corresponds to enhanced tensile strength and burst strength of paper prepared from holocellulose fibers with similar curl and kink values. Nonetheless, both burst strength and tensile strength depend on other factors, such as interfiber bond strength,



web structure, and inherent fiber strength. By comparing the results of holocellulose pulps M/K6 and M/K5, it shows that a 50% increase in fiber charge of holocellulose fibers enhances tensile and burst index by 7% and 8%, respectively.

Table 4.2. Paper physical strength and FQA results of holocellulose fibers from M/K1, M/K2, M/K5 and M/K6 kraft pulps.

Holocellulose sample of M/K kraft pulps	Fiber charge of holocellulose fibers after refining (mmol/100 g o.d. pulp)	Tensile Index of holocellulose fibers after refining (Nm/g)	Burst Index of holocellulose fibers after refining (kPa.m <sup>2</sup> /g)	Curl of holocellulose fibers after refining	Kink of holocellulose fibers after refining (l/mm)
#M/K 1	8.44±0.09	58.87±1.66	7.21±0.21	0.064±0.006	0.82
#M/K 2	5.35±0.09	54.03±1.08	6.94±0.18	0.066±0.006	0.90
#M/K 5	8.35±0.09	57.79±1.54	7.33±0.22	0.061±0.006	0.78
#M/K 6	5.58±0.09	54.14±0.97	6.78±0.18	0.068±0.006	0.86

AFM is used to evaluate surface morphology and properties of a large number of materials which also include wood, fibers, and cellulose.[192, 207-209] Handsheets of unrefined and refined holocellulose fibers from M/K1, M/K2, M/K5 and M/K6 kraft pulps were analyzed by AFM. Figures 4.5 and 4.6 show AFM phase images of the holocellulose fibers.

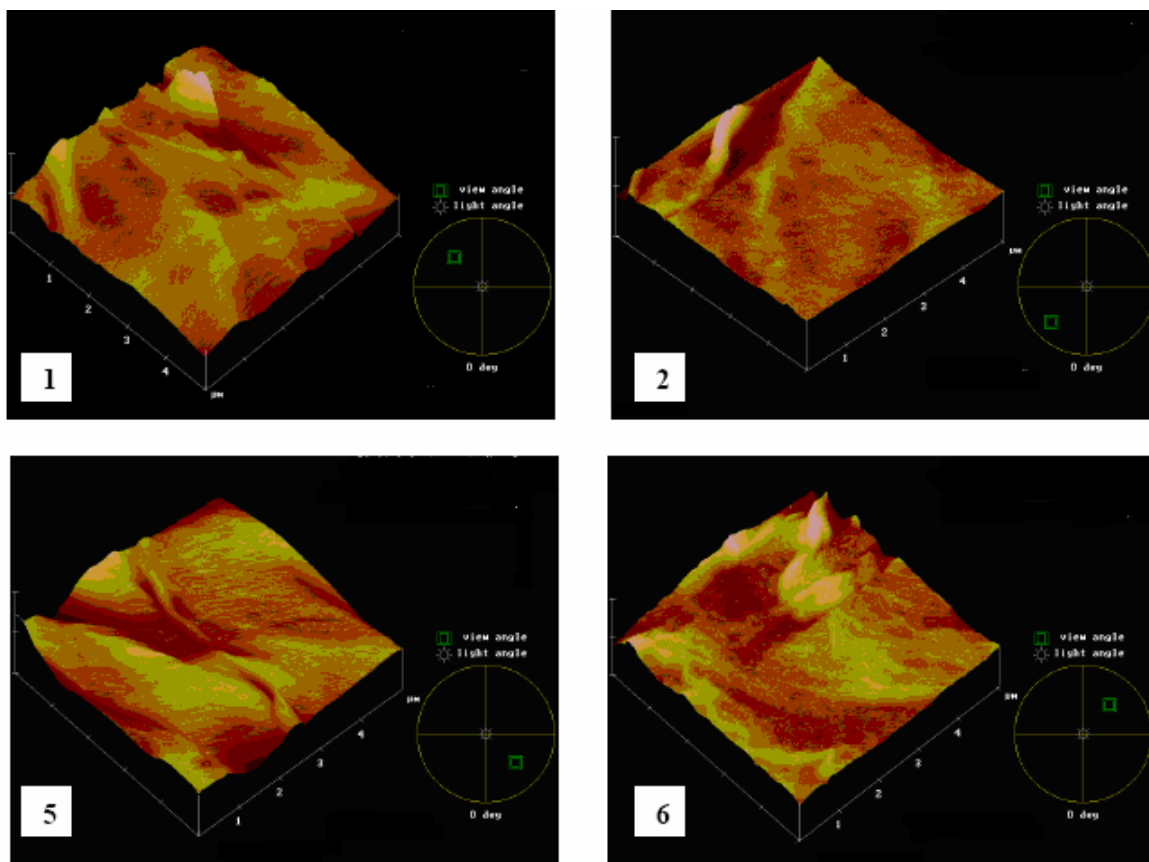


Figure 4.5. Atomic force microscopy (AFM) phase images of holocellulose fibers. (1), (2), (5), and (6) are holocellulose fibers from M/K1, M/K2, M/K5 and M/K6 kraft pulps, respectively.

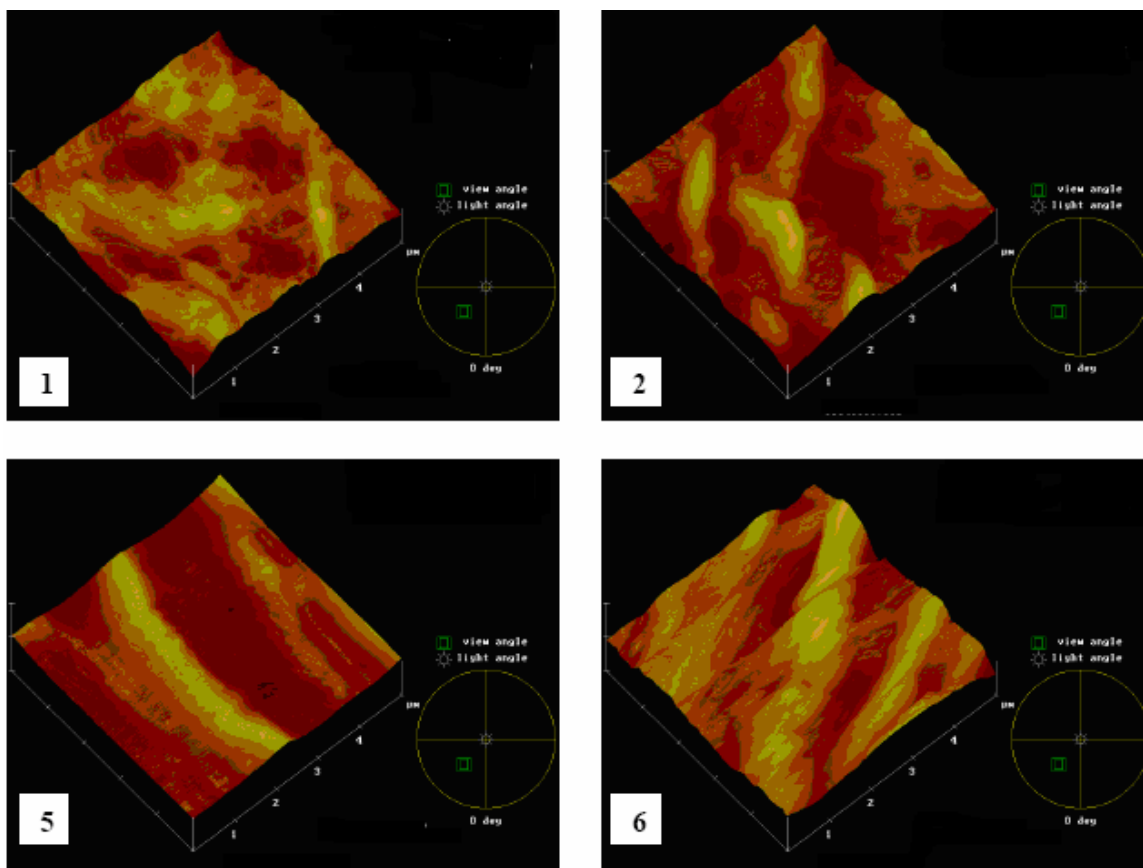


Figure 4.6. Atomic force microscopy (AFM) phase images of holocellulose fibers treated by 2000 rev. PFI refining. (1), (2), (5), and (6) are holocellulose fibers from M/K1, M/K2, M/K5 and M/K6 kraft pulps, respectively.

Based on the AFM Phase Images of samples, there are no striking differences in the surface topographies between high fiber charge (Holocellulose fibers M/K1 and M/K5) and low fiber charge (Holocellulose fibers M/K2 and M/K6). Figure 4.7 presents the RMS-roughness values for holocellulose fiber M/K1, M/K2, M/K5, and M/K6. As expected, the unrefined samples exhibited at least 26% lower RMS values when compared to refined samples. However, no marked differences in RMS were noted between the high surface charge samples and low surface charge samples. Based on the research by Pang and Gray[210], it was found that the force acting on the AFM tip as it

approaches a pulp fiber surface can be measured using the AFM tip as a probe. Higher fibrillation of a pulp surface corresponds to high force acting on the tip as it approaches the pulp surface. Mechanical action causes fibrillation of the fiber surface, which can be detected from the tip-fiber force-distance curves.[210] PFI refining increased the fibrillation of fiber surfaces, which might lead to higher roughness value of refined pulp surface compared to unrefined pulp fiber surface.

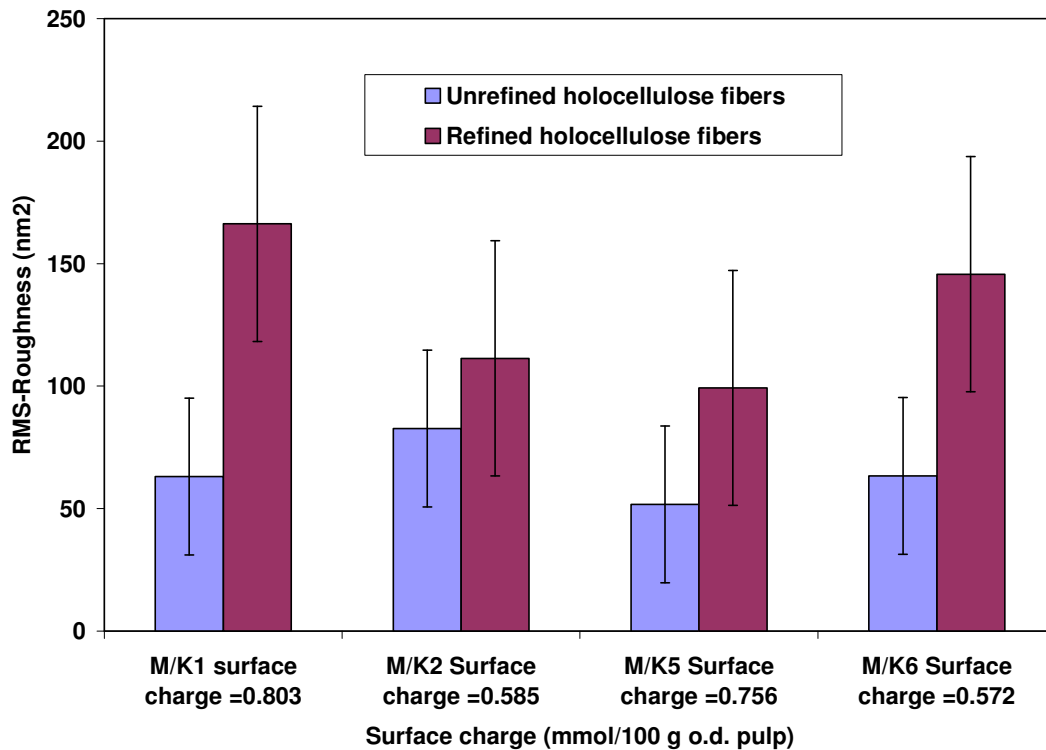


Figure 4.7. Comparison between holocellulose fibers RMS-roughness measured by AFM and surface charge on holocellulose fibers of M/K1, M/K2, M/K5, and M/K6 kraft pulps.

#### 4.2.6 Investigation of batch vs. continuous Lo-Solids pulping on fiber charge

A series of lab produced kraft pulps were prepared employing conventional pulping (CK), and simulated continuous low solids (LS) pulping from kappa number 14.7

to 39.9. Kraft pulping parameters and pulp properties are summarized in Table 3.2. The primary parameters investigated in this study were H-factor and pulping protocols. The remaining pulping parameters were kept constant within experimental control capabilities.

From Table 3.2, it is apparent that the values of viscosity of Lo-Solids kraft pulps were higher than those of conventional kraft pulps, when pulping was conducted under the same conditions. This is in accordance with literature results.[90] Kappa number was plotted against bulk fiber charge for all the pulps in Table 2 in Figure 4.8.

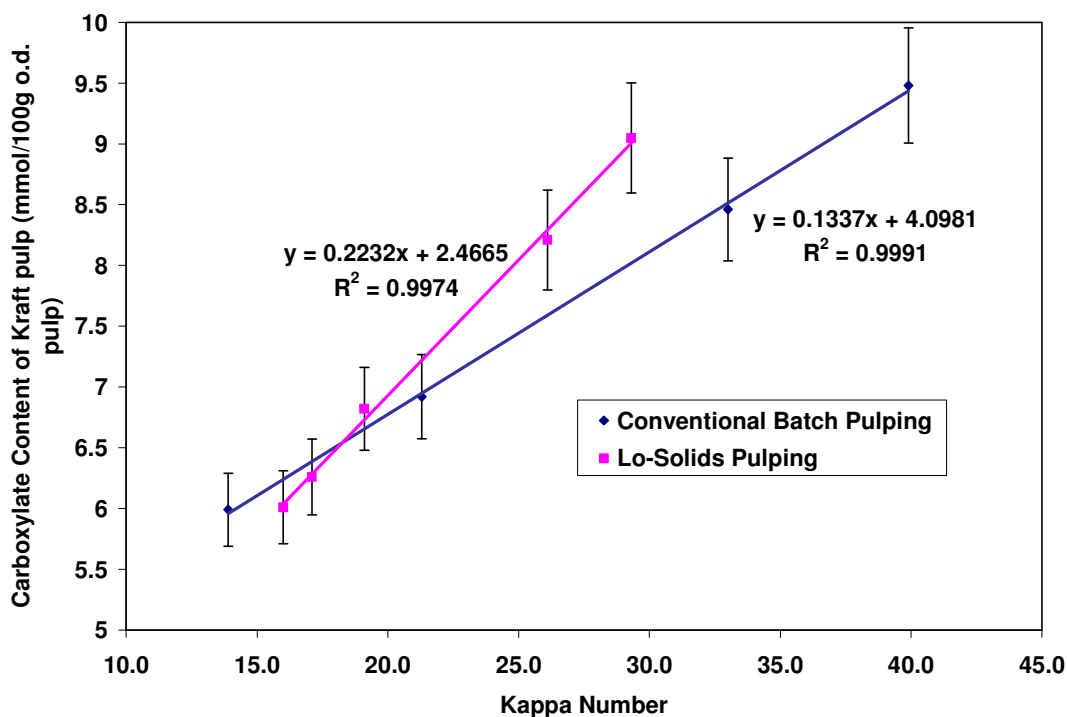


Figure 4.8. The comparison between carboxylate content and kappa number of conventional and Lo-Solids pulping loblolly pine kraft pulps underwent 20.5% EA and 170°C maximum temperature pulping.

It appears in Figure 4.8 that there is a linear relationship between kappa number and fiber charge. Although no linear relationship between fiber charge and kappa number of Lo-Solids pulps was found in Bhardwaj's study[93], fiber charge was found to be positively proportional to kappa number which is widely accepted in numbers of studies of kraft pulps.[15, 87, 93, 131, 203, 211]

Also from Figure 4.8, the fiber charge of LS pulps had a higher slope value than the conventional pulping pulps. The two trend lines intersect at a kappa number of 18.2. This suggests that LS pulps with kappa number higher than 18.2 have higher fiber charge than CK pulps. On the contrary, LS pulps with kappa number lower than 18.2 have lower fiber charge than CK pulps. These data indicate that LS pulps should not be pulped to a high H-factor if the desired effect is to produce high fiber charge pulps. This is the first time that fiber charge has been compared between conventional and Lo-Solids pulping.

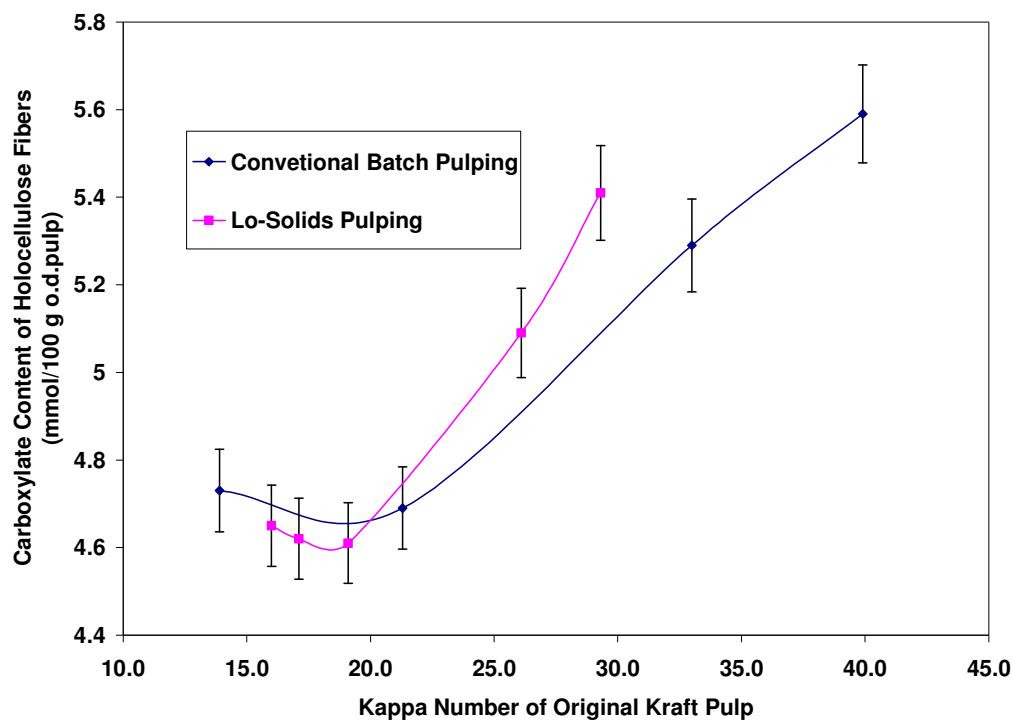


Figure 4.9. Holocellulose fibers charge vs. kappa number of conventional and low solids pulping kraft pulps prepared from loblolly woodchips with 20.5% EA and 170°C maximum cooking temperature.

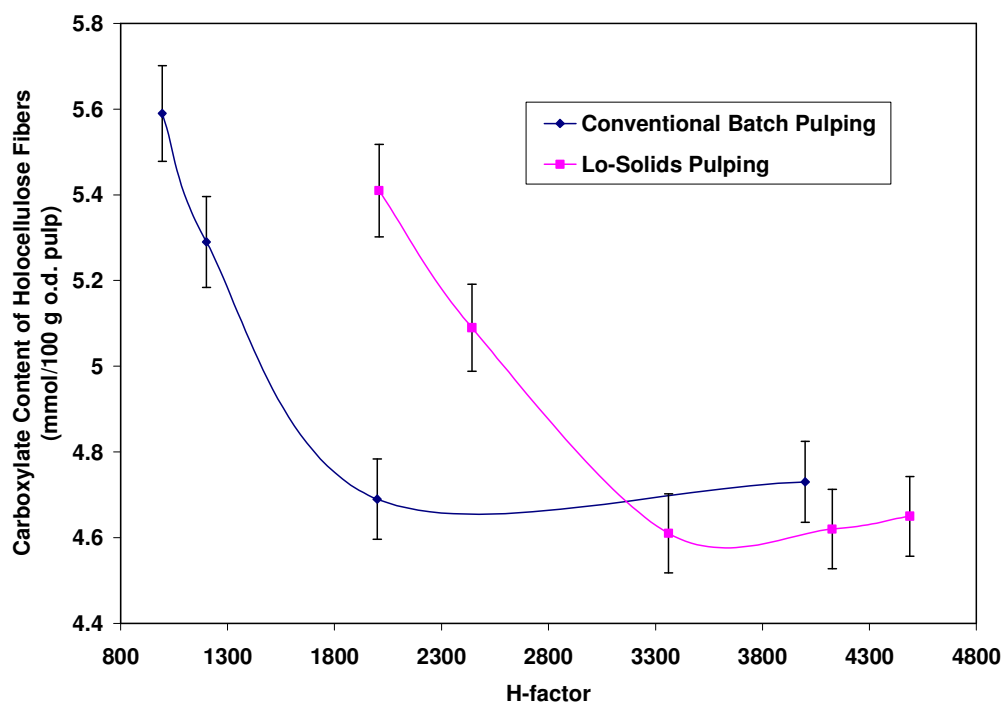


Figure 4.10. Holocellulose fibers charge versus pulping H-factor of conventional and low solids pulping kraft pulps prepared from loblolly woodchips with 20.5% EA and 170°C maximum cooking temperature.

Figures 4.9 and 4.10 present the fiber charge of holocellulose fibers against kappa number of original kraft pulps and pulping H-factor, respectively. From these data, it is apparent that the charge of holocellulose fibers reached a constant value as pulping advanced. This constant value for the LS pulps (4.62 mmol/100g o.d. pulp) was a somewhat lower than the value of CK pulps (4.70 mmol/100g o.d. pulp). From Figure 4.9, fiber charge of holocellulose LS pulps has higher values than that of CK pulps when pulps have the same kappa number. This is the first study to compare the charge of polysaccharides against H-factor. In Buchert's study of kraft pulps,[87] the results showed that the carboxyl content of kraft pulps tended to be constant with the extension of cooking time, which is an indication of the H-factor.



### 4.3 Conclusions

The results of laboratory pulping loblolly pine kraft pulps, which are generated in an M/K digester, show that EA charge is the key factor in controlling fiber charge when kraft pulping was performed at same H-factor. Low EA charge and low pulping temperature were favorable for increasing carboxylic acid group content of bulk fibers. Carboxylic acid group content of lignin and HexA contributes approximately 14-44% of the total carboxylic acid group content of bulk fibers, depending on the level of lignin content. The surface charge on fibers accounts for 4% to 7% of the bulk fiber charge. Higher fiber charge correlated with enhanced paper physical strength by measuring tensile strength and burst strength of holocellulose fibers handsheets, with different fiber charge. The roughness data measured by AFM does not show a correlation with surface charge of holocellulose fibers. The results of another set of lab produced pulp, conventional pulping and Lo-Solids pulping, were investigated to determine the effect of pulping protocol on fiber charge. Kappa number was linearly related with fiber charge. The fiber charge of LS pulps had a higher slope value than the conventional pulping pulps when bulk fiber charge and kappa number were plotted. The charge of holocellulose fibers reaches a constant value as pulping advanced for both types of pulps. Fiber charge of holocellulose LS pulps has higher values than the CK pulps when cooked to the same kappa number.

## CHAPTER 5

### ALKALINE PEROXIDE TREATMENT OF ECF BLEACHED SOFTWOOD KRAFT PULPS

This chapter is in part reproduced with the kind permission from [Holzforschung].  
*Copyright © 2007 by Walter de Gruyter GmbH & Co. KG.*<sup>iv</sup> The first part investigates the effect of alkaline peroxide treatment on carboxyl groups of fibers. The second one examines the effect of increased fiber charge on refining, wet-end application, and hornification.

#### **5.1 Characterizing the effect of alkaline peroxide treatment on carboxyl groups of fibers**

##### **5.1.1 Introduction and objective**

This section studies the effect of peroxide bleaching of ECF bleached softwood kraft pulp on fiber charge and carbonyl group contents. We also investigated the effect of sodium borohydride pretreatment of bleached kraft pulps prior to peroxide treatment aiming at the clarification of the role of carbonyl groups in the course of carboxyl group formation during the subsequent peroxide treatment.

In our preliminary study[141] and Toven's[21] work of peroxide bleaching of

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<sup>iv</sup> This study was accepted by Holzforschung and is in the process of publishing. Two manuscripts were created based on this work. They are titled as "Alkaline peroxide treatment of ECF bleached softwood kraft pulp. Part I. Characterizing the effect of alkaline peroxide treatment on carboxyl groups of fibers." and "Part II. Effect of increased fiber charge on refining, wet-end application, and hornification"

fully bleached pulps, it has been reported that the fiber charge can be increased, which results in enhanced swelling of fibers, and better tensile strength and stiffness. In the present paper, the alkaline peroxide treatment of ECF bleached pulp is studied in regards to fiber charge and carbonyl group content.

### **5.1.2 Results and discussion**

#### **5.1.2.1 The effect of peroxide charge on fiber charge**

An ECF bleached softwood kraft pulp was subjected to alkaline peroxide treatment by employing a series of peroxide charges from 0 to 8.0%. The remaining parameters of the experiment were 2.0% NaOH, 2.0 hour treatment time, 10.0% consistency, and temperatures of 60.0 and 90.0°C. Figure 5.1 shows the effect of peroxide treatment on fiber charge of the treated ECF bleached SW kraft pulp.

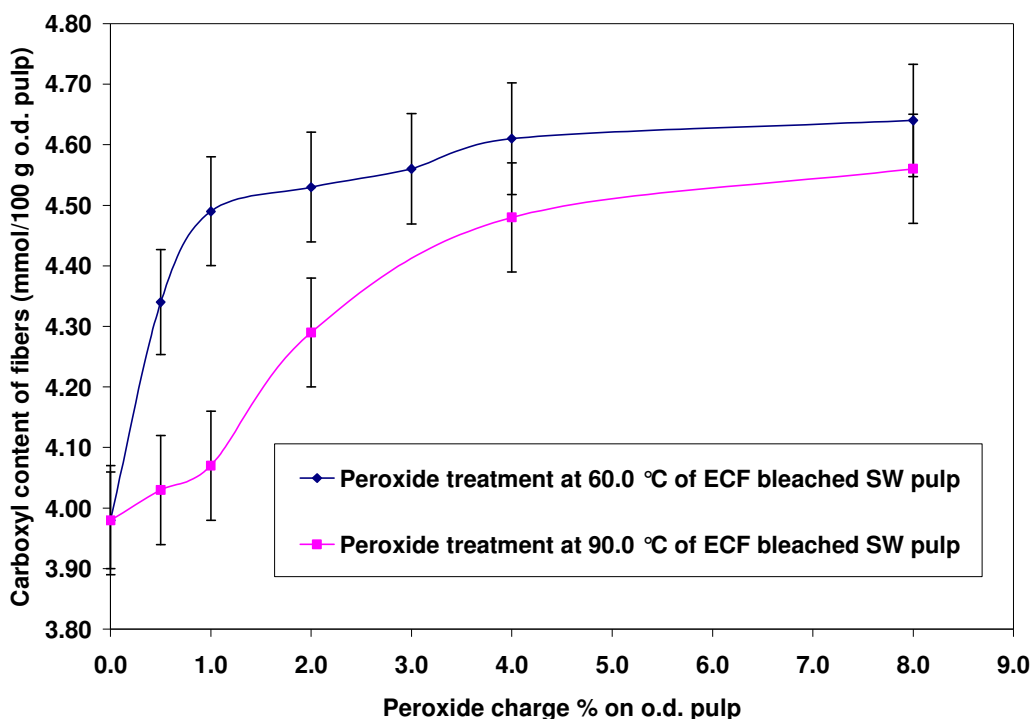


Figure 5.1. Relation between peroxide charge on o.d. pulp and fiber charge after ECF bleached softwood kraft pulp was treated at 2.0% NaOH, 2.0 h treatment time and temperatures of 60.0°C and 90.0°C.

The results in Figure 5.1 indicate that fiber charge is increased by an alkaline peroxide treatment. However, the charge value is approximately constant when peroxide charge is increased to 4.0% or greater. The maximum increase in fiber charge achieved by peroxide treatment was 16.6%. The treatment was performed at 60.0 and 90.0°C. It is obvious that an elevated temperature of 90.0°C was detrimental to fiber charge development. The influence of temperature was further studied in the range of 40.0 to 90.0°C with 2.0% NaOH, 2.0% H<sub>2</sub>O<sub>2</sub>, 10.0% consistency, and 2.0 hour treatment (Figure 5.2).

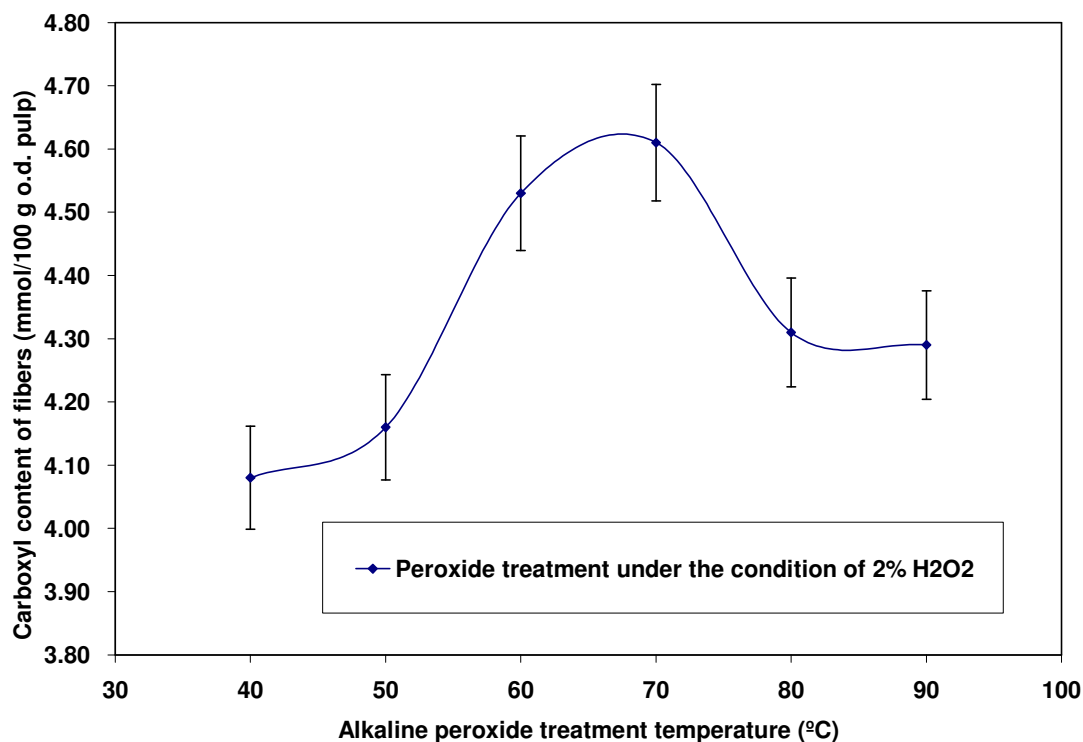


Figure 5.2. Relation between the temperature of alkaline peroxide treatment and fiber charge after ECF bleached softwood kraft pulp was treated at 2.0% NaOH and 2.0% H<sub>2</sub>O<sub>2</sub> on o.d. pulp, 10.0% consistency, and 2.0 h treatment.

Based on the data we suggest that the optimal temperature of alkaline peroxide treatment in terms of fiber charge development is between 60.0 and 70.0°C. Low temperature does not provide enough energy to activate the peroxide's oxidizing power which is necessary for fiber charge formation. A too high temperature may lead to a high decomposition rate of peroxide, i.e., to another limiting factor for fiber charge formation.[97, 118]

#### 5.1.2.2 The effect of peroxide charge on intrinsic viscosity of pulp

Intrinsic viscosity is related to the molecular weight of the carbohydrates. Reduced viscosity is a hint to reduced strength of pulp fiber. Cellulose and hemicelluloses are readily attacked during alkaline oxygen delignification and peroxide bleaching. Hydroxyl radicals, the strongest one-electron oxidant in aqueous media, are responsible for cellulose degradation.[212, 213]

Data of intrinsic viscosity are summarized in Figure 5.3. Accordingly, intrinsic viscosity decreases with increasing peroxide charge. As for the temperature effect, the intrinsic viscosity is lower after peroxide treatment at 90.0°C than that after peroxide treatment at 60.0°C. This observation is in accordance with literature reports.[97]

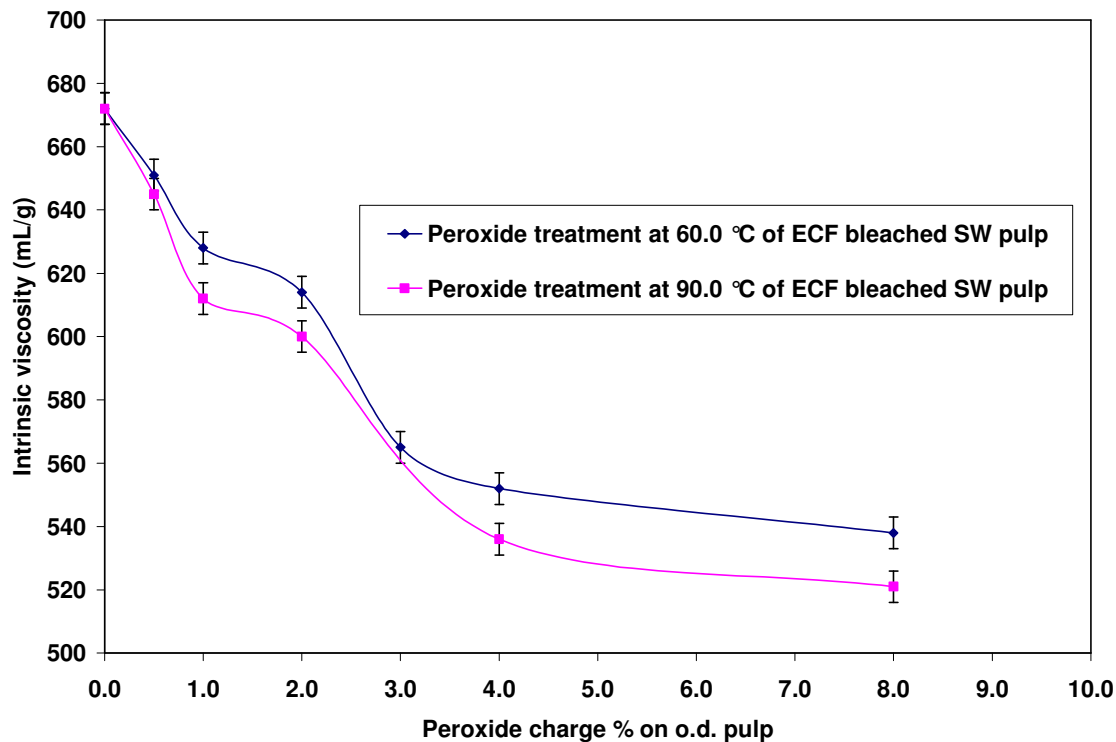


Figure 5.3. Relation between peroxide charge on o.d. pulp and intrinsic viscosity of fibers after ECF bleached softwood kraft pulp was treated at 2.0% NaOH, 2.0 h and temperatures of 60.0°C and 90.0°C.

#### 5.1.2.3 The effect of fiber charge on paper tensile strength

It is well established that higher carboxyl group content leads to enhanced paper strength.[9, 128, 206, 214, 215] Peroxide bleaching is usually the final step in a sequence before refining. Refining improves the final tensile strength. However, it has been also found that grafting with carboxymethyl cellulose (CMC) has the potential to replace the refining operation and its application leads to better paper properties than PFI-refining, e.g., concerning the relationship between tensile strength and light scattering

coefficient.[216] In this study, the unrefined pulp was modified by peroxide treatment which led to the improved fiber charge. Subsequently, the effect of the improved fiber charge on refining will be described in Section 5.2. Pulp fibers, treated with peroxide at 60.0°C in this study, were selected to investigate the influence of improved fiber charge on the tensile strength of the final paper (Table 5.1).

Table 5.1. The results of tensile index of ECF bleached softwood pulp after alkaline peroxide treatment at 60.0°C, 2.0% NaOH, 2.0 h and 10.0% consistency. Data are based on oven dried pulp.

Peroxide charge (%)	Carboxyl group content (mmol/100g)	Tensile index (Nm g <sup>-1</sup> )
Untreated ECF bleached SW pulp	3.98	32.8
0.0 (Alkaline extr.)	3.98	34.9
0.5	4.34	35.8
1.0	4.49	36.0
2.0	4.53	36.2
3.0	4.56	36.2
4.0	4.61	36.3
8.0	4.64	36.5

The tensile index of the untreated ECF bleached pulp was 32.8 Nm g<sup>-1</sup>. The fiber charge of ECF bleached pulp did not change at only 2.0% NaOH treatment. However, the tensile strength increased after 2.0% NaOH treatment to a value of 34.9 Nm g<sup>-1</sup>. This result can be explained by the increased swelling properties of fibers after alkali treatment.[139, 217] And swelling can lead to higher tensile strength.[21] In Table 5.1, it can be seen that tensile strength is enhanced as fiber charge is increased by the alkaline peroxide treatment. The tensile index of the pulp after alkaline treatment increased 6.4%



comparing to the control, while the maximum value of tensile index increased by 11.3% after 8% peroxide treatment. However, the alkaline treatment did not change the carboxyl group content which is of primary importance to retention of wet end chemicals. The densities were in the range of  $0.426 \pm 0.011 \text{ g cm}^{-3}$  which did not show correlation between the control and the peroxide treated samples. Obviously, the increase in tensile index of the enhanced fiber charge sample did not relate to the change of the sheet density.

#### 5.1.2.4 The effect of peroxide charge on copper number

In Figure 5.4, it can be seen that the pulp copper number decreases when the peroxide charge is low, but increases when the peroxide charge is elevated from 0.5% (at 60.0°C) and 1.0% (at 90.0°C). It is clear that there is an optimal peroxide charge between 0.5 and 1.0%, at which the carbonyl groups could be removed. This contributes to an increase in brightness stability. At high charges of peroxide, new carbonyl groups are generated which leads to an increase in copper number. The copper number reaches to a constant value at peroxide charge of 4.0% (Figure 5.4). The coincidence of a maximum fiber charge and the copper number at a peroxide charge of 4.0% is remarkable. We suggest that the peroxide treatment has a limitation to oxidize cellulose fibers with respect to forming carbonyl and carboxyl groups. Peroxide charges at the 4.0% level or higher will not change any more the carbonyl and carboxyl group contents.

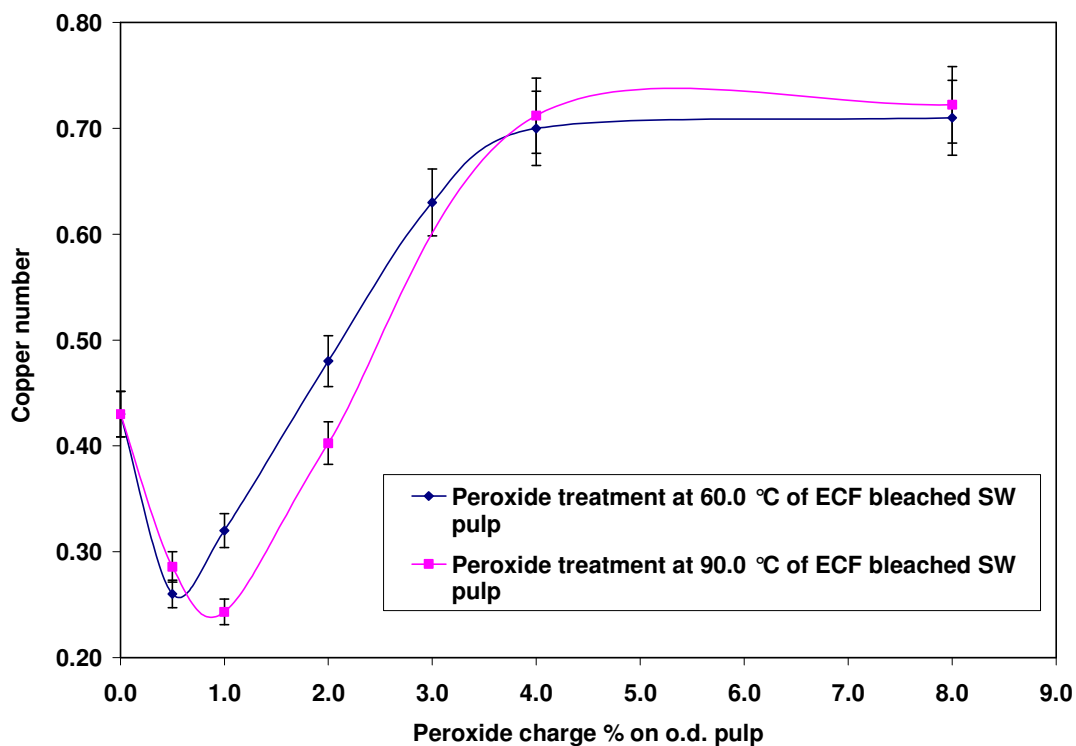


Figure 5.4. Relation between peroxide charge on o.d. pulp and copper number of ECF bleached softwood kraft pulp fibers treated at 2.0% NaOH, for 2.0 h and temperatures of 60.0°C and 90.0°C.

#### 5.1.2.5 The effect of carbonyl groups of fibers on subsequent peroxide treatment

The ECF bleached SW kraft pulp was treated with NaBH<sub>4</sub> (Figure 5.5). The carbonyl group content drops to zero after the ECF bleached kraft pulp fibers are treated with 0.5% sodium borohydride, the addition of which does not affect fiber charge.

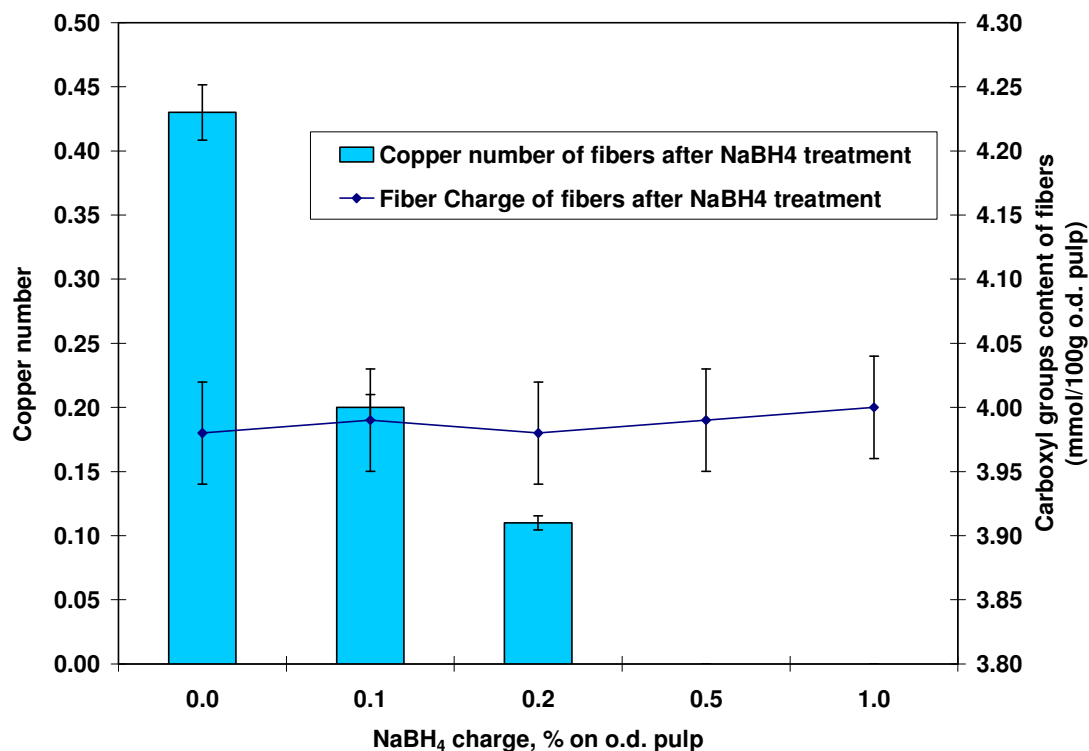


Figure 5.5. The relationship between sodium borohydride addition, copper number, and fiber charge after fibers were treated with 2.0% NaOH, for 2.0 h, at 60.0°C, with different charges of sodium borohydride.

The original pulp fiber was reduced with 0.5% NaBH<sub>4</sub>; thereafter, the reduced fibers were bleached with alkaline peroxide, at rates of 0.5 to 8.0% peroxide on o.d. pulp. The parameters during the alkaline treatment were: 2.0% NaOH on o.d. pulp, 60.0°C, 10.0% consistency, and 2.0 h.

Based on these experiments, the results of peroxide treatment on sodium borohydride reduced ECF bleached pulp can be compared with those of the peroxide treatment on original ECF bleached pulp. Three cases were considered:

- Case 1. The comparison of intrinsic viscosity (Figure 5.6).

- Case 2. The comparison of fiber charge (Figure 5.7).
- Case 3. The comparison of copper number (Figure 5.8).

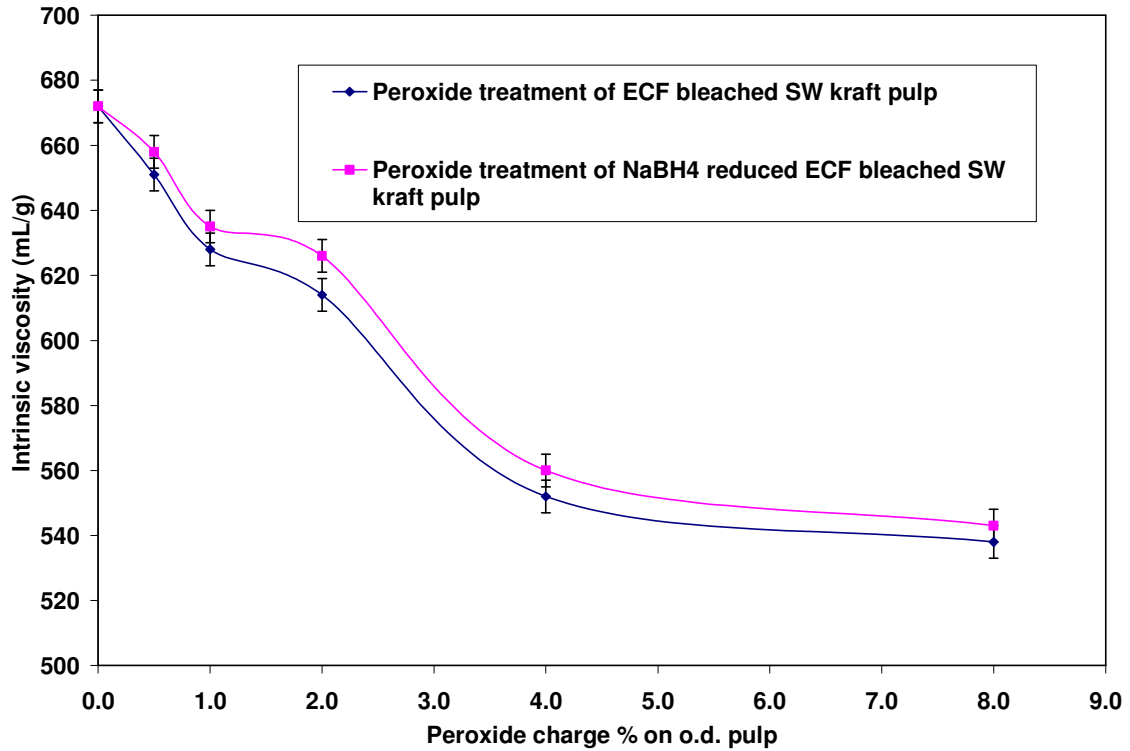


Figure 5.6. Comparison of the intrinsic viscosity after peroxide treatment on original ECF bleached kraft pulp with NaBH<sub>4</sub> reduced ECF bleached kraft pulp.

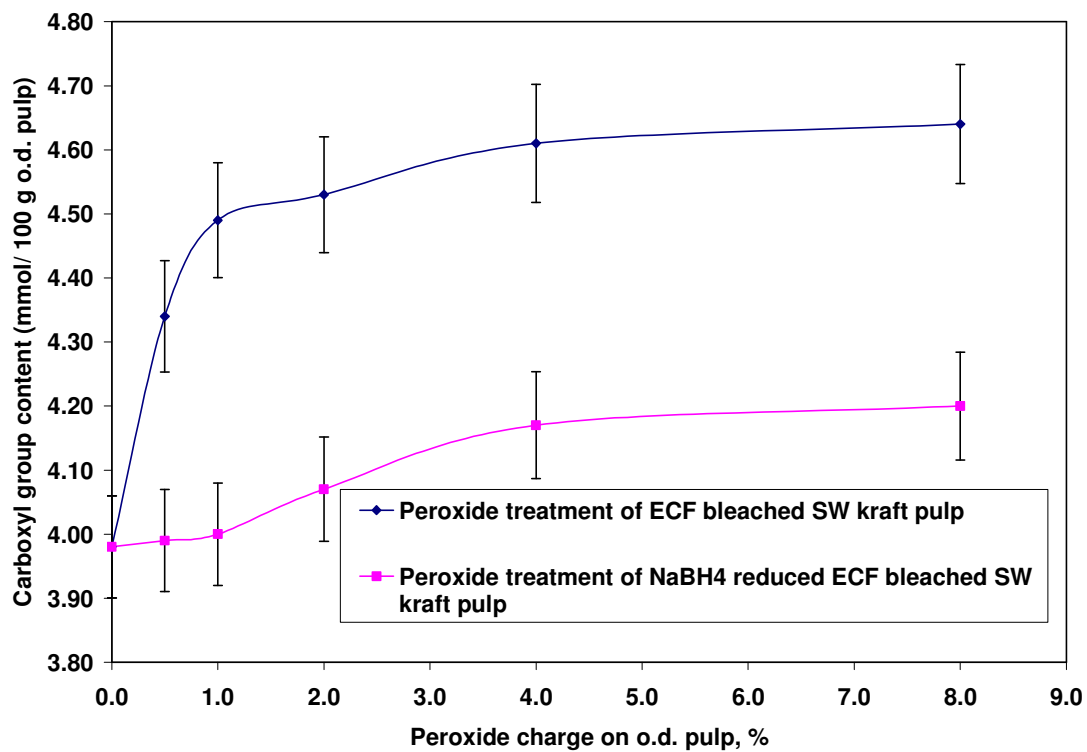


Figure 5.7. Comparison of the fiber charge after peroxide treatment on original ECF bleached kraft pulp with NaBH<sub>4</sub> reduced ECF bleached kraft pulp.

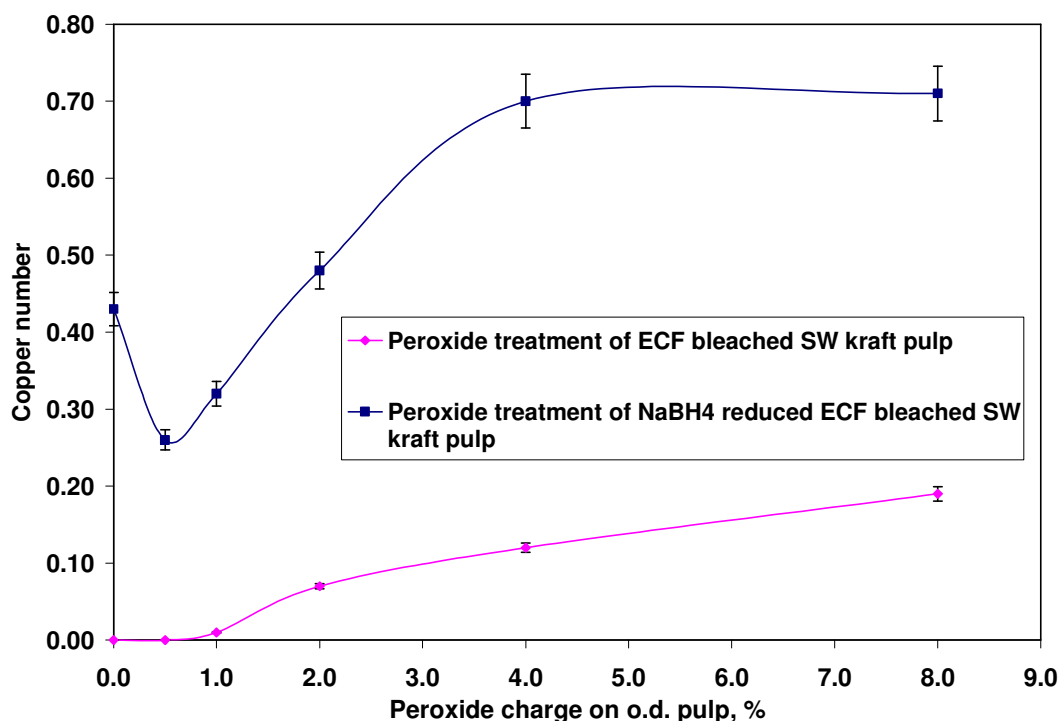


Figure 5.8. Comparison of the copper number after peroxide treatment on original ECF bleached kraft pulp with NaBH<sub>4</sub> reduced ECF bleached kraft pulp.

Peroxide bleaching of NaBH<sub>4</sub> reduced pulps resulted in a higher intrinsic viscosity values compared to the blank (with no reductive pretreatment) (Figure 5.6). This is probably due to the NaBH<sub>4</sub> reduction of carbonyl groups, which decreases the chelating power and helps remove of heavy metals.[165, 166]

Figure 5.7 is a comparison of fiber charge after peroxide treatment of original ECF bleached kraft pulp and that after NaBH<sub>4</sub> reduction. It is apparent that the best fiber charge improvement is 5.53%, and this value is much lower than that of original fibers obtained by peroxide treatment (16.6%). Copper numbers of the two types of pulps after peroxide treatment are illustrated in Figure 5.8. The maximum copper number increase

after peroxide treatment was 0.19 units for the reduced pulp fibers, while it was 0.28 for original pulp fibers. At 0.5% peroxide charge on the reduced pulp (i.e., the pulp without carbonyl groups) the copper number and the carboxyl group content did not increase at all. However, at the same peroxide charge on the original pulp, the copper number dropped from 0.43 to 0.26 and the carboxyl group content increased by 9.1%. Accordingly, the virgin pulp carbonyl groups are the source for the carboxyl groups increment after peroxide treatment.

### **5.1.3 Conclusions**

Treatment of an ECF bleached kraft pulp with alkaline peroxide at 60.0°C was shown to increase fiber charge by 16.6% at a peroxide charge of 8.0% (base on o.d. pulp). When a low peroxide charge of 0.5% employed at 60.0°C, the copper number was reduced by 39.5% and an increase of fiber charge by 9.0% was observed. At 90.0°C, the same alkaline peroxide treatment resulted in lower fiber charge and intrinsic viscosity. Optimal temperature during the peroxide treatment with respect to fiber charge was found to be between 60 and 70°C. Peroxide treatment of ECF bleached kraft pulp was compared with NaBH<sub>4</sub> reduced ECF bleached kraft pulp. The results with respect to fiber charge and copper number indicated that the carbonyl groups are source for the elevated carboxyl group contents observed after peroxide treatment.

## **5.2 The effect of increased fiber charge on refining, wet-end application, and hornification**

### 5.2.1 Introduction and objective

The intent of this paper is to study how improved fiber charge obtained from a peroxide-stage treatment affects refining, wet-end application, and hornification. On the basis of Section 5.1, an ECF bleached SW-KP was treated with 2% NaOH, and 1% H<sub>2</sub>O<sub>2</sub>, at 60°C resulting in a 12.8% increase in fiber charge. This study examines the effect of the change in fiber charge with respect to refining, cationic starch adsorption, and drying.

The properties of the control pulp and the high fiber charge pulp (HCP) are summarized in Table 5.2. The freeness values do not show an obvious difference between the two pulps. Given these results, the effects of enhanced fiber charge were investigated on refinability, cationic starch adsorption, and hornification.

Table 5.2. The properties of the control pulp and HCP.

Pulp properties	Pulp samples	
	Control pulp	HCP
Brightness (Tappi standard)	84.5	87.3
Intrinsic viscosity (ml g <sup>-1</sup> )	672	628
Carboxyl group content (mmol/100 g o.d. pulp)	3.98	4.49
Freeness (ml)	696±5	690±5
FQA of fibers		
Fiber length (mm)	1.090±0.034	0.995±0.032
Curl	0.144±0.006	0.128±0.006
Kink index (l mm <sup>-1</sup> )	1.48	1.38



## **5.2.2 Results and discussion**

### **5.2.2.1 The influence of elevated fiber charge on refining**

HCP and control pulp were PFI refined at 500, 1000, 2000, 4000, and 8000 r. Fiber charge values of 3.98 – 4.00 mmol/100 g (control pulp) and 4.45 – 4.51 mmol/100 g (HCP) were observed. Total fiber charge properties of both pulps remained relatively constant throughout the refining. Thus PFI refining does not appear to alter total fiber charge properties, a finding which is in agreement with the results of Bhardwaj et al. [176]

The surface charge, on the other hand, increased as a function of PFI revolution (Figure 5.9-A). Expectedly, the refined pulp adsorbs more cationic polymers onto the fiber surface than the unrefined pulp. Surface charges of the two pulps without refining were statistically the same (Figure 5.9.-A). We can safely conclude that peroxide treatment of ECF bleached pulp does not affect significantly the surface charge.

Figure 5.9-B shows the tensile indices plotted against the level of PFI refining. The initial tensile strength of the HCP was 10% higher than the control pulp. The differences in tensile indices between the two pulps were increased to 15.4% when refining took place at 1000 r. On the basis of Figure 5.9-B, the tensile indices of the two pulps are identical if refined at 2000 to 4000 revolutions. The control pulp exhibits a reduction in tensile strength when the revolution is elevated from 4000 to 8000.

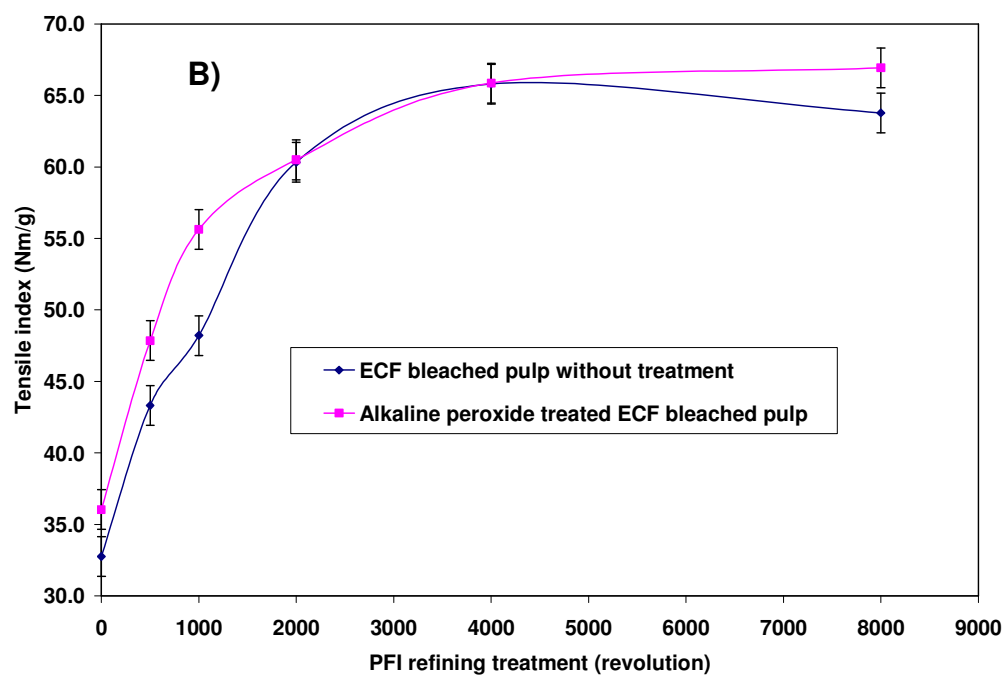
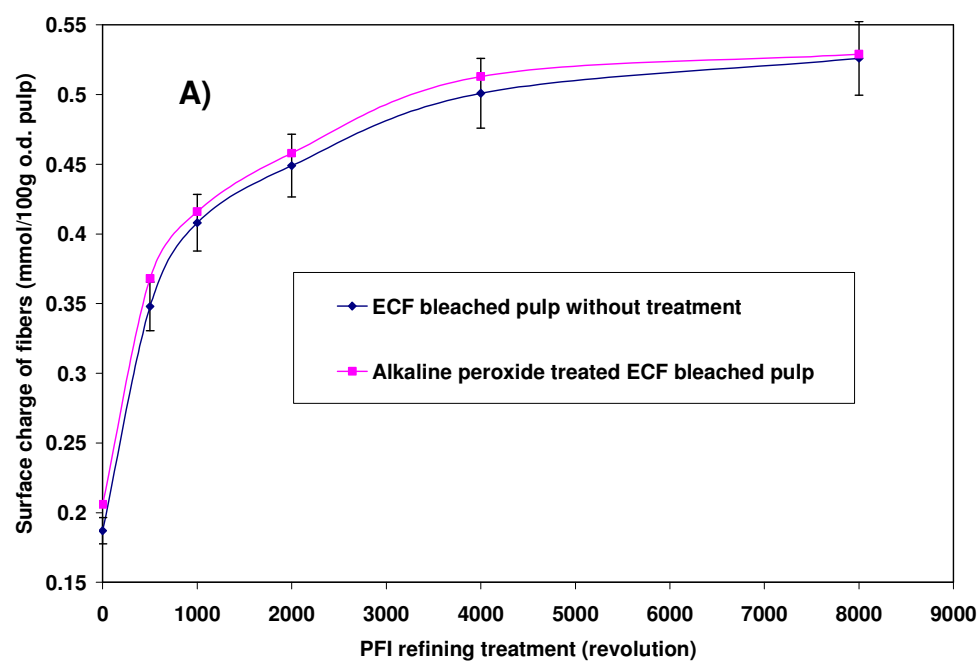


Figure 5.9. The effect of increased fiber charge on PFI refining. A) surface charge and B) tensile strength against refining treatment of the control pulp and the alkaline peroxide treated pulp.

It is well known that refining enhances the surface area of fibers.[218-220] Also, Carrasco et al.[221] found that freeness is related the total surface area of fibers after refining. The tensile strength is plotted against the freeness in Figure 5.10. It is obvious that HCP has better tensile indices of than those of the control pulp in the freeness range between 540 and 670 ml and below 260 ml. This observation is in agreement with the results illustrated in Figure 5.9-B.

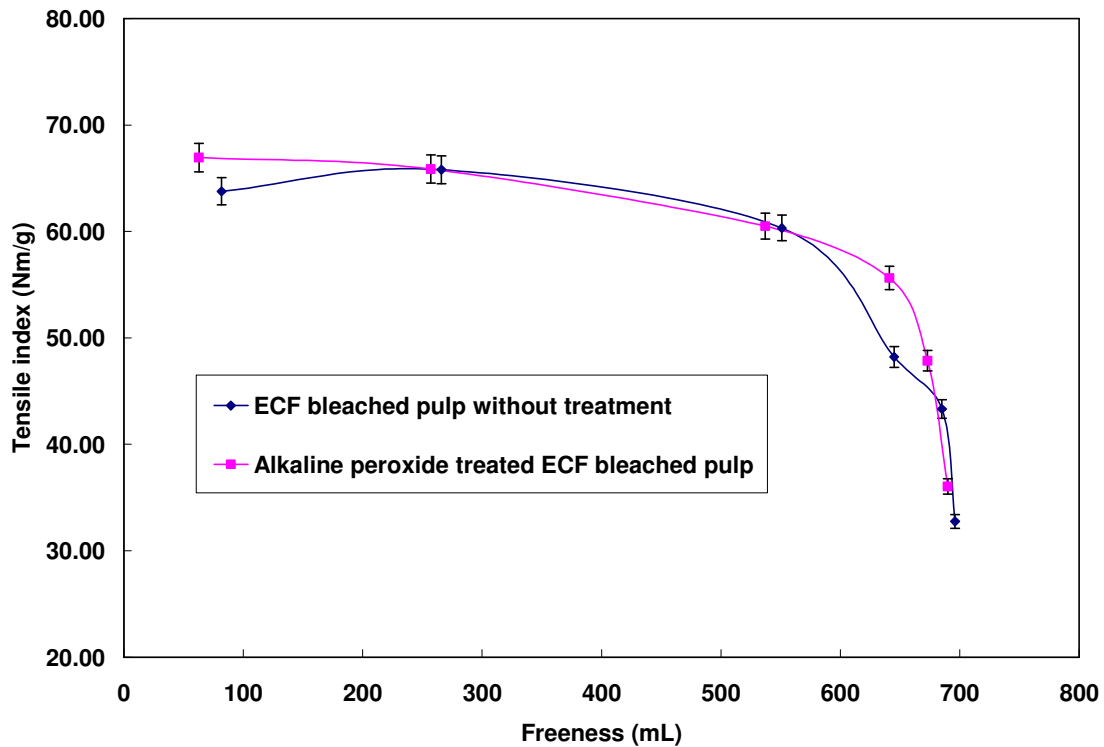


Figure 5.10. Comparison between tensile strength and freeness of the control pulp and the alkaline peroxide treated pulp after refining.

The increased surface area of fibers after milling also leads to better bonding[222], but may damage the fiber quality which results in lower single fiber strength and lower final paper strength[223]. In this study is also confirmed that the

tensile strength of the control pulp increases under the mild refining treatment, but decreases at the higher levels of refinement. It is well established that the strength of final paper is primarily controlled by fiber-fiber bonding at low levels of mechanical treatment, but the single fiber strength may become more important with high levels of refining. However, this is not the case for the HCP; it is more sensitive to mechanical refining from the very beginning.

#### 5.2.2.2 The influence of increased fiber charge on the cationic starch adsorption onto fibers

The wet-end behavior of the pulps was evaluated in the context of cationic starch as additive. Usually, papermakers apply about  $4.54 \text{ kg ton}^{-1}$  ( $10 \text{ lb ton}^{-1}$ ), i.e. 0.454%, of cationic starch into the system and then gradually optimize it from that point.[224] In this study, dosages of 0.25, 0.50, 1.0, and 2.0% (based on o.d. pulp) were applied to both pulps in focus. Figures 5.11 and 5.12 show the results concerning of tensile and burst strength. It is apparent (Figure 5.11) that the tensile index was increased 23.7% with 2% cationic starch application onto the HCP in comparison to a 13.7% increment of the control pulp. The tensile index did not change too much around 1% cationic starch addition to the control pulp. However, the tensile index of the peroxide treated pulp exhibited a continuing increase even at higher application levels. As shown in Figure 5.12, the greatest increase of burst indices is 47.4% (control) and 57.9% (HCP) when 2% cationic starch is applied. Clearly, the efficiency of cationic starch adsorption is better in the case of HCP.

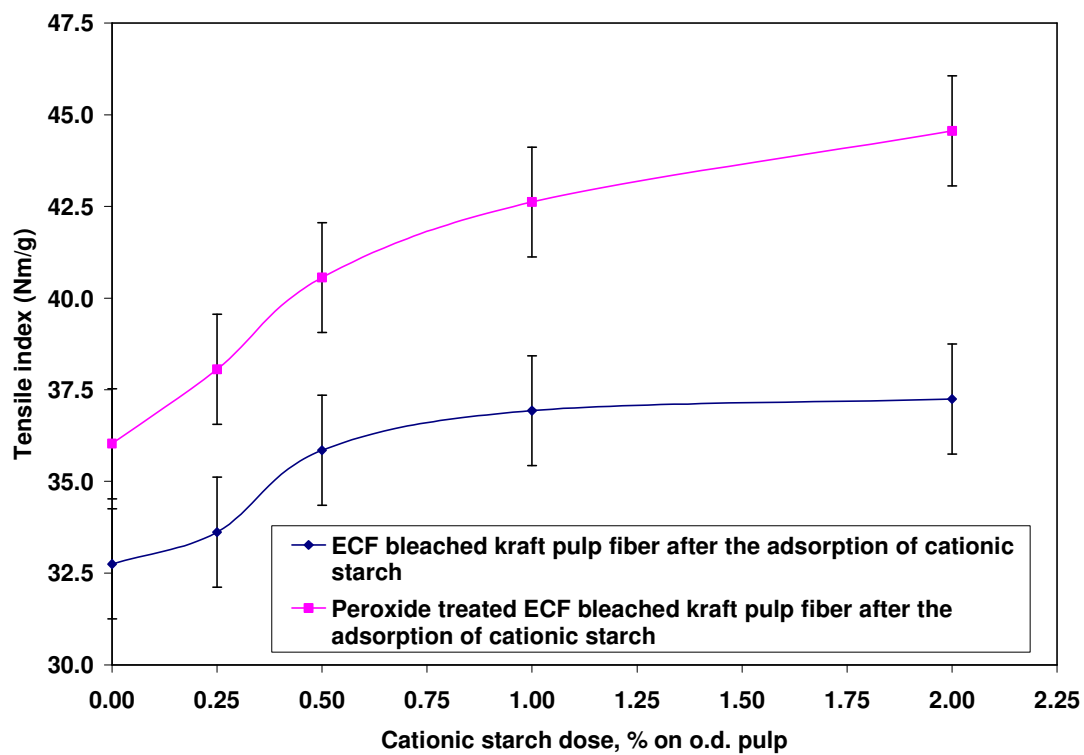


Figure 5.11. Comparison of tensile index between the control pulp and the alkaline peroxide treated pulp after the adsorption of cationic starch onto fibers.

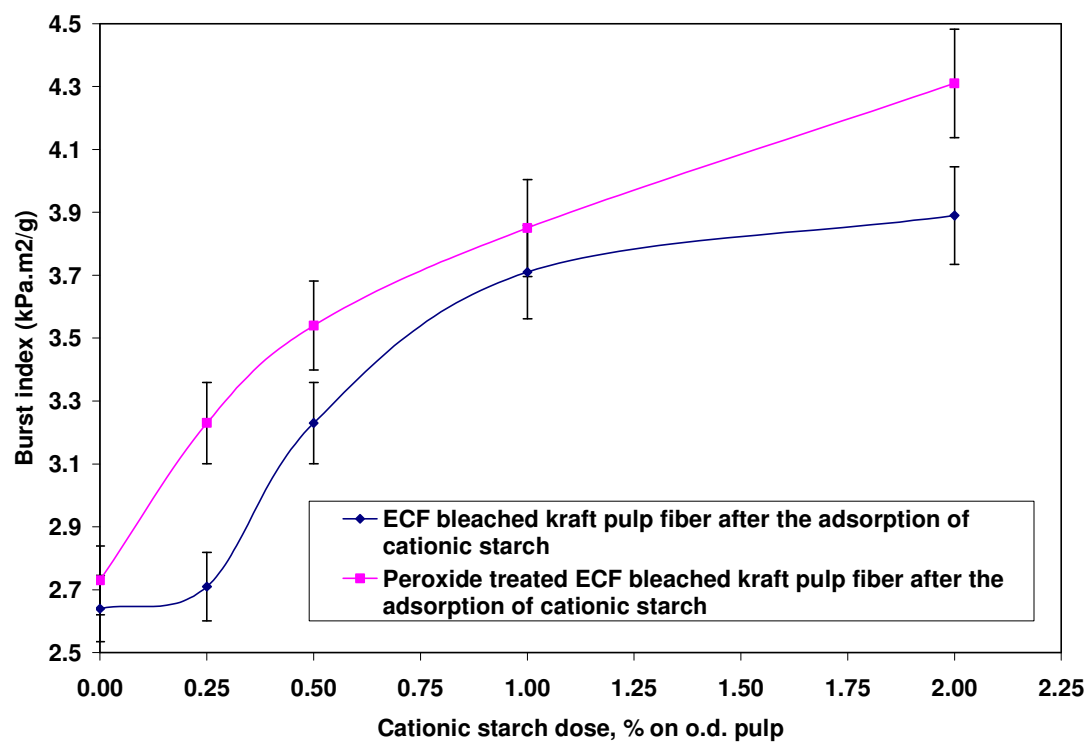


Figure 5.12. Comparison of burst index between the control pulp and the alkaline peroxide treated pulp after the adsorption of cationic starch onto fibers.

Tensile index has a linear relationship with burst index (Figure 5.13). The slope of the control sample trend line is lower than that of the enhanced fiber charge pulp.

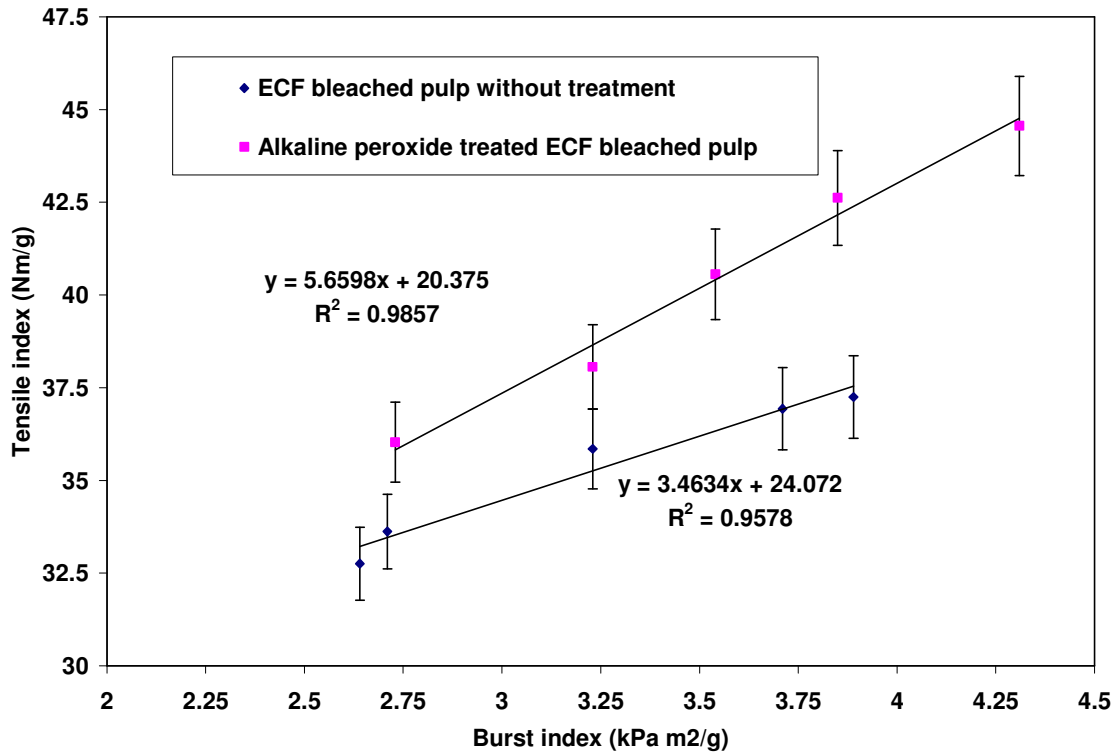


Figure 5.13. Comparison of burst index against tensile index of the control pulp and the alkaline peroxide treated pulp after the adsorption of cationic starch onto fibers.

#### 5.2.2.3 Surface morphology of cationic starch treated fibers measured by AFM

AFM is an effective tool for evaluating surface morphology and properties of wood, fibers, and cellulose. In our previous study on holocellulose fibers, we had reported that there was no apparent relationship between roughness and surface charge of fibers.[225] Figure 5.14 shows AFM phase images of the control, the control treated with

2% cationic starch, the HCP, and the HCP treated with 2% cationic starch. No striking differences in the surface topographies among the samples were found.

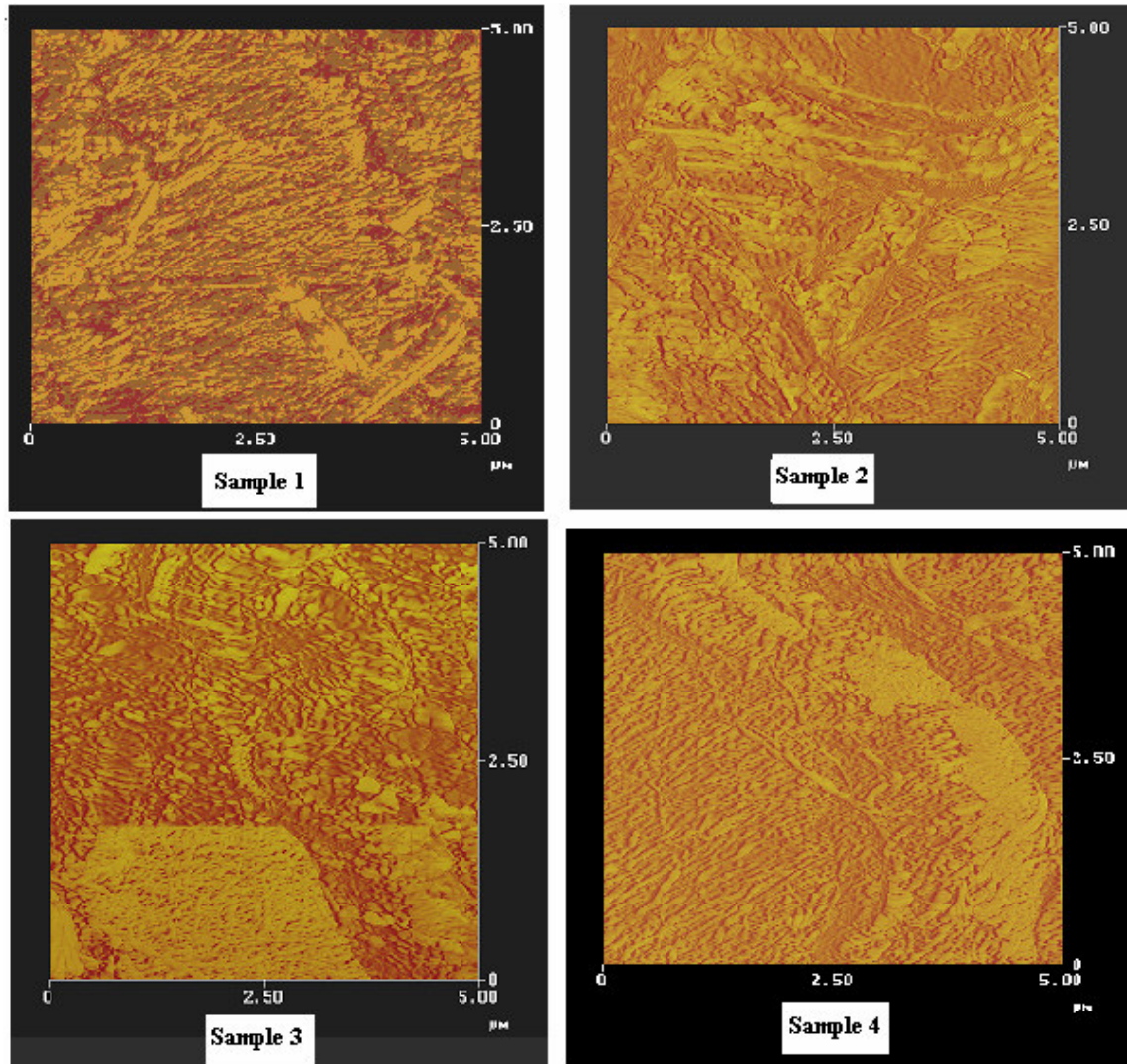


Figure 5.14. Atomic force microscopy (AFM) phase images of pulp fibers: 1. control pulp, 2. control pulp treated with 2% cationic starch, 3. HCP, 4. HCP treated with 2% cationic starch.

#### 5.2.2.4 The influence of the increased fiber charge on hornification



Table 5.3. The results of pulp properties of the control pulp and HCP dried at 23°C and 105°C.

Pulp samples	Drying at (°C)	Intrinsic viscosity (ml g <sup>-1</sup> )	Total carboxyl group content (mmol/100 g)	Tensile index (Nm g <sup>-1</sup> )	Burst index (kPa m <sup>2</sup> g <sup>-1</sup> )
1. Control pulp	23	672	3.98	32.8	2.6
2. Control pulp	105	667	3.97	29.0	2.1
3. Peroxide* treated pulp	23	628	4.49	36.0	2.7
4. Peroxide* treated pulp	105	616	4.45	31.5	2.4
5. Control pulp**	105 and 23	544	4.12	23.2	1.6
6. Control pulp***	105 and 105	542	4.11	19.2	1.0

\* Peroxide treatment condition: 2% NaOH, 1% H<sub>2</sub>O<sub>2</sub>, 60°C, 10% consistency, and 2 h treatment.

\*\* First dried at 105°C, peroxide\* treated, and finally dried at 23°C

\*\*\* First dried at 105°C, peroxide\* treated, and finally dried at 105°C

Six samples were prepared and the data are summarized in Table 5.3. By comparing the results of pulps dried at 23°C (samples 1, 3, and 5) with those dried at 105°C (samples 2, 4, and 6), it can be seen that drying at elevated temperature does not have an obvious effect on intrinsic viscosity and fiber charge. However, high temperature drying does decrease physical strength properties including tensile and burst strength for both control pulp and HCP.

The tensile index of sample 2 decreased 11.6% compared to that of sample 1, while the decrement was 12.5% in the case between samples 4 and 3. In terms of the effect of peroxide treatment on hornification, the tensile and the burst indices of sample 4 were respectively 8.6% and 14.3% higher than those of sample 2. Accordingly, increased fiber charge can reduce the effect of hornification for never dried fibers to some extent. On the contrary, the tensile and burst indices of sample 6 showed a drastic decrease compared with those of samples 2 and 4. Although the carboxyl group content of sample

6 was 3.5% greater compared to sample 2, the tensile index of sample 6 dropped 33.8% (against sample 2) and 39.0% (against sample 4). Similar to the results of tensile index determination, the burst index dropped 52.4% and 58.3%. These results indicate that the peroxide treatment of oven dried pulps can not be used to recover physical strength properties. This treatment is in some cases detrimental.

### **5.2.3 Conclusions**

The increased fiber charge can enhance the efficiency of refining between freeness values of 540 and 670 ml and lower than 260 ml. In this ranges, the tensile index of the HCP is greater than that of the control pulp. The tensile index increased 23.7% with 2% starch application to the HCP, while the tensile index of the control pulp was improved 13.7%. The burst index of the control pulp and HCP increased 47.4% and 57.9% after 2% cationic starch addition, respectively. When the never dried pulp was treated by peroxide, the increased fiber charge reduced the hornification at 105°C in comparison to the control pulp. The peroxide treatment of the once dried pulp at 105°C increased the hornification. The manifestation of this was very low intrinsic viscosity, tensile and burst indices.

## CHAPTER 6

### CHARACTERIZING TEMPO-MEDIATED OXIDATION OF ECF BLEACHED SOFTWOOD KRAFT PULPS

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#### 6.1 Introduction and objective

Softwood and hardwood kraft pulps are often used for absorbency materials. However, softwood fibers are judged to have much better water absorbency property than hardwood fibers.[226] Therefore, they are often preferably used as absorbency materials.[227] The objective of this study is to investigate TEMPO-mediated oxidation of an ECF bleached softwood kraft pulp which has not been previously examined. The effect of the oxidation parameters on carboxyl group content, copper number, water absorbency, and intrinsic viscosity of SW bleached kraft pulp were examined. NMR analyses and SEM images were employed to study the crystallinity index and surface morphology of oxidized fibers, respectively.

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<sup>v</sup> This manuscript was accepted by Carbohydrate Polymers and is in the process of publishing. It was titled as “Characterizing TEMPO-mediated oxidation of ECF bleached softwood kraft pulps”. The other two authors are Dr. Jianguo Zhang and Dr. Arthur J. Ragauskas from the School of Chemistry and Biochemistry at the Georgia Institute of Technology.

## 6.2 Results and discussion

### 6.2.1 The effect of charge of NaClO on carboxyl group content, carbonyl group content, intrinsic viscosity of fibers after TEMPO-mediated oxidation

Figure 6.1 presents the carboxyl group content, carbonyl group content, and intrinsic viscosity of pulp fiber after treatment with different levels of NaClO charge. These results indicate that the carboxyl group content increased from 3.98 to 23.1 mmol/100 g o.d. fibers in a near linear relationship of NaClO addition. The change in the degree of cellulose polymerization was monitored by intrinsic viscosity measurement. These results are in agreement with recent studies by Kitaoka et al.[26] and Saito & Isogai[32]. Evans & Wallis[228] developed an equation relating the degree of polymerization (DP) to the intrinsic viscosity  $[\eta]$  of the carbohydrates (equation 6.1). The DP of the control ECF bleached fibers was estimated as 2416, while the DP of the TEMPO oxidized fibers after 1.701 mmol NaClO/g o.d. pulp charge was 688.

$$DP^{0.9} = 1.65 \times [\eta] \quad (6.1)$$

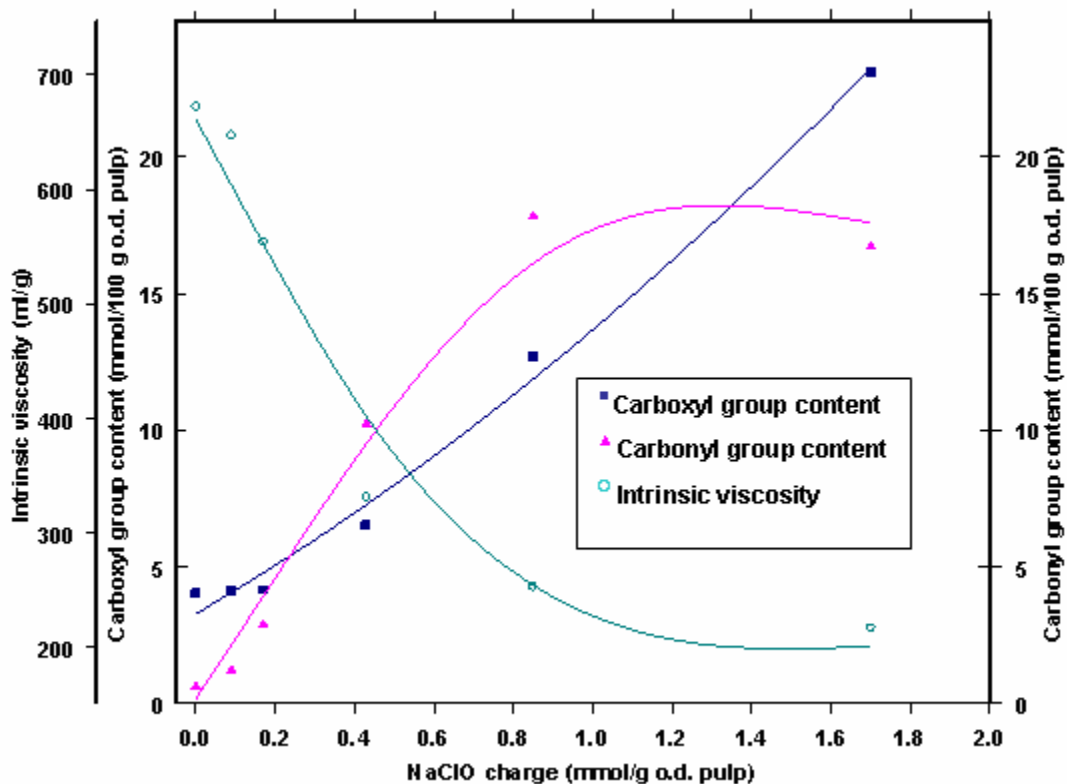


Figure 6.1. Carboxyl group content, carbonyl group content, and intrinsic viscosity of ECF bleached SW kraft pulps prepared with varying NaClO charge on pulps during TEMPO-mediated oxidation.

The copper number ( $\text{Cu}^\#$ ) is an indication of aldehyde groups in fibers and the analysis for the TEMPO oxidized pulps is presented in Figure 6.1. Röhring et al.[159] reported a linear relationship between the carbonyl group content and copper number shown in equation 3.3. In this study, this equation was applied to convert  $\text{Cu}^\#$  to carbonyl group content.

The aldehyde group is generated by oxidizing C6 hydroxyl group during TEMPO-mediated system. The results of carbonyl group content measurements are summarized in Figure 6.1. This data shows that the aldehyde groups enhanced with

increasing NaClO charge approaching a maximum value of 17.8 mmol/100g o.d. pulp with NaClO charge of 0.85 mmol/g o.d. fibers. These results suggest that the TEMPO-oxidation process is not yet fully optimized for the formation of acid groups.

### 6.2.2 <sup>13</sup>C CP/MAS NMR spectra of the oxidized fibers

<sup>13</sup>C CP/MAS NMR analysis of the starting and TEMPO oxidized pulp were recorded, and the crystallinity index was determined following a literature method.[47] As summarized in Table 6.1, these results indicate that there was a minor increase in the crystallinity for the oxidized fibers. This suggests that the amorphous regions in fiber are slightly more prone to oxidation.

Table 6.1. Crystallinity index results from <sup>13</sup>C-CP/MAS NMR analysis of original ECF bleached SW kraft pulp fibers and TEMPO-mediated oxidized fibers.

Sample I.D.	Crystallinity index
Original ECF bleached SW pulp fibers	0.52
Oxidized fibers (0.43 mmol NaClO/g o.d. pulp charge)	0.52
Oxidized fibers (0.85 mmol NaClO/g o.d. pulp charge)	0.53
Oxidized fibers (1.70 mmol NaClO/g o.d. pulp charge)	0.54

### 6.2.3 SEM images of the oxidized fibers

Figure 6.2 illustrates the SEM images of the original ECF bleached SW kraft pulp fibers and TEMPO-mediated oxidized pulps (NaClO charge of 1.70 mmol/g o.d. pulp). Figure 6.2-A provides a clear illustration of the primary wall of a fiber. The fibrils inside the fibers can be clearly seen from Figure 6.2-B. This result suggests that the primary wall or even the S1 sublayer, i.e. the outer layer of second wall, of the fibers were partially peeled by the alkaline TEMPO-mediated oxidation.

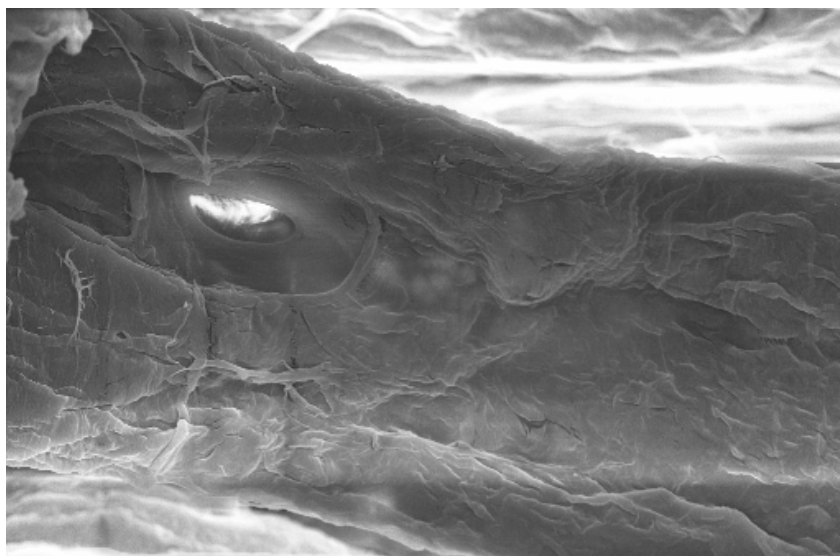


Figure 6.2-A. SEM image of original ECF bleached SW kraft pulp fibers.

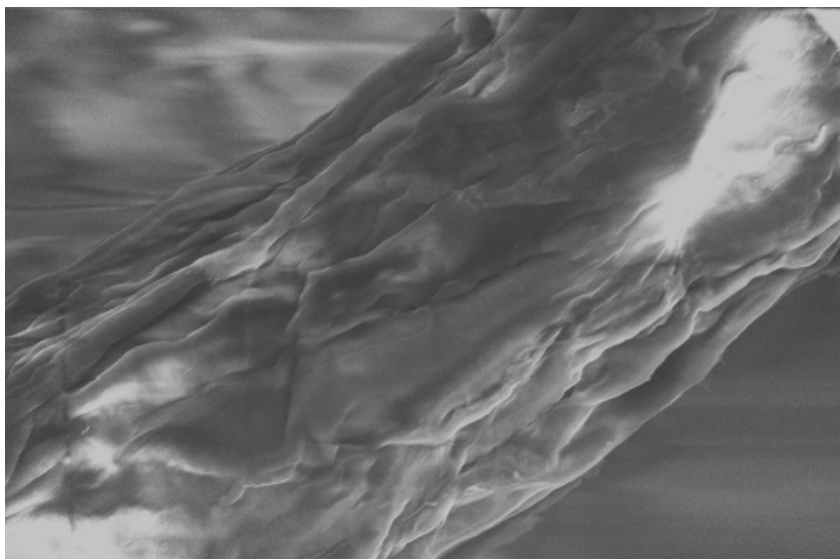


Figure 6.2-B. SEM image of TEMPO-mediated oxidized ECF bleached SW kraft pulp fibers (1.70 mmol NaClO/g o.d. pulp charge).

#### **6.2.4 The effect of temperature during TEMPO-mediated oxidation on carboxyl group content and intrinsic viscosity of fibers**

As discussed previously, hypochlorite degrades carbohydrates which results in the loss of fiber viscosity. Usually, hypochlorite bleaching of kraft pulps is limited to high alkalinity (pH~10) and low temperature.[70] To investigate the effect of reaction temperature on carboxylate content and fiber viscosity, the TEMPO oxidation was conducted at varying reaction temperatures with a fixed charge of 0.85 mmol NaClO/g o.d. pulp (see Figure 6.3). These results show that the carboxyl group content of SW bleached fibers reaches a maximum value at 23 °C. The intrinsic viscosity of fibers after TEMPO oxidation at 23 °C was found to be the lowest.



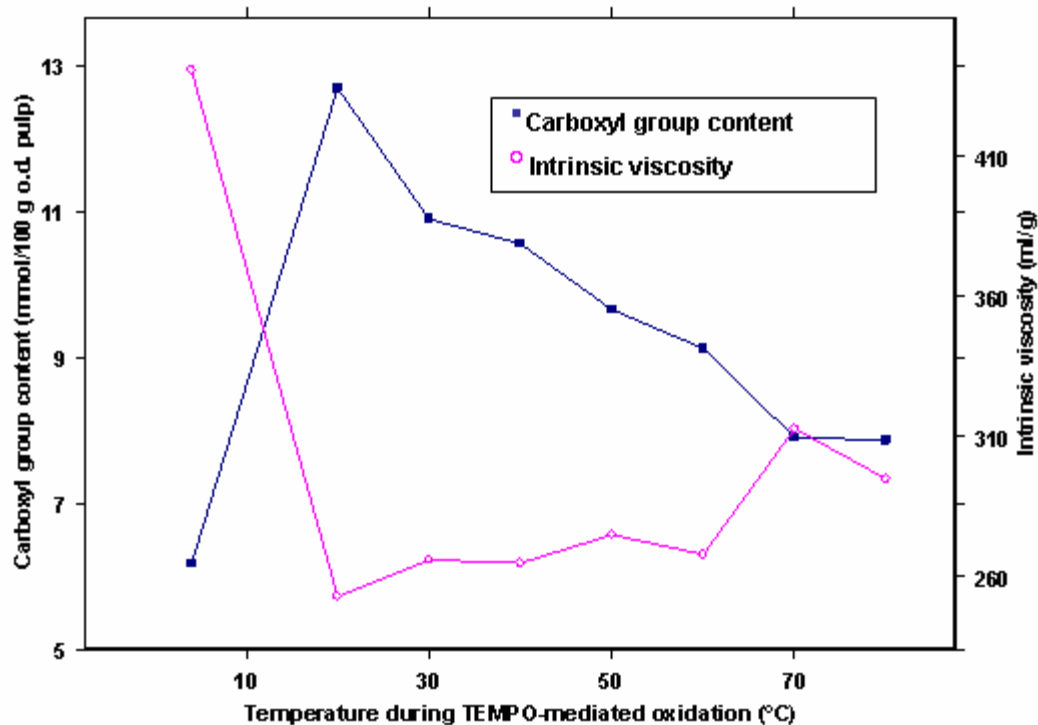


Figure 6.3. The effect of temperature during TEMPO-mediated oxidation on carboxyl group content and intrinsic viscosity of ECF bleached SW kraft pulps at the condition of 0.85 mmol NaClO/g o.d. pulp charge.

#### 6.2.5 The effect of pH value during TEMPO-mediated oxidation on carboxyl group content, carbonyl group content, and intrinsic viscosity of fibers

It's been reported that the solution pH value has an impact on the TEMPO-mediated oxidation with respect to the formation of carboxyl group and the reaction rate.[27] To evaluate this effect for SW bleached kraft pulp, five reaction pH values were examined including 7.10, 8.00, 8.60, 9.10, and 10.00. The remaining experimental conditions were kept constant including a reaction temperature of 23°C, 2.0 h reaction

time, and 0.85 mmol NaClO/g o.d. pulp. Figure 6.4 shows the results of carboxyl and carbonyl group content, and intrinsic viscosity of fibers after the ECF bleached SW kraft pulp was oxidized by the TEMPO-mediated system with 0.85 mmol NaClO/g o.d. pulp. In terms of the formation of carboxyl group content of fibers, the optimal result was obtained at pH 9.10. At this pH value, the carbonyl group content was the lowest, and the intrinsic viscosity was next to the highest value observed.

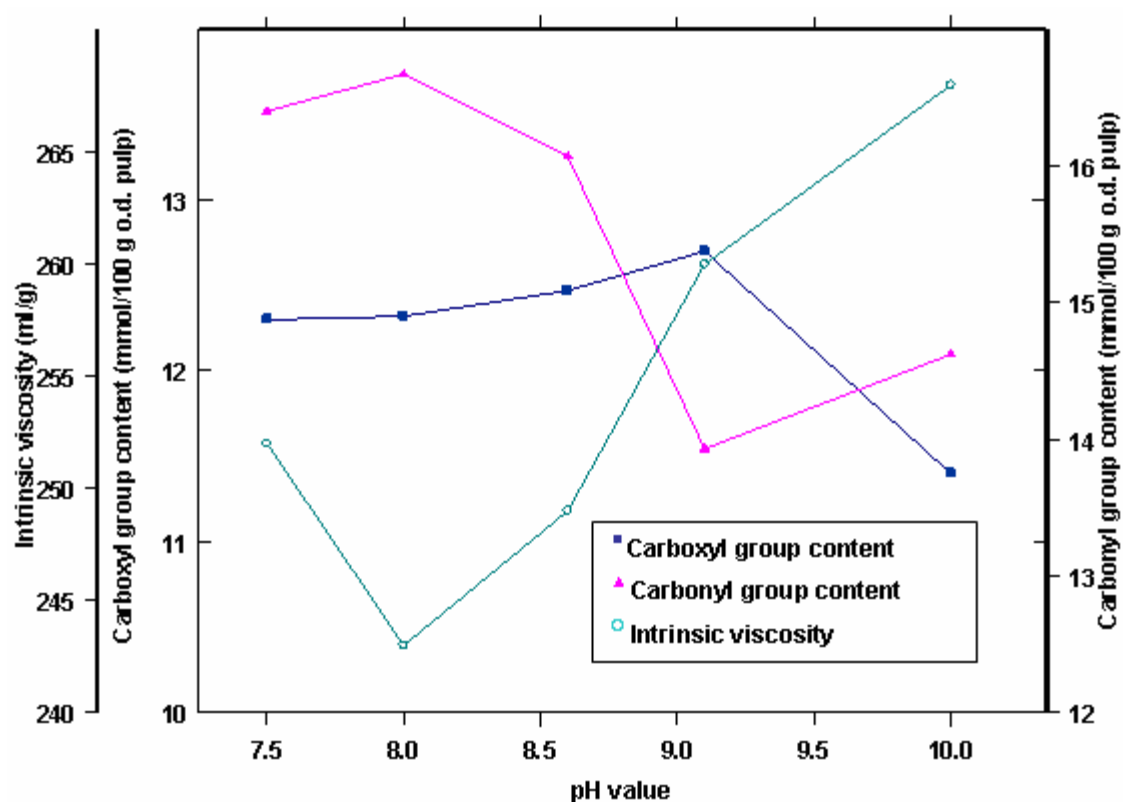


Figure 6.4. The effect of pH value during TEMPO-mediated oxidation on carboxyl group content, carbonyl group content, and intrinsic viscosity of ECF bleached SW kraft pulps at the condition of 0.85 mmol NaClO/g o.d. pulp charge.

#### **6.2.6 The effect of PEG addition on water retention value of fibers after TEMPO-mediated oxidation**

Pulp water retention values characterize the swelling capability of pulps.[138] It is commonly acknowledged that enhanced fiber swelling relates to increased concentration of acid groups in the mechanical pulps[8, 138] and kraft pulp[225]. In our previous study of the effect of carboxyl group content on WRV, it was found that there is a linear relationship between the carboxyl group content and WRV of the softwood kraft pulp.[225]

PEG is widely used to cross-link pulp fibers to enhance the water absorbency property of fibers.[229, 230] It has been reported that PEG-hydroxyl end groups can form ester crosslinking with cellulosic hydroxyl groups and carboxyl groups.[231, 232] Ibrahim et al.[233] studied the addition of PEG in the citric acid treated cotton and reported that the carboxyl group content was decreased due to the esterification. The imparting of a more hydrophilic crosslinked structure leads to enhanced swellability of the cellulose structure and higher moisture absorption.[233] In addition, PEG treatment of textile fabric shows enhancement of the fabric properties including antistatic behavior, wrinkle recovery, and abrasion resistance.[234, 235]

The glycols used in this study to cross-link fibers were PEG with a MW of 3,350 and 10,000. The water retention values of the original ECF bleached SW kraft pulp, TEMPO oxidized, and PEG cross-linked pulps were studied. Table 6.2 summarizes the results of water retention studies.

The WRV of oxidized fibers is greater than that of the original fibers by 62.9%. This result indicates that, the higher value of carboxyl group content, the higher is the

water retention value of the fibers. Kitaoka et al.[26] studied the chemical modification of bleached hardwood kraft pulp fibers by TEMPO-mediated oxidation. They reported that WRVs of pulps were roughly constant, even though these pulps had carboxyl contents from 0.06 to 0.47 mmol/g after TEMPO oxidation. In comparison, the softwood kraft pulps in this study present an enhanced water absorbency property after TEMPO oxidation.

The WRV of fibers after PEG cross-linking was increased compared to the untreated fibers. This is consistent with the study by Barcus & Bjorkquist[229]. As for the original fibers, the WRVs were increased by 59.6% and 22.6% after cross-linking by PEG 3,350 and 10,000, respectively. However, they increased by 18.1% and 3.0% when the oxidized fibers were cross-linked by PEG 3,350 and 10,000, respectively. Based on the performance of PEG 3,350 and PEG 10,000 on fibers, the low molecular weight polymer appears to provide enhanced improvement of fiber WRV.

Table 6.2. The results of water retention values of ECF bleached SW kraft pulps with and without cross-linking.

Sample I.D.	Water retention value (g water/ g o.d. pulp fibers)		
	Control	Cross-linked by PEG 3,350	Cross-linked by PEG 10,000
Original ECF bleached SW pulp fibers	0.733	1.170	0.899
Oxidized fibers (0.85 mmol NaClO/g o.d. fiber)	1.194	1.410	1.230

### 6.2.7 The paper physical properties of fibers after TEMPO-mediated oxidation

Tensile and zero-span strength of the paper test sheets prepared from the two oxidized pulp samples described in section 6.2.6 were measured. The results are summarized in Table 6.3.

Due to the higher carboxyl group content, the tensile strength of the paper test sheet prepared from the oxidized pulp fibers was higher than that of the original pulp fibers. Zero-span index indicates the average ultimate strength of the longitudinal structure of individual fibers in a paper test sheet. The zero-span strength of the oxidized pulp fibers was lower than that of the original pulp fibers. Since the TEMPO-mediated oxidation drastically drops the intrinsic viscosity, it leads to the lower single fiber strength.

Table 6.3. The results of paper physical properties of original ECF bleached SW kraft pulp fibers and oxidized fibers.

Sample I.D.	Paper physical strength	
	Tensile Index (Nm/g)	Zero-span Index (Nm/g)
Original ECF bleached SW pulp fibers	26.8	119.7
Oxidized fibers (0.85 mmol NaClO/g o.d. fiber)	30.5	99.3

### 6.3 Conclusions

This study demonstrates the potential of the TEMPO-KBr-NaClO system to oxidize ECF bleached SW kraft pulp fibers providing a 480% increase in carboxyl group at the charge of 1.701 mmol NaClO/g o.d. pulp. In addition, at this high oxidative charge the carbonyl group content of pulp was increased by a factor of 28. A comparison of the SEM images between the original fibers and the oxidized fibers indicated that the primary wall can be peeled by TEMPO-mediated oxidation. In terms of the carboxyl group formation of fibers after TEMPO-mediated oxidation, the optimum temperature and pH value were found to be around room temperature, and 9.10, respectively. Water retention value of the oxidized fibers had higher value than the original fibers. Fibers after PEG cross-linking showed increased water retention value. The zero-span strength of the paper test sheets prepared from the oxidized pulp fibers were lower than the original bleached pulp fibers due to oxidatively induced changes in the fibers.

## CHAPTER 7

### CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Conclusions

In the experiments reported here, the carboxyl groups of pulp fibers were carefully investigated during kraft pulping, alkaline peroxide bleaching, and TEMPO-mediated oxidation. This study provides a practical way to control the carboxyl group content of kraft pulps by kraft pulping, an effective technique to enhance the carboxyl group content of fully bleached pulps by peroxide bleaching, and a novel method to enrich the carboxyl groups into fibers.

##### 7.1.1 Effect of kraft pulping on fiber charge

Laboratory kraft pulping of loblolly pine was carried out to study the influence of pulping conditions, including: effective alkali (EA), sulfidity, and pulping temperature, on fiber charge. The results indicated that when pulping to the same H-factor, low EA charge and low pulping temperature are favorable for increasing bulk carboxylic acid group content of fibers. Sulfidity did not have an obvious effect on bulk or surface carboxylic acid group content of fibers. Surface charge was not significantly affected by pulping temperature. Bulk fiber charge has a linear relationship with water retention value. Another set of kraft pulps distinguished by conventional pulping and Lo-Solids

pulping were investigated to determine the effect of H-factor and pulping protocol on fiber charge. When bulk fiber charge was plotted against kappa number, pulps from Lo-Solids pulping had a higher slope value than the conventional pulping pulps. The charge on holocellulose fibers approaches a constant value as pulping advances for both types of pulping processes.

#### **7.1.2 Effect of peroxide bleaching on fiber charge**

The influence of alkaline peroxide treatment has been characterized on ECF bleached SW kraft pulp. The results indicated that fiber charge was increased with the increase of peroxide charge. Two primary bleaching temperatures at 60.0°C and 90.0°C were investigated during peroxide treatment. Copper number was decreased when peroxide charges were 0.5% and 1.0% at 60.0°C and 90.0°C treatments, respectively, then increased with the increase of peroxide charge. Both fiber charge and copper number approached constant values when a 4.0% or higher peroxide charge was applied. Peroxide treatment on a bleached kraft pulp at 90.0°C resulted in lower fiber charge and lower intrinsic viscosity compared to a treatment at 60.0°C. Fiber charge and copper number were compared after peroxide treatment of ECF bleached kraft pulp versus sodium borohydride reduced ECF bleached kraft pulp. The results indicated that carbonyl group content of fibers is favorable for improving fiber charge after peroxide treatment.

The effect of increased fiber charge on refining, cationic starch adsorption, and hornification was examined. It was shown that the increased fiber charge can improve the efficiency of the refining treatment. Upon the addition of 2% cationic starch to both



pulps, the tensile index of the control pulp increased by 13.7% and that of higher fiber charge pulp by 23.7%. Increased fiber charge was beneficial in reducing hornification when pulp was dried at 105°C.

### **7.1.3 Effect of TEMPO-mediated oxidation on fiber charge**

An ECF bleached SW-KP was catalytically oxidized with TEMPO-mediated system. This work shows a promising way to enrich carboxyl groups into fibers. However, the degree of polymerization of fibers drastically decreased from 2416 to 688 depending on the increase of NaClO charge during the TEMPO-mediated oxidation. The optimum reaction temperature and pH for TEMPO-mediated oxidative generation of carboxyl groups was found to be 23°C at a pH of 9.10. Oxidized fibers were shown to exhibit 62.9% higher water retention values (WRV) than the original fibers. Due to the enhanced carboxyl group content after oxidation, the paper physical strength presented that the tensile index of the oxidized fibers is 13.8% greater than that of the original fibers. The individual fiber strength of the oxidized fibers was lower than that of the original fibers, as determined by zero-span strength measurement showing a 17.0% decrease.

## **7.2 Recommendations**

The current work suggests several other studies that might be conducted to further explore the enrichment of carboxyl groups into fibers.

- The effect of adding additives or catalysts on the retention of carboxyl groups during kraft pulping.
- Peroxide activators should be explored to understand how it affects the carboxyl group content during peroxide bleaching.
- TEMPO is an expensive reagent for paper industry. A fundamental study of the decomposition of the TEMPO should be explored during the oxidation of fibers. This can bring the ideas of reusing it.
- An approach of how to avoid the drastic depolymerization of cellulose should be employed. That means the selectivity of TEMPO-oxidation should be increased to meet the requirements from industry.

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## **APPENDIX B. PROCEDURE OF THE MEASUREMENT OF CARBOXYLIC**

### **ACID GROUP CONTENT OF PULP**

**(Based on Tappi T-237: Carboxyl content of pulp)**

#### **1. Apparatus and Materials**

- 1.1 Conductivity meter, EC Meter Model 2052
- 1.2 Filtering funnels (coarse, fritted glass, 250mL)
- 1.3 Filtering flask (2000mL)
- 1.4 Beakers (400mL)
- 1.5 Glass stirring rods
- 1.6 Magnetic stir plates
- 1.7 Magnetic stir bars
- 1.8 Graduated cylinders (250mL and 500mL)
- 1.9 Volumetric flasks (1000mL)

#### **2. Reagents**

- 2.1 Hydrochloric acid (HCl), 0.1N
- 2.2 Sodium chloride (NaCl), 0.001N
- 2.3 Sodium hydroxide (NaOH), 0.05N
- 2.4 Nitrogen gas (N<sub>2</sub>)

#### **3. Sample Collection, Preservation, and Holding Times**

Samples should either stored in refrigerator or air dried.

#### **4. Procedure**

- 4.1 Sample Preparation

- 4.1.1 Determination the moisture content of the sample
- 4.1.2 Weight out 1.500 gram of over-dry pulp into a 400mL beaker, to the nearest 0.0001g
- 4.1.3 Add 300mL of 0.1N HCl to the pulp and stir for one hour, and make sure the pulp is well dispersed
- 4.1.4 Filter the pulp using a vacuum flask and fritted glass filter funnel. Use a water aspirator as the vacuum source. Wash the sample with at least 2000mL of deionized water, breaking up the pulp and stirring with a glass rod. Dump the filtrate and then wash the pulp with 200mL deionized water again. Check the conductivity reading of filtrate to see whether it's close to 0 which is almost same as the conductivity of deionized water. If not, wash the pulp till it's close to 0.

## 4.2 Titration

Figure B.1 presents a picture of the equipment set for fiber charge measurement.

- 4.2.1 Quantitatively transfer the filtered pulp back into the 400mL beaker and add 250mL NaCl. Use the glass rod and the sodium chloride solution to aid in transfer of the fiber.
- 4.2.2 Add 1.5mL of the standard 0.1N HCl to the beaker. Begin stirring and bubbling nitrogen through the solution. With the EC meter range set at D, dip the conductivity probe up and down and side to side to ensure fresh solution in the cell. Record the conductivity at 0mL NaOH added and multiply by 1000. A typical reading is 0.390, multiplying by 100 give 390 for ease in recording a plotting.

- 4.2.3 While stirring and bubbling nitrogen through the mixture, titrate with 0.05N NaOH in 0.25mL aliquots, taking conductivity readings after each addition. Be sure to dip the probe up and down and side to side before taking each reading.
- 4.2.4 Titrate until the conductivity reading is the same or about the same as it was before began, typically about 9-10mL.
- 4.2.5 Rinse the conductivity probe with water between samples.

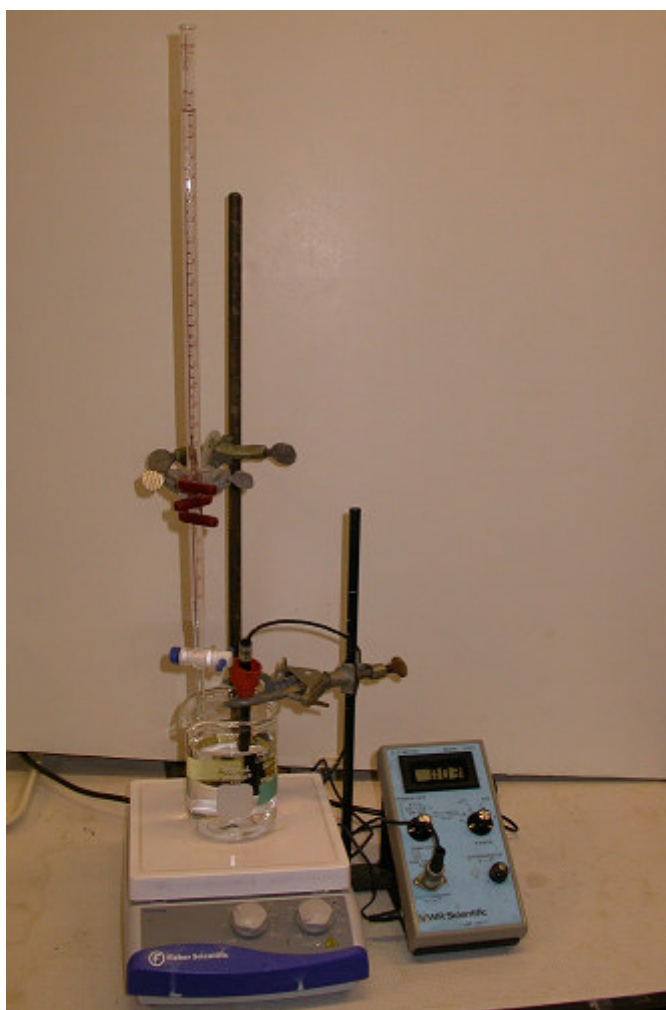


Figure B.1. Photograph of the equipment set for fiber charge measurement.

#### 4.3 Cleanup

Clean the glass filter when they become slow to drain, by soaking it into strong sulfuric acid and then rinse with deionized water.

#### 4.4 Calculations

Refer section 3.2.1 for the calculation of carboxylic acid group content.

Repeatability: Duplicate the tests, the difference between two data should accord to:

<u><i>Carboxylic acid content, meq/100 g pulp</i></u>	<u><i>Repeatability, meq/100g pulp</i></u>
---	--

0.20 to 5.0	0.13
-------------	------

5.1 to 10	0.18
-----------	------

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## **VITA**

Zheng Dang was born in Xi'an, P.R. China. He attended Nanjing University of Science and Technology in Nanjing and graduated in 1995 with a Bachelor's degree in Chemical Engineering. He attended Northwest University in Xi'an in 1996 and obtained his Master's degree in Biochemical Engineering in 1999. After completing his study in China, he joined the University of Maine in the spring of 2000 and received his M.S. degree in Chemical Engineering in August, 2002. He then moved to Atlanta to pursue a Ph.D. degree in Institute of Paper Science and Technology at the Georgia Institute of Technology.

Zheng is a candidate for the Ph.D. degree in Paper Science and Engineering from School of Chemical and Biomolecular Engineering at the Georgia Institute of Technology in August, 2007.