STRUCTURAL CHANGES IN LIGNIN DURING KRAFT PULPING AND CHLORINE DIOXIDE BLEACHING

A Dissertation Submitted by

Peter M. Froass

B.S. 1991, Hobart College

M.S. 1993, Institute of Paper Science and Technology

in partial fulfillment of the requirements

from the Institute of Paper Science and Technology

for the degree of Doctor of Philosophy

Atlanta, Georgia

October 1996

TABLE OF CONTENTS

LIST OF FIGURES viii

LIST OF TABLES xvii

LIST OF LIGNIN IDENTIFICATIONS xxii

ABSTRACT xxvi

INTRODUCTION 1

LITERATURE REVIEW 4

LIGNIN 4

KRAFT DELIGNIFICATION 7

Modified Kraft Delignification 9

Kraft Delignification Chemistry 11

Degradation reactions 11

Condensation reactions 16

Other reactions 18

Lignin-Carbohydrate Complexes 20

ANALYSIS OF RESIDUAL AND KRAFT LIGNINS 22

Phenolic Hydroxyl Groups 22

β-O-4 Structures 24

Distribution of Carbon-Carbon Linkages 26

Condensation Products 29

Other Functional Groups 30

Linkages to Carbohydrates 32

ClO_2 DELIGNIFICATION 33

ClO_2 Delignification Chemistry 34

Model compound studies 35

Phenolic structures 35

Non-phenolic structures 45

Ring-conjugated structures 45

Reactions of products from ClO_2-treated lignin model with NaOH 46

Interpretations of ClO_2 bleaching by model compound studies 47

Summary 49

Analysis of Residual and Dissolved Lignins 50

NMR TECHNIQUES TO CHARACTERIZE LIGNINS 54

Quantitative ^{13}C-NMR 54

^{1}H-NMR 58

^{31}P-NMR 62

THESIS OBJECTIVES AND EXPERIMENTAL APPROACH 65

THESIS OBJECTIVES 65

EXPERIMENTAL APPROACH 66

MATERIALS AND METHODS 69

CHEMICALS 69

WOOD SOURCE AND CHIP PROCESSING 69

PULPING AND BLEACHING 70

Kraft Pulping 70

ASAQ Pulping 72

ClO_2 Bleaching 72

RESIDUAL LIGNIN ISOLATION 75

Unbleached Pulps 75

ClO_2-Bleached and Alkaline-Extracted Pulps 76

Comments on the Isolation of Residual Lignin 77

DISSOLVED LIGNIN ISOLATION 78

Kraft Lignins 78

Extraction Stage Dissolved Lignins 79

REACTION PROCEDURES 80

Acetylation 80

Kraft Treatment of Lignins 82

ClO_2 Treatment of Residual Lignins 83

Alkaline Treatment of ClO_2-Bleached Residual Lignin 85

Alkaline Treatment of ClO_2-Reacted Residual Lignin 87

Residual Lignin Permanganate Consumption 88

NMR SPECTROSCOPY 90

^{13}C-NMR Spectroscopy 90

^{1}H-NMR Spectroscopy 92

Lignin acetates 93

Underivatized lignins 95

^{31}P-NMR Spectroscopy 96

Comments on the ^{31}P-NMR and ^{1}H-NMR Analyses 98

RESULTS AND DISCUSSION 100

CHAPTER 1. ANALYSIS OF RESIDUAL LIGNIN DURING KRAFT PULPING 101

INTRODUCTION 101

Analysis Overview 102

RESULTS AND DISCUSSION 102

Aliphatic Hydroxyl Content 102

Kraft-treated residual lignins 103

Discussion of results 104

Phenolic Hydroxyl Content 105

Kraft-treated residual lignins 110

Discussion of results 112

Carboxylic Acid Content 113

Kraft-treated residual lignins 114

Discussion of results 115

β-O-4 Structures 116

Kraft-treated residual lignins 118

Discussion of results 122

Condensed Structures 124

Aromatic proton content 124

Substituted aromatic carbons 126

Kraft-treated residual lignins 127

Discussion of results 129

CONCLUSIONS 130

CHAPTER 2. ANALYSIS OF DISSOLVED LIGNIN DURING KRAFT PULPING 133

INTRODUCTION 133

RESULTS AND DISCUSSION 134

Phenolic Hydroxyl Content 134

β-O-4 Structures 136

^{1}H-NMR analysis 136

^{13}C-NMR analysis 137

Condensed Structures 139

^{1}H-NMR analysis 140

^{13}C-NMR analysis 141

Kraft Treatment of E14-ai 143

Comparison between CK and EK Kraft Lignins 147

Comparison between Residual and Kraft Lignins 149

CONCLUSIONS 152

CHAPTER 3. RELATIONSHIP BETWEEN BLEACHABILITY AND RESIDUAL LIGNIN STRUCTURE 155

INTRODUCTION 155

RESULTS AND DISCUSSION 156

Bleachability of Kraft Pulps 156

Delignification in the D stage 157

Delignification in the D(EO) partial sequence 157

Relationship between Residual Lignin Structure and Bleachability 158

Reactivity of Residual Lignin with ClO_2 160

Introduction of carboxylic acid groups 162

Loss of phenolic groups 168

CONCLUSIONS 174

CHAPTER 4. ClO_2-BLEACHED RESIDUAL AND DISSOLVED LIGNINS 176

INTRODUCTION 176

ClO_2 CHEMISTRY 177

Qualitative Analysis of ^{13}C-NMR Spectra 178

Quantitative ^{13}C-NMR and ^{1}H-NMR Analysis 182

Carboxylic acid content 183

Phenolic hydroxyl content 185

Methoxyl content 185

Aromatic proton content 186

Substituted aromatic carbons 190

Aliphatic carbons linked to oxygen 190

ALKALINE EXTRACTION CHEMISTRY 191

Analysis Overview 191

Qualitative Analysis of ^{13}C-NMR Spectra 192

Quantitative Analysis of Residual and Dissolved Lignins 195

Carboxylic acid content 195

Phenolic hydroxyl content 198

TREATMENT OF ClO_2-REACTED LIGNINS UNDER ALKALINE CONDITIONS 200

ClO_2-Bleached Residual Lignin 201

ClO_2-Treated Isolated Unbleached Residual Lignin 206

Comments on the Alkaline Extraction Stage 209

CONCLUSIONS 210

CONCLUSIONS 212

RECOMENDATIONS FOR FUTURE WORK 215

ACKNOWLEDGMENTS 218

LITERATURE CITED 219

APPENICES 228

APPENDIX I. BLEACHING EXPERIMENTS 229

APPENDIX II. RESIDUAL LIGNIN ISOLATION 232

APPENDIX III. QUANTITATIVE ^{13}C-NMR ANALYSIS 240

APPENDIX IV. QUANTITATIVE ^{1}H-NMR ANALYSIS 246

APPENDIX V. QUANTITATIVE ^{31}P-NMR ANALYSIS 256

APPENDIX VI. PERMANGANATE CONSUMPTION EXPERIMENTS 260

LIST OF FIGURES

Figure 1. The most common interunit linkages in lignin (14)....................................5

Figure 2. Schematic model of the constitution of spruce lignin (20)..........................7

Figure 3. Lignin content (% on wood) versus reaction time for conventional kraft pulping (22)..9

Figure 4. Alkaline cleavage of α-aryl ether bonds in phenolic arylpropane units (21)..12

Figure 5. Sulfidolytic cleavage of β-aryl ether bonds in phenolic arylpropane units and conversion into enol ether structures (21).............14

Figure 6. Alkaline cleavage of β-aryl ether linkages in non-phenolic arylpropane units (21)..15

Figure 7. Alkaline cleavage of carbon-carbon linkages by retro aldol reactions (21)..15

Figure 8. Competitive addition of external and internal nucleophiles to quinone methide intermediates (30). OAr = aroxyl group; Ar = aryl group; DPM = Diphenyl-methane..17

Figure 9. Alkali-promoted condensation reaction of phenolic units (30)................18

Figure 10. Competing reactions during kraft pulping (31).......................................19

Figure 11. Structures that are resistant to kraft delignification conditions.................20

Figure 12. Formation of an LCC under kraft pulping conditions by the reaction between carbohydrate and a non-phenolic β-O-4 lignin model (25)...21

Figure 13. Frequency of phenolic hydroxyl groups as a function of cooking time in wood and in the residual lignin in kraft pulps (open symbols) and corresponding dissolved lignins (closed symbols) (8)..23

Figure 14. The phenolic hydroxyl content of residual lignin as related to the kappa number of unbleached pine kraft pulp (34)..............................24

Figure 15. Relative amount of β-aryl ether structures per gram of lignin in kraft pulps and in dissolved lignins as a function of the degree of delignification (23)....25

Figure 16. Amount of carbohydrates present in dissolved kraft lignin fractions from a laboratory cook of pine wood (23)....33

Figure 17. Oxidation of phenolic structures by chlorine dioxide (55,61)....37

Figure 18. Identified chlorination products during the reaction of creosol with ClO_2 (55)....40

Figure 19. Products identified in the reaction of creosol with ClO_2. Estimated % yields are in parenthesis below the structures (59)....41

Figure 20. Reaction of a lignin model dimer similar to the 5-5 structure found in residual kraft lignin with ClO_2 (56,58)....43

Figure 21. Reaction of dihydroeugenol-β-4-methylguaiacyl ether with ClO_2 (57)....44

Figure 22. Reaction of monomeric lactones 7 and 8 with NaOH (59)....47

Figure 23. Quantitative ^{13}C-NMR spectrum of milled wood lignin (MWL) from spruce (*Picea glauca*) by Inverse Gated Decoupling (IGD) pulse sequence. Solvent: DMSO-d_6. Reprinted from reference (48) page 435 by courtesy of Marcel Dekker, Inc....56

Figure 24. ^{1}H-NMR (270 MHz) spectrum of acetylated milled wood lignin from spruce (87)....60

Figure 25. The spectral range δ 8.0-10.5 (400 MHz, solvent DMSO-d_6) of MWL from spruce. The assignments of the peaks are indicated in the figure (the peak at δ8.14 is due to an unidentified contaminant) (88)....62

Figure 26. The reaction of labile protons present in lignins with 2-chloro-4,4,5,5 tetramethyl-1,3,2-dioxaphospholane (36)....63

Figure 27. Quantitative ^{31}P-NMR spectra and signal assignment of a milled wood lignin obtained from black spruce and the three kraft lignins at various degrees of delignification. Reprinted with permission from (36), Copyright 1995, American Chemical Society....64

Figure 1.1. Aliphatic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l. 103

Figure 1.2. Aliphatic hydroxyl content of residual lignins treated under kraft pulping conditions for different lengths of time. The aliphatic hydroxyl content was determined by ^{31}P-NMR. Duplicates of each sample were performed and the averages graphed. C28 r.l.-120' is a replicate of C28 r.l. treated for 120 minutes 104

Figure 1.3. Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.' and four replicates of C28 r.l. 107

Figure 1.4. Guaiacyl phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l. 107

Figure 1.5. Condensed phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l. 108

Figure 1.6. Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates. Also included are A26 r.l. and E29 r.l.' 109

Figure 1.7. Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of underivatized lignins 110

Figure 1.8. Total phenolic hydroxyl content of residual lignins treated under kraft pulping conditions for different lengths of time as determined by ^{31}P-NMR. Duplicates of each sample were performed and the averages graphed. C28 r.l.-120' is a replicate of C28 r.l. treated for 120 minutes 111

Figure 1.9. Change in the guaiacyl and condensed phenolic hydroxyl content of C28 r.l. during the kraft treatment 111

Figure 1.10. Change in the guaiacyl and condensed phenolic hydroxyl content of E14 r.l. during the kraft treatment..112

Figure 1.11. Carboxylic acid content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l..114

Figure 1.12. Carboxylic acid content of residual lignins treated under kraft pulping conditions for different lengths of time as determined by ^{31}P-NMR. Duplicates of each sample were performed and the averages graphed. C28 r.l.-120' is a replicate of C28 r.l. treated for 120 minutes...115

Figure 1.13. β-O-4 content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates. Also included are A26 r.l. and E29 r.l.'.........................117

Figure 1.14. Quantitative ^{13}C-NMR spectra of residual lignins E29 r.l. and E14 r.l. Signal assignments are presented in Table 20 on page 91..........118

Figure 1.15. Content of Cβ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK residual lignins as determined by the integration of region 8 in the quantitative ^{13}C-NMR spectra. Also included are A26 r.l. and E29 r.l.'...119

Figure 1.16. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK residual lignins as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra. Also included are A26 r.l. and E29 r.l.'...120

Figure 1.17. Quantitative ^{13}C-NMR spectra of residual lignin C28 before and after a two-hour treatment under kraft pulping conditions. Signal assignments are presented in Table 20 on page 91.......................120

Figure 1.18. Content of Cβ in β-O-4 structures (expressed as number of C atoms per aromatic unit) in untreated and kraft-treated residual lignins C28 r.l. and E14 r.l. as determined by the integration of region 8 in the quantitative ^{13}C-NMR spectra...121

Figure 1.19. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) in untreated and kraft-treated residual lignins C28 r.l. and E14 r.l. as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra....122

Figure 1.20. Apparent aromatic proton content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates. Also included are A26 r.l. and E29 r.l.'....125

Figure 1.21. Apparent aromatic proton content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of underivatized lignins....126

Figure 1.22. Content of substituted aromatic carbon atoms (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for CK and EK residual lignins as determined by ^{13}C-NMR. Also included are A26 r.l. and E29 r.l.'....127

Figure 1.23. Apparent aromatic proton content in untreated and kraft treated residual lignins C28 r.l. and E14 r.l. as determined by ^{1}H-NMR analysis of underivatized lignins....128

Figure 1.24. Content of substituted aromatic carbon atoms (expressed as number of carbon atoms per aromatic unit) in untreated and kraft-treated residual lignins C28 r.l. and E14 r.l. as determined by quantitative ^{13}C-NMR analysis....128

Figure 2.1. Phenolic hydroxyl content for various CK and EK end of cook kraft lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR. Also included in the analysis is C13-eoc'....135

Figure 2.2. β-O-4 content of various CK and EK end of cook kraft lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of lignin acetates. Also included in the analysis is C13-eoc'....137

Figure 2.3. Content of Cβ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK eoc kraft lignins as determined by the integration of region 8 in the quantitative ^{13}C-NMR spectra....................138

Figure 2.4. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK end of cook kraft lignins as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra....................139

Figure 2.5. Apparent aromatic proton content of various CK and EK end of cook kraft lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of lignin acetates. Also included in the analysis is C13-eoc'....................140

Figure 2.6. Content of substituted aromatic carbons (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK end of cook kraft lignins as determined by the integration of region 2-4 in the quantitative ^{13}C-NMR spectra....................142

Figure 2.7. Quantitative ^{13}C-NMR spectra of E14-ai before and after a 2-hour treatment under kraft pulping conditions. Signal assignments are presented in Table 20 on page 91....................145

Figure 2.8. Phenolic hydroxyl content of various CK and EK kraft and residual lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of acetylated lignin....................150

Figure 2.9. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) for various CK and EK kraft and residual lignin versus unbleached kappa number as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra......150

Figure 2.10. Apparent aromatic proton content of various CK and EK kraft and residual lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of acetylated lignin....................151

Figure 3.1. TAC per unit kappa number drop over the D(EO) partial delignification sequence for the various unbleached CK and EK kraft pulps....................158

Figure 3.2. ^{31}P-NMR spectra of unbleached residual lignin and the same lignin reacted with two charges of ClO_2 corresponding to charges of 0.05 and 0.10 KF......161

Figure 3.3. Increase in carboxylic acid groups of various residual lignins isolated from EK pulps after being treated with various charges of ClO_2 as determined by ^{31}P-NMR......163

Figure 3.4. Increase in carboxylic acid groups of E29 r.l., A26 r.l., and C28 r.l. after being treated with various charges of ClO_2 as determined by ^{31}P-NMR......164

Figure 3.5. Increase in carboxylic acid groups of C18 r.l., E18 r.l., and E14 r.l. after being treated with various charges of ClO_2 as determined by ^{31}P-NMR......164

Figure 3.6. Increase in carboxylic acid groups of various residual lignins isolated from CK and EK pulps after a treatment with a charge of ClO_2 equivalent to 0.05 kappa factor versus the unbleached kappa number of the pulp from which the residual lignin was isolated from. The carboxylic acid content was determined by ^{31}P-NMR......167

Figure 3.7. Loss of phenolic hydroxyl groups from various residual lignins isolated from EK pulps after being treated with various charges of ClO_2 as determined by ^{31}P-NMR......169

Figure 3.8. Percentage of reacted phenolic hydroxyl groups converted in carboxylic acid groups for the various EK residual lignins reacted with three charges of ClO_2. (Percent converted = (Increase in COOH / Loss in phenolic) * 100)......170

Figure 3.9. Loss of guaiacyl and condensed phenolic hydroxyl groups from E29 r.l. treated with three charges of ClO_2 as determined by ^{31}P-NMR......172

Figure 3.10. Loss of guaiacyl and condensed phenolic hydroxyl groups for various residual lignins treated with three charges of ClO_2 as determined by ^{31}P-NMR......173

Figure 4.1. Quantitative ^{13}C-NMR spectra of residual lignins isolated from unbleached and ClO_2-bleached kraft pulps. The spectra have been labeled with areas of interest......179

Figure 4.2. Quantitative ^{13}C-NMR spectra of residual lignin isolated from the unbleached C33 pulp and the spectra of this residual lignin treated with two charges of ClO_2 corresponding to 0.05 and 0.20 KF. The spectra have been labeled with areas of interest.........180

Figure 4.3. Ring-opening reaction between ClO_2 and a guaiacyl structure resulting in the formation of a muconic acid methyl ester (MAME) and its cyclized lactone. The approximate ^{13}C-NMR chemical shift of the carbonyl carbons is shown....................................181

Figure 4.4. Ring-opening reaction between ClO_2 and a guaiacyl structure resulting in the formation of a muconic acid methyl ester (MAME) and its cyclized lactone. The approximate ^{13}C-NMR chemical shift of the methoxyl carbons is included (59,62)..................................182

Figure 4.5. Aromatic proton content of various isolated unbleached residual lignins reacted with three charges of ClO_2. The aromatic proton content was determined by quantitative ^{1}H-NMR using underivatized lignins..187

Figure 4.6. ^{1}H-NMR spectra of C28 r.l. and C28 r.l. treated with 0.05 KF ClO_2 and 0.20 KF ClO_2..189

Figure 4.7. Quantitative ^{13}C-NMR spectra of residual lignin isolated from ClO_2-bleached C28 pulp (C28 D r.l. (0.20)), residual lignin isolated from this same pulp after an alkaline extraction (C28 DE r.l. (0.20)), and dissolved lignin isolated from its alkaline extraction stage effluent (C28 DE d.l. (0.20))......................193

Figure 4.8. Saponification of the methyl ester group in muconic acid methyl ester and its cyclized lactone under alkaline extraction conditions.........194

Figure 4.9. Phenolic content of various residual and dissolved lignins produced during the bleaching of C28 pulp with ClO_2 with kappa factors of 0.05 and 0.20. (data taken from Table 4.2 on page 196).........198

Figure 4.10. Carboxylic acid content of residual lignin isolated from a ClO_2-bleached pulp (C28 D r.l. (0.20)) and after a blank alkaline extraction treatment (Blank), an alkaline extraction treatment without oxygen reinforcement (E), and an alkaline extraction treatment with oxygen reinforcement (EO). For conditions, see Table 18 on page 88. The carboxylic acid content was determined by quantitative ^{1}H-NMR and the averages of two samples reported...201

Figure 4.11. Quantitative ^{31}P-NMR spectra of residual lignin from ClO_2-bleached pulp and of this lignin after its treatment under various alkaline extraction conditions....................203

Figure 4.12. Phenolic content of same lignins analyzed in Figure 4.7. The phenolic contents were determined by quantitative ^{1}H-NMR..........205

Figure 4.13. Content of carboxylic acid and phenolic groups in ClO_2-bleached residual lignin treated under alkaline extraction conditions in the presence and complete absence of oxygen....................205

Figure 4.14. Carboxylic acid content of isolated unbleached residual lignins treated with ClO_2 and their contents after being treated under alkaline extraction stage conditions as determined by quantitative ^{1}H-NMR....................208

Figure AII.1. Yield of residual lignin from the acid hydrolysis of various CK and EK pulps plotted against the kappa number of the pulp. The yield was calculated as weight percent of the theoretical amount of lignin in the pulp as determined by the kappa number / lignin content relationship....................238

LIST OF LIGNIN IDENTIFICATIONS

Type of Lignin	Lignin ID	Description
Unbleached residual lignin	E29 r.l.	Residual lignin isolated from the 29.1 kappa EK pulp
	E29 r.l.'	Residual lignin isolated from the 29.1 kappa EK pulp (replicated isolation)
	E18 r.l.	Residual lignin isolated from the 18.5 kappa EK pulp
	E14 r.l.	Residual lignin isolated from the 14.5 kappa EK pulp
	C28 r.l.	Residual lignin isolated from the 28.0 kappa CK pulp
	C18 r.l.	Residual lignin isolated from the 18.5 kappa CK pulp
	C13 r.l.	Residual lignin isolated from the 13.5 kappa CK pulp
	A26 r.l.	Residual lignin isolated from the 25.6 kappa ASAQ pulp
Kraft lignin	E14-ai	Kraft lignin isolated from the after impregnation black liquor of the 14.5 kappa EK cook
	C18-ai	Kraft lignin isolated from the after impregnation black liquor of the 18.5 kappa CK cook
	E14-eo1	Kraft lignin isolated from the after co-current stage black liquor of the 14.5 kappa EK cook
	E29-eoc	Kraft lignin isolated from the eoc of cook black liquor of the 29.1 kappa EK cook
	E18-eoc	Kraft lignin isolated from the eoc of cook black liquor of the 18.5 kappa EK cook
	E14-eoc	Kraft lignin isolated from the eoc of cook black liquor of the 14.5 kappa EK cook
	C28-eoc	Kraft lignin isolated from the eoc of cook black liquor of the 28.0 kappa CK cook
	C18-eoc	Kraft lignin isolated from the eoc of cook black liquor of the 18.5 kappa CK cook
	C13-eoc	Kraft lignin isolated from the eoc of cook black liquor of the 13.5 kappa CK cook
	C13-eoc'	Kraft lignin isolated from the eoc of cook black liquor of the 13.5 kappa CK cook (replicated isolation)
Kraft-treated residual and kraft lignins	C28 r.l.-15	C28 r.l. treated for 15 minutes under kraft pulping conditions
	C28 r.l.-120	C28 r.l. treated for 120 minutes under kraft pulping conditions
	C28 r.l.-120'	C28 r.l. treated for 120 minutes under kraft pulping conditions (replicated kraft treatment)
	E14 r.l.-15	E14 r.l. treated for 15 minutes under kraft pulping conditions
	E14 r.l.-120	E14 r.l. treated for 120 minutes under kraft pulping conditions
	E14-ai-120	E14-ai kraft lignin treated for 120 minutes under kraft pulping conditions

Type of Lignin	Lignin ID	Description
ClO_2 treated residual lignins	E29 r.l.-0.05	E29 r.l. treated with a 0.05 KF charge of ClO_2
	E18 r.l.-0.05	E18 r.l. treated with a 0.05 KF charge of ClO_2
	E14 r.l.-0.05	E14 r.l. treated with a 0.05 KF charge of ClO_2
	C28 r.l.-0.05	C28 r.l. treated with a 0.05 KF charge of ClO_2
	C18 r.l.-0.05	C18 r.l. treated with a 0.05 KF charge of ClO_2
	C13 r.l.-0.05	C13 r.l. treated with a 0.05 KF charge of ClO_2
	A26 r.l.-0.05	A26 r.l. treated with a 0.05 KF charge of ClO_2
	E29 r.l.-0.10	E29 r.l. treated with a 0.10 KF charge of ClO_2
	E18 r.l.- 0.10	E18 r.l. treated with a 0.10 KF charge of ClO_2
	E14 r.l.- 0.10	E14 r.l. treated with a 0.10 KF charge of ClO_2
	C28 r.l.- 0.10	C28 r.l. treated with a 0.10 KF charge of ClO_2
	C18 r.l.- 0.10	C18 r.l. treated with a 0.10 KF charge of ClO_2
	C13 r.l.- 0.10	C13 r.l. treated with a 0.10 KF charge of ClO_2
	A26 r.l.- 0.10	A26 r.l. treated with a 0.10 KF charge of ClO_2
	E29 r.l.- 0.20	E29 r.l. treated with a 0.20 KF charge of ClO_2
	E18 r.l.- 0.20	E18 r.l. treated with a 0.20 KF charge of ClO_2
	E14 r.l.- 0.20	E14 r.l. treated with a 0.20 KF charge of ClO_2
	C28 r.l.- 0.20	C28 r.l. treated with a 0.20 KF charge of ClO_2
	C18 r.l.- 0.20	C18 r.l. treated with a 0.20 KF charge of ClO_2
	C13 r.l.- 0.20	C13 r.l. treated with a 0.20 KF charge of ClO_2
	A26 r.l.- 0.20	A26 r.l. treated with a 0.20 KF charge of ClO_2
	C33 r.l.-0.05	C33 r.l. treated with a 0.05 KF charge of ClO_2
	C33 r.l.-0.20	C33 r.l. treated with a 0.20 KF charge of ClO_2
ClO_2 bleached residual lignin	C28 D r.l. (0.05)	Residual lignin isolated from the 0.05 KF ClO_2-bleached C28 pulp
	C28 D r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached C28 pulp
	C18 D r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached C18 pulp
	E29 D r.l. (0.10)	Residual lignin isolated from the 0.10 KF ClO_2-bleached E29 pulp
	E29 D r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached E29 pulp
	E18 D r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached E18 pulp

Type of Lignin	Lignin ID	Description
ClO_2 bleached and alkaline extracted residual lignin	C28 DE r.l. (0.05)	Residual lignin isolated from the 0.05 KF ClO_2-bleached and alkaline-extracted C28 pulp
	C28 DE r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted C28 pulp
	C28 D(EO) r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted (with oxygen reinforcement) C28 pulp
	C18 D(EO) r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted (with oxygen reinforcement) C18 pulp
	E29 r.l. (0.10)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted E29 pulp
	E29 D(EO) r.l. (0.10)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted (with oxygen reinforcement) E29 pulp
	E29 D(EO) r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted (with oxygen reinforcement) E29 pulp
	E18 D(EO) r.l. (0.20)	Residual lignin isolated from the 0.20 KF ClO_2-bleached and alkaline-extracted (with oxygen reinforcement) E18 pulp
Alkaline extraction dissolved lignin	C28 DE d.l. (0.05)	Dissolved lignin isolated from the alkaline extraction effluent of the C28 pulp bleached with a 0.05 KF
	C28 DE d.l. (0.20)	Dissolved lignin isolated from the alkaline extraction effluent of the C28 pulp bleached with a 0.20 KF
	C28 D(EO) d.l. (0.20)	Dissolved lignin isolated from the oxygen-reinforced alkaline extraction effluent of the C28 pulp bleached with a 0.20 KF
	C18 D(EO) d.l. (0.20)	Dissolved lignin isolated from the oxygen-reinforced alkaline extraction effluent of the C18 pulp bleached with a 0.20 KF
	E29 d.l. (0.10)	Dissolved lignin isolated from the alkaline extraction effluent of the E29 pulp bleached with a 0.10 KF
	E29 D(EO) d.l. (0.10)	Dissolved lignin isolated from the oxygen-reinforced alkaline extraction effluent of the E29 pulp bleached with a 0.10 KF
	E29 D(EO) d.l. (0.20)	Dissolved lignin isolated from the oxygen-reinforced alkaline extraction effluent of the E29 pulp bleached with a 0.20 KF
	E18 D(EO) d.l. (0.20)	Dissolved lignin isolated from the oxygen-reinforced alkaline extraction effluent of the C18 pulp bleached with a 0.20 KF

Type of Lignin	Lignin ID	Description
ClO_2-reacted lignins treated under alkaline conditions	Blank	C28 D r.l. (0.20) treated under blank alkaline extraction conditions
	E	C28 D r.l. (0.20) treated under alkaline extraction conditions under atmospheric conditions
	EO	C28 D r.l. (0.20) treated under alkaline extraction conditions with oxygen reinforcement
	EO w/o O_2	C28 D r.l. (0.20) treated under alkaline extraction conditions under argon (complete absence of oxygen)
	C33 r.l.-0.05-pH 11	C33 r.l.-0.05 treated under alkaline extraction conditions at a pH of 11
	C33 r.l.-0.20-pH 11	C33 r.l.-0.20 treated under alkaline extraction conditions at a pH of 11
	C33 r.l.-0.20-pH 9	C33 r.l.-0.20 treated under alkaline extraction conditions at a pH of 9

ABSTRACT

Conventional kraft pulps were produced from loblolly pine wood chips with kappa numbers 28, 18, and 13. Simulated EMCC® kraft pulps having similar kappa numbers were also produced from the same wood chips. Residual lignins in these pulps and kraft lignins from black liquor samples extracted during these cooks were isolated and structurally characterized by advanced NMR spectroscopic techniques. Results from these analyses showed that residual lignin structure is quite different in these various kappa number pulps. The lower kappa number residual lignins had lower contents of aliphatic hydroxyl groups and β-O-4 structures and higher contents of phenolic hydroxyl groups, carboxylic acid groups, and condensed structures compared to higher kappa number residual lignins. Comparisons between conventional and EMCC® residual lignins with similar kappa numbers showed that conventional residual lignins had slightly lower contents of β-O-4 structures and slightly higher contents of condensed structures. These differences may help in explaining the improved delignification selectivity of EMCC® kraft pulping because residual lignins with higher contents of β-O-4 structures and lower contents of condensed structures would be more reactive under pulping conditions. Isolated residual lignins treated under kraft pulping conditions showed that residual lignin is still reactive under pulping conditions as additional aryl ether fragmentation was observed.

Kraft lignin isolated from black liquor extracted early during the cook had higher phenolic contents, lower β-O-4 contents, and higher contents of condensed structures

compared to kraft lignins isolated from black liquors extracted later during the cook. Comparisons between the conventional and EMCC® kraft lignins extracted at similar extents of delignification showed that conventional kraft lignins had higher contents of phenolic groups, lower contents of β-O-4 structures, and lower contents of condensed structures. These differences have been explained in terms of kraft delignification chemistry and the different process variables used in conventional and modified kraft pulping.

The bleachability of these pulps was measured by bleaching the pulps in a D(EO) sequence and calculating the consumption of ClO_2 per unit kappa number drop over this partial delignification sequence. The results showed that the lower kappa number pulps were more difficult to delignify than the higher kappa number pulps which seems to be directly related to the structure and reactivity of the unbleached residual lignin. The lower kappa residual lignin compared to the higher kappa residual lignin had a lower content of aryl ether linkages and a higher content of condensed structures, which may be the cause for the different reactivity of these lignins. Experiments in which the isolated residual lignins were reacted in homogeneous solutions with similar charges of ClO_2 showed that higher kappa residual lignins were more reactive toward ClO_2 as evidenced from the greater introduction of carboxylic acid groups. The introduction of such groups would increase the water solubility of the lignin enhancing its dissolution.

Residual lignins were isolated from ClO_2 bleached and alkaline-extracted pulps and dissolved lignins isolated from the alkaline extraction effluents and characterized by NMR techniques to provide greater insights into the chemical mechanisms causing the oxidation and dissolution of residual lignin during ClO_2 bleaching. Results from this analysis found that lignin is oxidized by chlorine dioxide, resulting in demethylation, the loss of phenolic groups, and the formation of significant quantities of carboxylic acids and methyl ester functional groups. During an alkaline extraction, an additional increase in the carboxylic acid content was observed, which was suggested to be due to the saponification of methyl ester groups. The further increase in carboxylic acid groups during the alkaline extraction enhances the solubility of the lignin during the alkaline extraction. The phenolic content of the lignin was found to decrease during the alkaline extraction as a result of such groups being oxidized by air (oxygen). This oxidation was found not to result in the formation of carboxylic acids. Reinforcing the alkaline extraction stage with oxygen resulted in a minor but noticeable increase in the carboxylic acid content compared to an alkaline extraction without oxygen reinforcement, suggesting that an intense treatment with oxygen can introduce carboxylic acid groups into the lignin.

INTRODUCTION

Chlorine is well-recognized as an effective delignification agent for kraft pulps; it oxidizes and degrades residual lignin in such a way that a substantial portion of the lignin is easily removed from the pulp by a subsequent alkali extraction. The effluents from chlorine bleaching contain chlorinated organic compounds, typically measured as adsorbable organic halide (AOX). Environmental pressures to reduce AOX levels have driven the development and implementation of oxygen-based delignification technologies for the manufacturing of fully bleached kraft pulp.

Two of the more viable delignification technologies that are emerging from these pressures are extended delignification during kraft pulping and elemental chlorine free (ECF) bleaching, employing chlorine dioxide (ClO_2) as the delignification and brightening reagent. Although both of these processes are currently being employed on an industrial scale, the need to advance these technologies further is required. Providing greater insights into the nature of residual and dissolved lignins produced during kraft pulping and ClO_2 bleaching will allow for future improvements in these operations.

Conventional kraft pulping removes approximately 92% of the lignin from wood. Further delignification results in an increased degree of carbohydrate degradation and dissolution, causing significant losses in yield and pulp strength (1,2). Kraft pulp, containing about 4% lignin, must be delignified further using alternative delignification procedures that do not cause significant yield losses. Recent advancements in kraft pulping technology have lead to the development of extended delignification processes capable of producing lower kappa kraft pulps with strength properties comparable to conventional higher kappa kraft pulps (3,4). Extended delignification ('modified') processes improve the selectivity of kraft pulping by changing some process variables of the cook (alkali and hydrosulfide concentration, dissolved lignin concentration, and temperature). Changing these conditions would seem to influence the chemistry of delignification and carbohydrate degradation. Extensive studies by Gellerstedt et al. on structural changes of lignin during kraft pulping have provided insight into the chemistry of kraft delignification (5-12). Because chemical mechanisms govern the dissolution of lignin during pulping, modifying pulping conditions so reactions that favor the dissolution of lignin are enhanced, an improved delignification selectivity is possible. A thorough structural investigation and comparison of dissolved and residual lignins produced during conventional and modified kraft pulping can provide further insights into the complex chemistry of kraft delignification. This analysis can also provide some chemical insights into the enhanced selectivity of modified kraft pulping.

Chlorine dioxide is an effective delignifier of kraft pulps, yet the chemical modifications of the residual lignin structure resulting in its dissolution during ClO_2 bleaching are not well-understood. Model compound studies have shown that ClO_2 can readily react with phenolic groups in lignin resulting in the creation of hydrophilic carboxylic acid groups, which increase the water solubility of the lignin. This would in part explain why pulps with low contents of phenolic groups are difficult to delignify. The model compound studies also suggest that the creation of carboxylic acid groups is just one of the many modifications that the lignin undergoes. Several products are formed that would not be expected to assist in the dissolution of the residual lignin, and perhaps, even hinder its dissolution. The model compound studies serve to illustrate the importance of understanding some of the basic chemical mechanisms occurring during ClO_2 delignification. A comprehensive understanding of the complex reaction of ClO_2 with lignin is best done, however, by characterizing and quantifying the structural changes residual lignin undergoes during its reaction with ClO_2.

Although some studies on the chemistry of the alkaline extraction stage have been performed, the chemistry occurring during the alkali treatment is still not completely understood. Characterizing the structure of residual lignin after a ClO_2 treatment and comparing its structure to the residual and dissolved lignins produced during a subsequent alkaline extraction can result in some valuable insights into this chemistry.

Advanced NMR spectroscopic methods offers a unique and informative way to characterize lignin during kraft pulping and ClO_2 bleaching. New insights into the chemistry have been detailed in this dissertation by performing such analyses.

LITERATURE REVIEW

LIGNIN

Wood is mainly composed of carbohydrates, lignin, and extractives. Lignin is a complex three-dimensional amorphous polymer embedded in the extracellular matrix of plants that provides the plant with a variety of functions. This macromolecule plays a vital role in the transport of water and nutrients by decreasing the permeability of water through the cell walls of the xylem. Lignin also provides a barrier to microorganism attack by impeding the penetration of harmful enzymes into the cell wall. Finally, lignin gives the cell wall a great deal of mechanical support against bending and compression (13).

The structure of this polymer has been studied for many years and has been found to consist of methoxylated phenylpropane repeating units. Linkages between these units, and the various functional groups on these units, give lignin a unique and very complex structure. Common approaches that have been taken to elucidate the structure of lignin include spectroscopic methods and analyses of degradation products. The results from these numerous studies have yielded what is believed to be an accurate representation of the structure of lignin. Figure 1 is a schematic diagram of some common linkages found in softwood lignin. The dominant linkage is the β-O-4 linkage. The percent abundance of this and other linkages found in spruce wood lignin has been determined (Table 1) (14). The frequency of some common functional groups found in spruce lignin is provided in Table 2. Figure 2 is a schematic representation of a softwood lignin derived

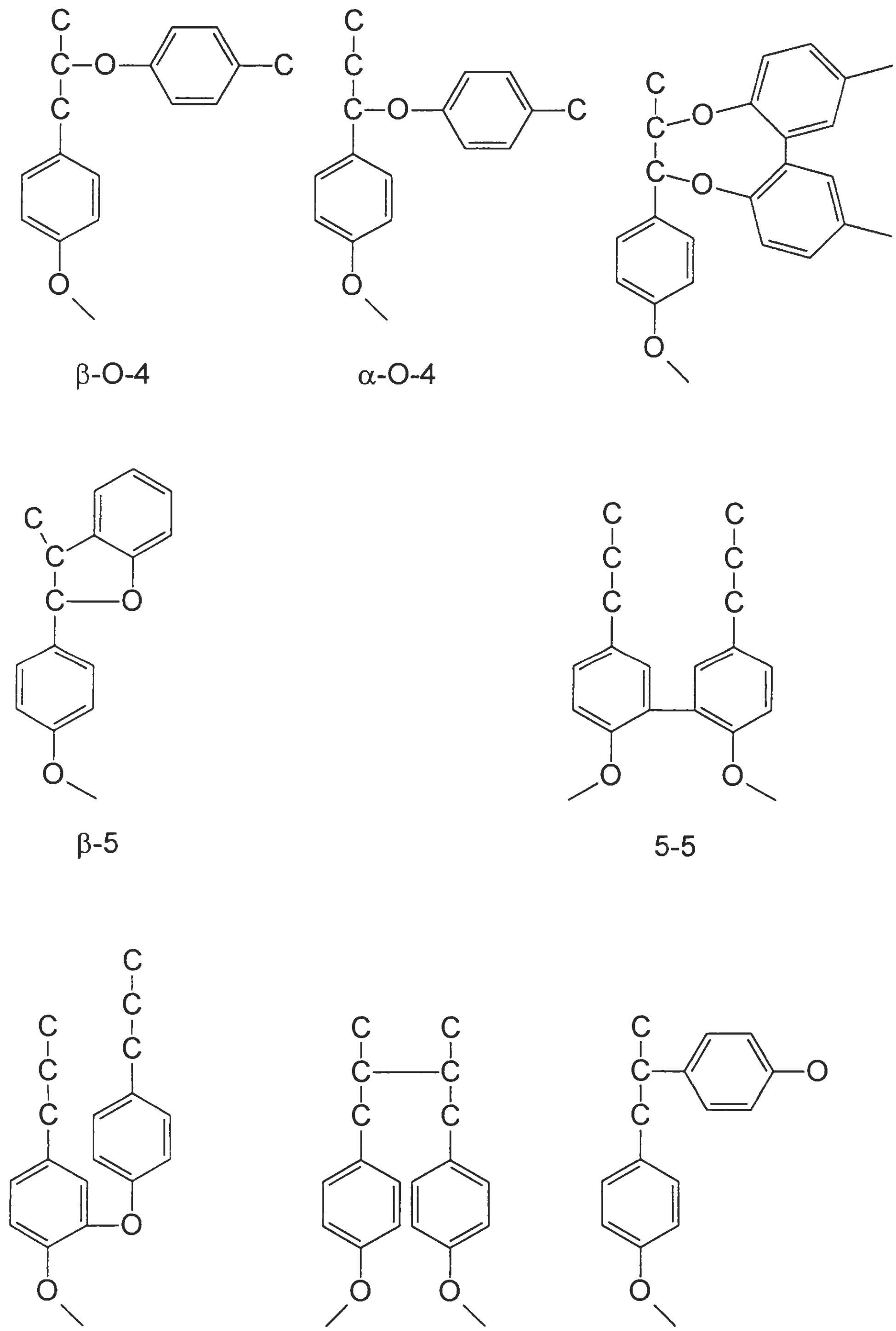


Figure 1. The most common interunit linkages in lignin (14).

by using the analysis of the frequency of certain linkages and functional groups. The C_9 (phenylpropane) units found in lignin are connected by either carbon-carbon or carbon-oxygen bonds or both. The frequency of such linkages is believed to have significant consequences on the lignin's overall reactivity toward delignification processes.

Studies have also suggested that covalent linkages between wood and hemi-celluloses exist in the native wood (15-19). These structures are typically referred to as lignin-carbohydrate complexes or simply LCC's.

Table 1. Percentages of different types of bonds in spruce lignin (MWL) (14).

Name	Bond Type	Percentage
β-O-4	Phenylpropane β-aryl ether	48
α-O-4	Phenylpropane α-aryl ether	6-8
β-5	Phenylcoumaran	9-12
5-5	Biphenyl	9.5-11
4-O-5	Diaryl ether	3.5-4
β-β	β-β-linked structures	2
β-1	1,2-Diarylpropane	7

Table 2. Functional groups of spruce lignin per 100 C_6C_3 units (14).

Functional Group	Spruce Lignin
Methoxyl	92-96
Phenolic hydroxyl (free)	15-30
Benzyl alcohol	15-20
Noncyclic benzyl ether	7-9
Carbonyl	20

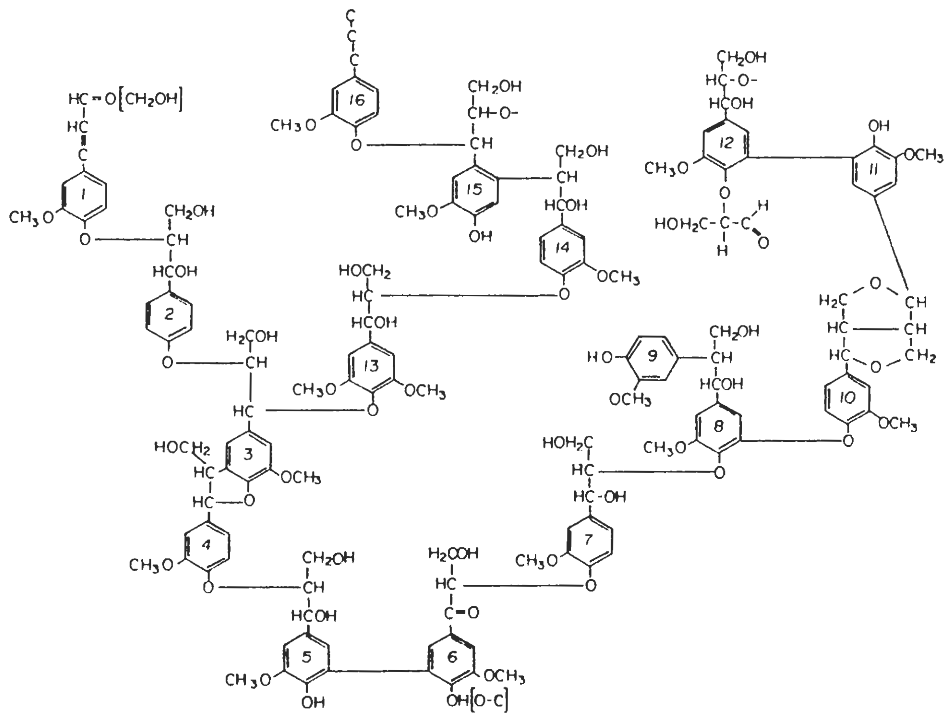


Figure 2. Schematic model of the constitution of spruce lignin. Reprinted from reference (20) with permission from Springer-Verlag.

KRAFT DELIGNIFICATION

The act of removing lignin from wood and lignin-containing pulps is referred to as delignification. The most commonly used commercial delignification procedure for wood is the kraft pulping process; wood chips are treated with chemicals that alter the structure of the lignin in such a way that soluble fragments of the polymer are produced (21). The pulping chemicals employed in the kraft process are sodium hydroxide (NaOH) and sodium sulfide (Na_2S); both are nucleophiles involved in the reaction with lignin, leading to the fragmentation and dissolution of lignin.

Delignification occurs by modifying lignin's structure in two ways to enhance its dissolution. The first is to degrade the lignin into smaller units by cleaving interunit linkages. The second is to introduce hydrophilic groups into the polymer and the cleaved fragments, making the lignin more soluble in the cooking liquor. During conventional kraft pulping, a concentrated aqueous solution of NaOH and Na_2S is added to wood chips in a digester, and the temperature is increased to and held at approximately 170°C for roughly 2 hours, depending upon the degree of delignification desired. The chemicals react with the lignin, leading to the fragmentation and dissolution of the lignin. There are three fairly distinct phases of delignification (known as initial, bulk, and residual) at which different rates of lignin removal are observed, as depicted graphically in Figure 3 (1,2,22). The bulk phase begins as the rate of delignification decreases after an initial rapid delignification phase. The majority of lignin is removed from the wood during this phase. The residual phase begins when roughly 90% of the lignin has been removed and is characterized by a significant decrease in the delignification rate. The selectivity of this phase is very poor, as evidenced from the increased degradation of the carbohydrates relative to the rate of delignification (selectivity is defined as the rate of delignification relative to the rate of cellulose degradation). The cook should be terminated at this point to prevent significant loss of pulp strength, and the remaining residual lignin should be removed using alternative delignification techniques, such as bleaching with ClO_2 and Cl_2.

The lignin content of a typical conventionally produced kraft pulp is in the range of 4-5% or 27-33 kappa number. Pulping to lower lignin contents under these conditions causes a severe degradation of the carbohydrate fraction, resulting in a pulp with poor papermaking qualities. The reasons for the poor selectivity of kraft pulping have been the subject of much debate. One reason given is that the structure of the residual lignin that remains in the fiber at the end of the cook has a low reactivity toward the pulping chemicals, making its fragmentation and dissolution difficult (6,10,23). Alternatively, it has been proposed that dissolution is hindered by the attachment of the residual lignin to carbohydrates (24,25).

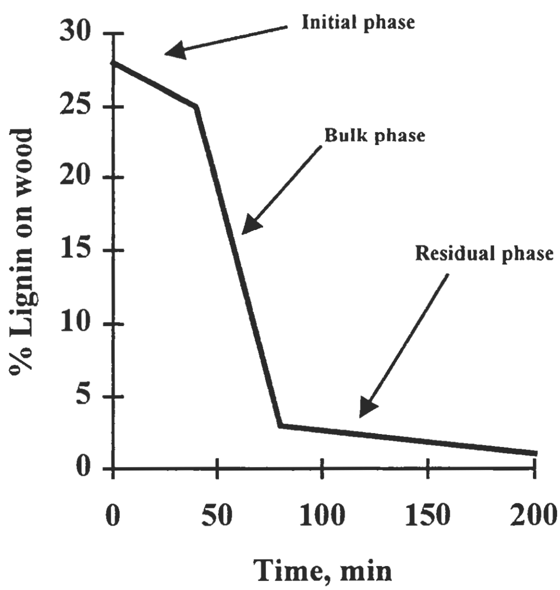


Figure 3. Lignin content (% on wood) versus reaction time for conventional kraft pulping (22).

Modified Kraft Delignification

Environmental pressures have been placed on the industry to use less chlorine-containing species to bleach kraft pulp. One method of addressing this challenge is to remove more of the lignin during pulping, so less bleaching chemicals are required to remove the remaining residual lignin. Attempts have therefore been made to improve the selectivity of kraft pulping by changing pulping process variables, so more lignin can be removed. Extensive research has been done in this area, and it has been recognized that a variety of process conditions can indeed be changed to increase delignification without significantly hurting the strength of the pulp (4). The important conditions that affect the selectivity are temperature, hydroxide ion concentration profile, hydrosulfide concentration, and dissolved lignin concentration (26,27).

Although the conditions required to improve the selectivity of kraft pulping have been understood for several years, they have only fairly recently been implemented on the production scale (28). Several types of new pulping technologies have been developed to extend delignification, including Kamyr's Extended Modified Continuous Cooking (EMCC® or EK, as will be used throughout this dissertation) kraft pulping process (3). The EK process has been shown to improve the selectivity of the kraft cook by employing some of the conditions mentioned above. The total white liquor addition is split, so a more "leveled-out" alkali concentration profile is maintained throughout the cook. The lower initial charge of alkali is believed to be less damaging to the carbohydrates. The concentration of dissolved lignin is kept low at the end of the cook by employing a prolonged counter-current cooking zone, which extracts black liquor while adding white liquor. The maximum cooking temperature is also lower than conventional temperatures, which is believed to hinder carbohydrate degradation reactions. Employing these conditions, softwood kraft pulps with kappa numbers as low as 18 with strength properties comparable to conventional kraft pulps at 30 kappa can be produced (3). Pulping to low kappa numbers, however, increases yield losses, and attempts have been focused on improving the yield by using additives such as anthraquinone and polysulfide, alone and in combination (4,29).

Kraft Delignification Chemistry

There are three categories of reactions that are believed to occur during kraft delignification: 1) degradation reactions that liberate lignin fragments and enhance solubility; 2) condensation reactions in which lignin fragments recombine to form alkali stable linkages; and 3) other reactions in which no net fragmentation occurs, but alkali stable structures, like stilbenes and vinyl ethers, are formed, making additional fragmentation difficult (21). These various reactions and their significance concerning the structural features of residual and dissolved lignins will be reviewed.

Degradation reactions

Degradation or fragmentation reactions are the most important reactions occurring during kraft delignification because these reactions assist in the fragmentation and dissolution of the lignin polymer. Aryl ether-type linkages (β-O-4 and α-O-4) are the most sensitive linkages in lignin under kraft pulping conditions. The reactivity of aryl alkyl ether linkages is greatly influenced by the phenolic position of the aromatic ring. Whether or not this position contains a free or etherified phenolic group affects the cleavage of the aryl ether linkage at the α and β positions of the propane side chain. The α-aryl ether linkage in phenolic structures is easily cleaved during the alkali-assisted formation of a quinone methide (Figure 4).

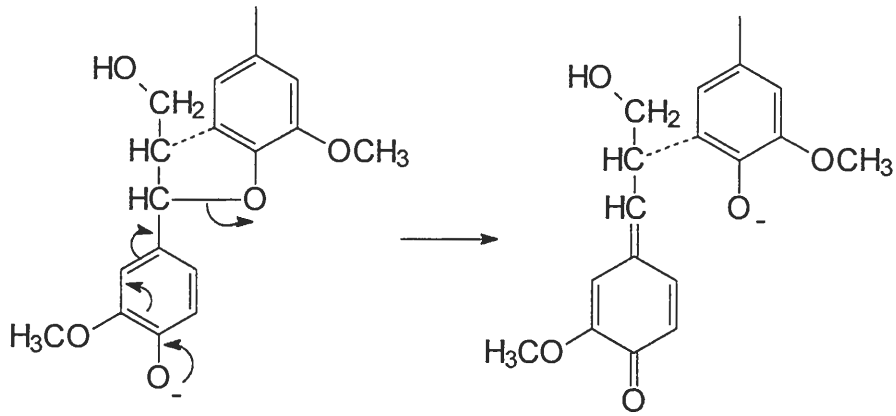


Figure 4. Alkaline cleavage of α-aryl ether bonds in phenolic arylpropane units (21).

β-aryl ether structures containing a free phenolic group can also undergo an alkali-assisted transformation into a quinone methide provided that the α position contains an appropriate leaving group (Figure 5). The quinone methide can then react in different ways to restore the aromaticity of the aromatic ring. The quinone methide intermediate could be converted to an alkali-stable enol ether structure by the elimination of the terminal hydroxymethyl group as formaldehyde. This reaction is more prominent in the absence of hydrosulfide ions, as is the case during soda pulping. Under kraft pulping conditions, a hydrosulfide nucleophile can react with the quinnone methide to restore the aromaticity of the ring. The mercaptide anion can attack the β carbon, forming a thiirane and eliminating the β-aroxy group. This reaction is often referred to as a neighboring group participation reaction. The thiirane structure can then lose elemental sulfur, forming a coniferyl alcohol-type structure. As with the cleavage of the free phenolic α-aryl ether linkages, the cleavage of the free phenolic β-aryl ether linkages proceeds rapidly in the presence of NaSH, with the formation of the quinone methide being the rate-determining step of the overall reaction (30). Although the presence of hydrosulfide ions is believed to influence the reaction pathway resulting in the fragmentation of the aryl ether linkage, enol ether structures have been detected in kraft lignin, suggesting that both reaction pathways occur during kraft pulping (10).

Cleavage of β-aryl ether linkages in non-phenolic structures is a relatively slow reaction that is greatly dependent upon the phenylpropane unit having a hydroxyl group at the alpha position. This group can dissociate under extreme alkali conditions, forming an alkoxide anion. A nucleophilic attack by this anion at the adjacent β carbon forming an oxirane ring eliminates the β aroxy substituent (Figure 6).

The high frequency of α- and β-aryl ether linkages in softwood lignin (as shown in Table 1) plays an important role in the fragmentation and dissolution of lignin during kraft pulping. In addition to forming new "reactive" free phenolic groups with the cleavage of these ether linkages, the increase in hydrophilic free phenolic groups helps promote the solubility of the lignin. These are the major fragmentation reactions occurring during kraft pulping that lead to the dissolution of lignin. By promoting an efficient and comprehensive fragmentation of these linkages, dissolution of lignin during pulping could possibly be optimized.

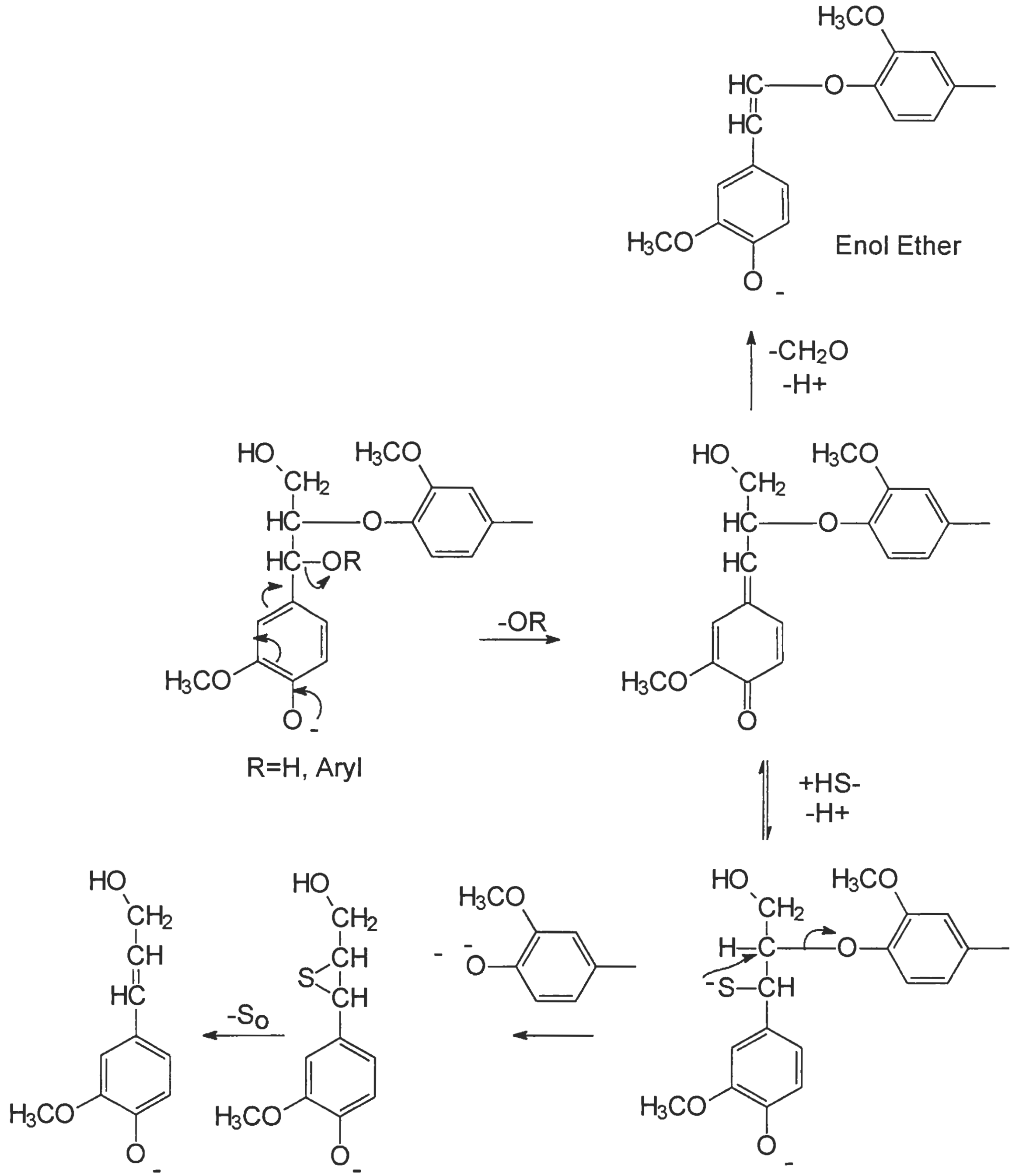


Figure 5. Sulfidolytic cleavage of β-aryl ether bonds in phenolic arylpropane units and conversion into enol ether structures (21).

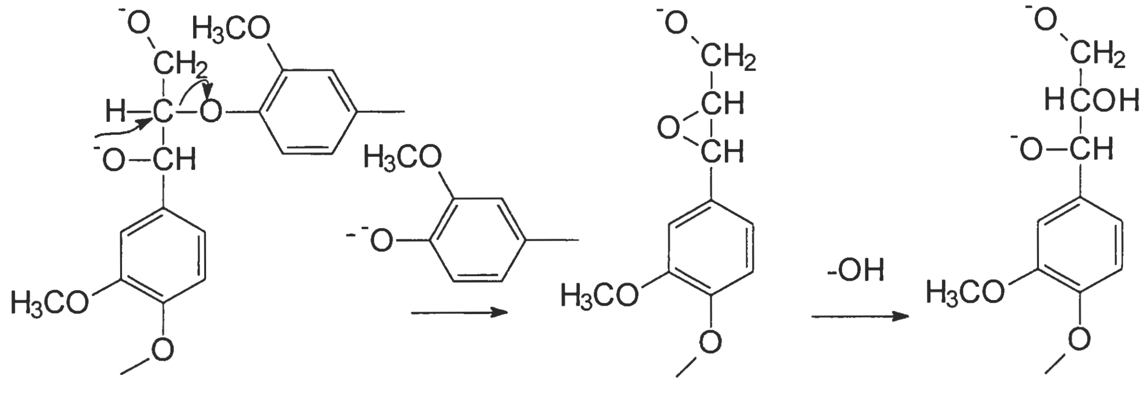


Figure 6. Alkaline cleavage of β-aryl ether linkages in non-phenolic arylpropane units (21).

Contrary to the cleavage of ether linkages, the cleavage of carbon-carbon linkages during kraft pulping is only responsible for a minor amount of the total lignin fragmentation. This cleavage occurs in side chains and between side chains and aromatic nuclei (Figure 7).

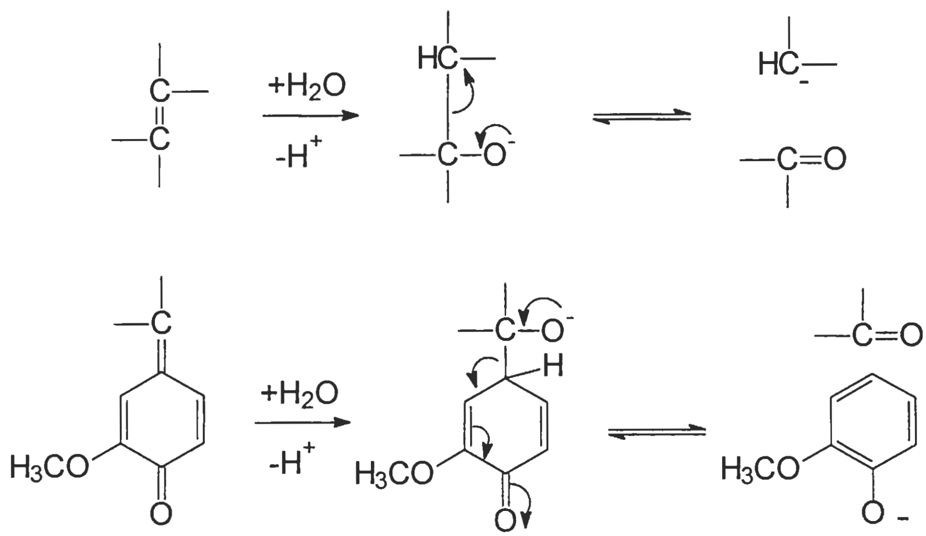


Figure 7. Alkaline cleavage of carbon-carbon linkages by retro aldol reactions (21).

Condensation reactions

Condensation reactions are the other main type of reactions that are believed to occur during kraft pulping (21). External nucleophiles, HS^- and ^-OH, have to compete with carbanions from fragmented phenolic units for quinone methide intermediates. The addition step of the nucleophile to the quinone methide is reversible and is therefore dependent on the nucleophilicity and the ability of the addition product to undergo a rapid irreversible reaction. Structures that contain an aroxyl substituent at the β position, which can be readily eliminated by the hydrosulfide nucleophile (via neighboring group participation), are susceptible to attack by the hydrosulfide nucleophile, resulting in a net fragmentation. However, if the quinone methide structure has a β substituent that cannot be readily eliminated, such as an aryl group, the addition of a phenolate ion, i.e., a cyclohexadienone anion, followed by irreversible rearomatization, can lead to a diphenylmethane structure. This competitive addition between external and internal nucleophiles is outlined schematically in Figure 8.

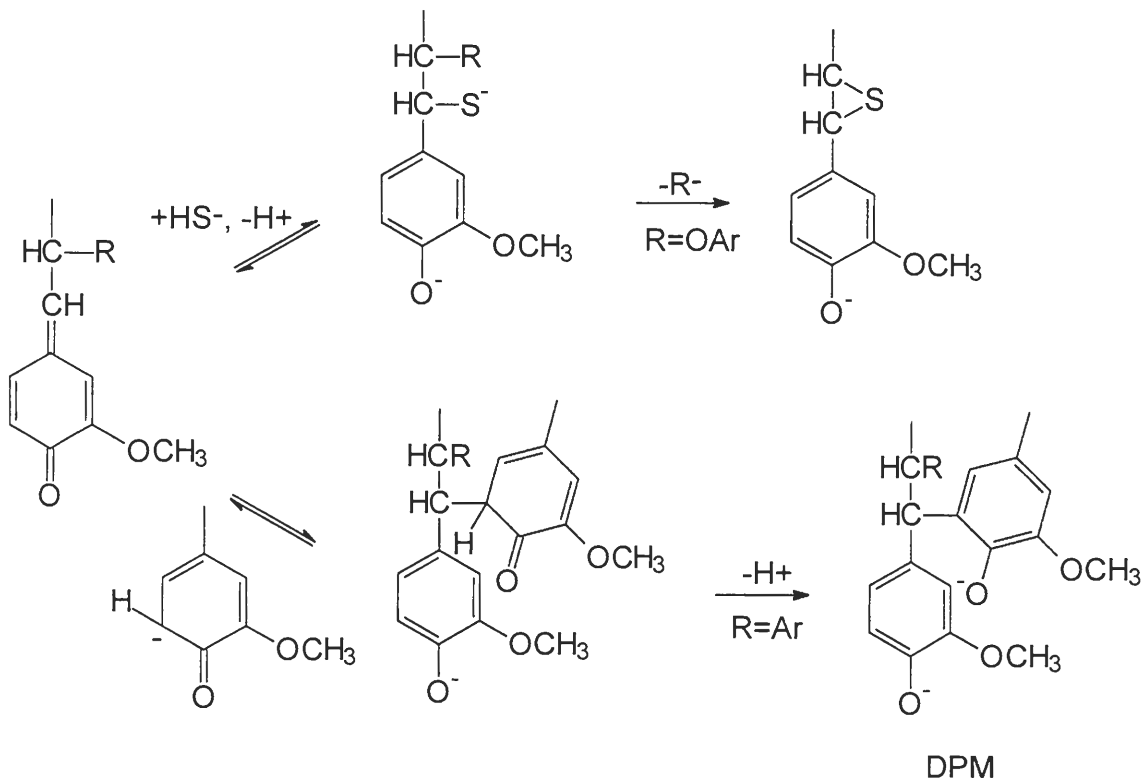


Figure 8. Competitive addition of external and internal nucleophiles to quinone methide intermediates (31). OAr = aroxyl group; Ar = aryl group; DPM = Diphenyl-methane.

Various other types of condensation reactions are also believed to occur during kraft pulping (31). Another condensation reaction that is believed to occur during kraft pulping involving two phenolic ions and formaldehyde has been drawn schematically in Figure 9.

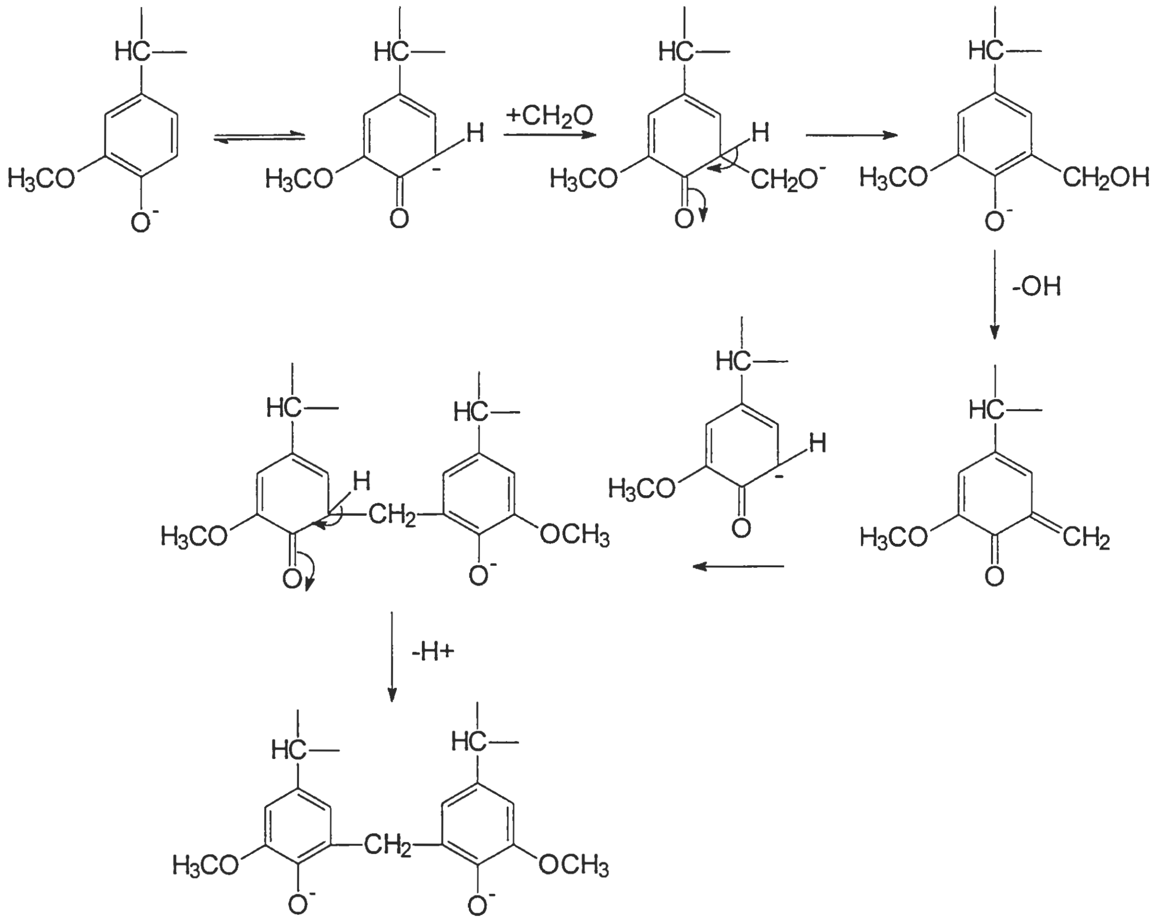
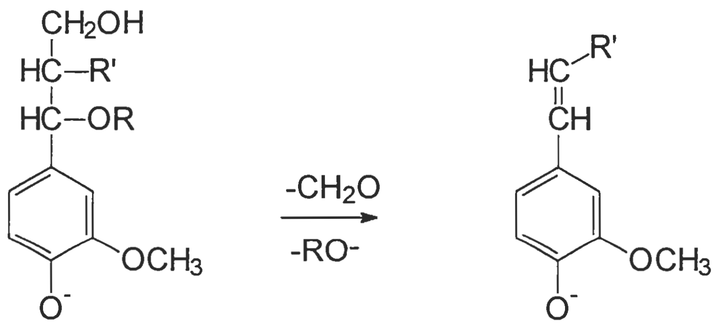


Figure 9. Alkali-promoted condensation reaction of phenolic units (31).

Other reactions

There are a variety of other reactions that occur during kraft pulping that are believed to contribute to the low reactivity of residual lignin. Enol ethers and stilbenes are formed during kraft pulping that do not assist in the fragmentation and dissolution of the lignin (Figure 10). Such structures are somewhat stable during pulping. These ring-conjugated structures are important to consider when studying the structure of residual and dissolved lignins because their presence, although in small quantities, contributes to the dark color of kraft pulp. A variety of reduced structures have been suggested to be present in the residual and dissolved lignins, as evidenced by the increase in the number of methylene and methine groups in the residual and kraft lignins (11). The formation of these structures is not well understood.



β-1 (R=H,Ar R'=Ar)
or
β-O-4 (R=H,Ar R'=OAr)

Stilbene (R'=Ar)
or
Enol ether (R'=OAr)

Figure 10. Competing reactions during kraft pulping (32).

Other structures that are resistant to kraft pulping are shown in Figure 11. Some of these structures contain ether linkages but are still resistant to kraft pulping due to their non-phenolic structure and poor leaving group at the alpha position. Many of the resistant structures contain carbon-carbon linkages. Such structures are believed to be enriched in the residual lignin of kraft pulps, leading to its unreactive nature.

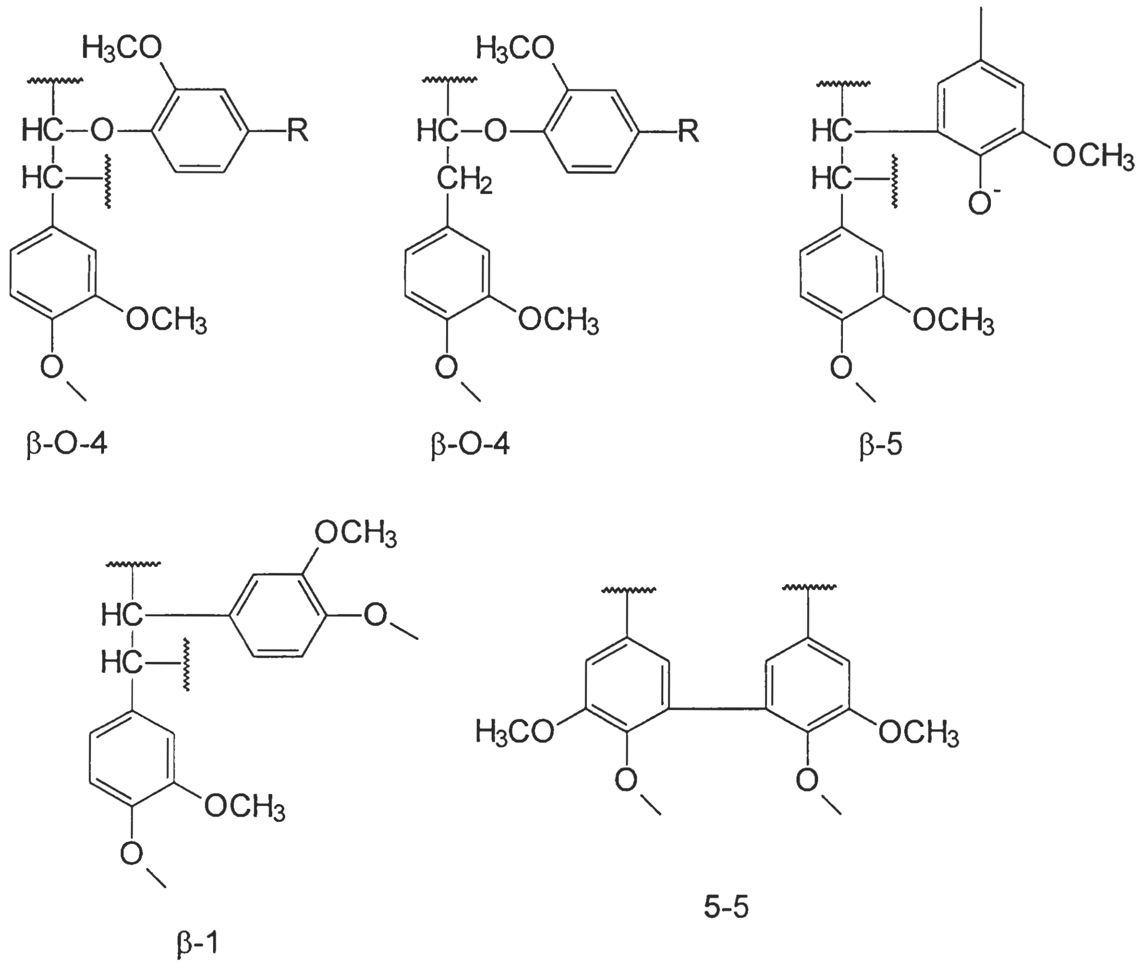


Figure 11. Structures that are resistant to kraft delignification conditions.

Lignin-Carbohydrate Complexes

Lignin-carbohydrate complexes (LCC's) are believed to be present in the native wood lignin (15-19). There are possibly several different linkage types between lignin and carbohydrate, and they can be generalized as either being alkali sensitive or alkali stable. The alkali-sensitive linkages are cleaved under the harsh alkali conditions of the kraft cook. The alkali-stable linkages survive the kraft cook and have been suggested to be present in kraft pulps (24,33). The linkage is believed to contribute to the difficulty in removing lignin at the end of the kraft cook (33). In addition to alkali-stable native LCC's surviving the kraft cook, alkali-stable LCC's may be formed during the cook (24,25). This has been demonstrated in both model compound studies of phenolic and non-phenolic model compounds. The formation of an LCC with a non-phenolic β-O-4-type structure is believed to occur by a carbohydrate hydroxyl group, acting as a nucleophile, reacting with an epoxide that is formed during the elimination of the β aroxy substituent, as demonstrated in Figure 12. The lignin fragment of native LCCs is believed to be linked exclusively with hemicelluloses, while the lignin fragment of the LCCs that are formed during pulping may be more frequently linked to cellulose (24,25,33).

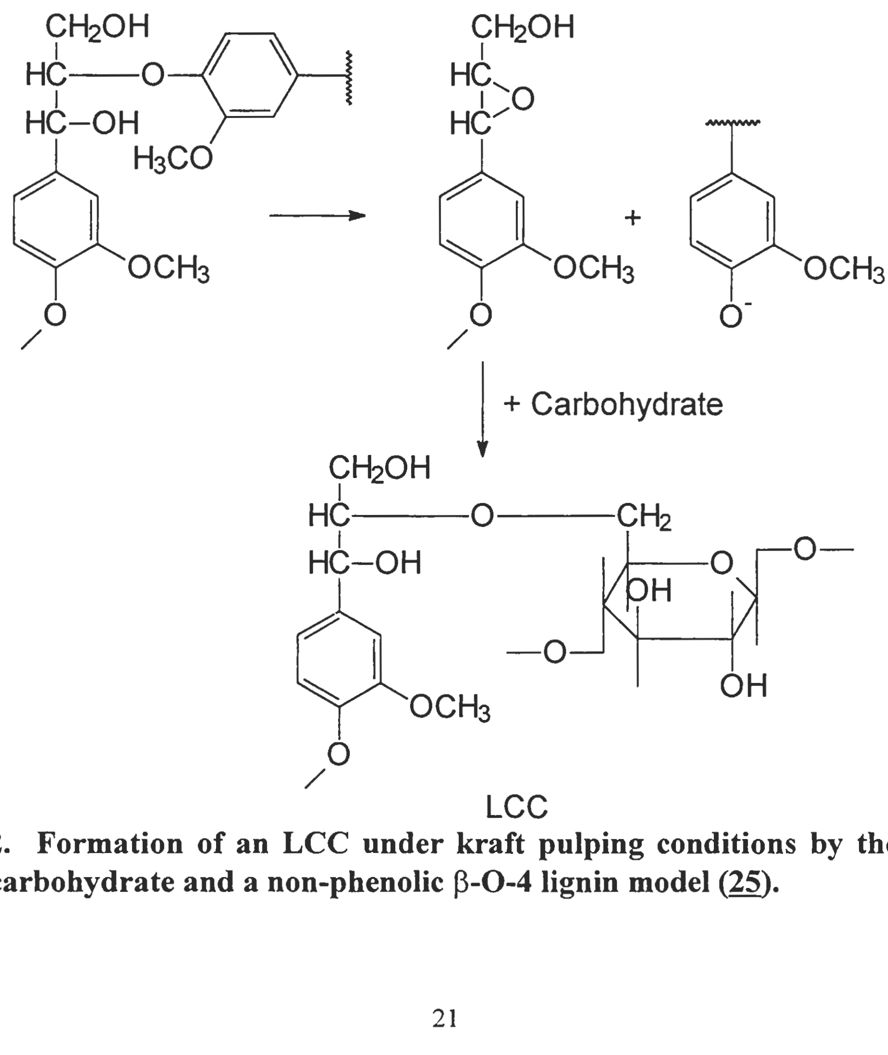


Figure 12. Formation of an LCC under kraft pulping conditions by the reaction between carbohydrate and a non-phenolic β-O-4 lignin model (25).

ANALYSIS OF RESIDUAL AND KRAFT LIGNINS

The chemistry of kraft delignification has been significantly advanced by characterizing the structural features of residual and kraft (dissolved) lignins. Monitoring the structural changes in lignins during pulping can provide valuable insights into the chemical reactions that contribute to the fragmentation and dissolution of the lignin and the poor reactivity of residual lignin. The following section will review literature studies, which characterize the structure of residual and kraft lignins.

Elucidating the precise structural features in lignin is very difficult. A common method is to determine the frequency of lignin functional groups and interunit linkages. The functional groups and linkages important for characterizing the structure of lignin include free phenolic hydroxyl groups, ether linkages (in particular β-O-4 structures), carbon-carbon linkages, condensed structures, and methoxyl groups. The distribution of these functional groups and linkages in a given lignin sample can be very informative.

Phenolic Hydroxyl Groups

The content of phenolic groups in kraft and residual lignins has been measured in a variety of studies (7,8,33-40). Compared to native wood lignin, the content of phenolic groups in kraft lignins is much higher. Values have been reported to be roughly 13 per 100 C9 units for wood lignin and as high as 70 per 100 C9 units for kraft lignin (7,8). Residual lignin has a phenolic content that is intermediate to these values, approximately 30 per 100 C9 units for a ~30 kappa kraft pulp (8,33-35). Figure 13 shows the phenolic hydroxyl content of kraft and residual lignins plotted against the percent delignification, showing the difference in phenolic hydroxyl contents of kraft and residual lignins at various times during the kraft cook (8). One interpretation for the discrepancy in the phenolic content of kraft and residual lignins is that a certain quantity of phenolic groups is necessary in order for the lignin to become soluble (8). This quantity is not reached in the residual lignins. Studies with a flow-through reactor found that the phenolic contents of lignins collected during the flow-through cook were comparable to the phenolic contents of lignins that had been isolated from a batch cook at a similar time during the cook. This result implies that the lignin dissolved from the wood/pulp requires a high phenolic content, which is reached while the lignin is still in the pulp.

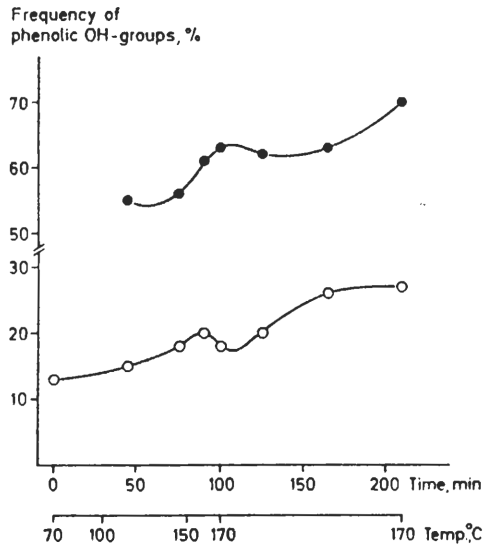


Figure 13. Frequency of phenolic hydroxyl groups as a function of cooking time in wood and in the residual lignin in kraft pulps (open symbols) and corresponding dissolved lignins (closed symbols). Reprinted from reference (8) with permission from Prof. Gellerstedt.

More recently a study on the variation in phenolic content in low kappa kraft pulps has found that as the kappa number is lowered the content of phenolic groups increases in the residual lignins, particularly when delignification is extended past a 20 kappa number (35,39). Figure 14 shows a plot of this data for pulps with kappa numbers ranging from 40 to 5 (35).

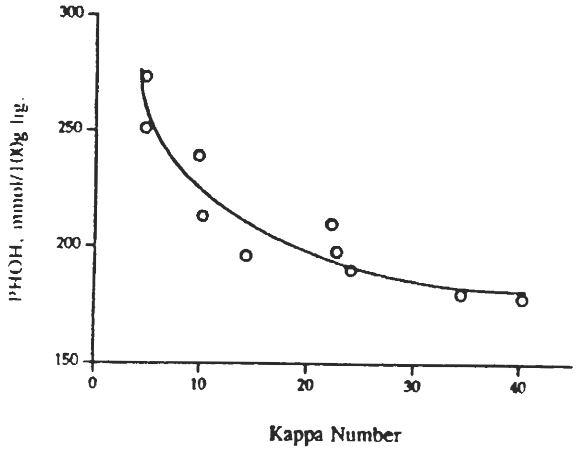


Figure 14. The phenolic hydroxyl content of residual lignin as related to the kappa number of unbleached pine kraft pulp (35).

β-O-4 Structures

Aryl ether linkages in kraft and residual lignins are important structural features that have been extensively characterized. Because the cleavage of these linkages results in fragmentation and assists in the dissolution by creating additional phenolic groups, monitoring the content of these linkages and how they change during pulping is very informative. In native wood lignin, every other linkage between subunits of lignin is of the β-O-4 type. After being exposed under pulping conditions for prolonged times, the kraft and residual lignins have a significantly decreased content of such linkages between subunits. The remaining linkages after kraft pulping are principally the carbon-carbon type.

The content of β-O-4 structures in kraft and residual lignins has been measured by Gellerstedt et al., employing a degradation analysis technique, acidolysis (6). The results from this analysis are shown in Figure 15 for both kraft and residual lignins. The kraft lignins have a relatively low content of such structures at the beginning of the cook and gradually decrease as the cook proceeds. In comparison, the content of these structures in the wood/pulp is quite high at the beginning of the cook and decreases more significantly as the cook proceeds, approaching the level in the kraft lignins. At the end of the cook (approximately 32 kappa), the content of β-O-4 structures in the residual lignin is similar to the content in the kraft lignin, an estimated 15% of the content in wood lignin.

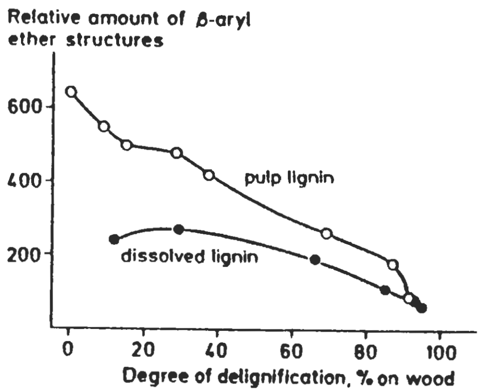


Figure 15. Relative amount of β-aryl ether structures per gram of lignin in kraft pulps and in dissolved lignins as a function of the degree of delignification. Reprinted from reference (23) with permission from Prof. Gellerstedt.

Kringstad and Morck used qualitative ^{13}C-NMR to analyze various kraft lignins for their contents of β-O-4 structures (41). The study involved determining the ^{13}C-NMR chemical shifts of 60 lignin model compounds, including the β-O-4 type; the kraft lignin spectra were interpreted, making reference to these model compounds. The signals arising from β-O-4 structures were found to diminish as the cook proceeded, indicating that the cleavage of such linkages was occurring to a significant degree.

The formation of enol ether structures competes with the cleavage of β-O-4 linkages (Figure 5). A ^{13}C-NMR analysis of kraft lignin suggested that vinyl ethers are present, implying that some β-O-4 structures are, indeed, converted into alkali-stable enol ethers (41). Gellerstedt and Lindfors have been able to detect and quantify these structures in residual and dissolved kraft lignins (10). The content of enol ether structures in both residual and kraft lignins reached a maximum when the cook reached its maximum cooking temperature. A deficiency of hydrogen sulfide ions at the β-O-4 reactive site was proposed to be the cause for this maximum content of enol ethers in the middle of the cook. The sulfide deficiency results in the formation of an alkali-stable enol ether instead of the fragmentation of the aryl ether linkage. The content of vinyl ether structures in residual and kraft lignins is quite low at the end of the cook, which may be a result of their possible fragmentation during pulping because they have been shown to be in equilibrium with quinone methides (30).

Distribution of Carbon-Carbon Linkages

Native wood lignin is known to contain some linkages between subunits that are the carbon-carbon type. These linkages include β-5, 5-5, and β-1 structures, as depicted in Figure 1. The alkali stability of these linkages implies that they would be difficult to cleave during pulping. The frequency of such linkages would be higher in kraft and residual lignins because most of the aryl ether linkages have been extensively cleaved.

The distribution of carbon-carbon linkages in kraft and residual lignins has been the focus of several investigations (9,37,39).

Oxidative degradation has been used to investigate the frequency of carbon-carbon linkages in lignin (42). The lignin is reacted with permanganate to selectively degrade all aliphatic side chains attached to aromatic units. The oxidized products are derivatized and analyzed by GC. Quantification of the degraded products provides information about the frequency of various linkages between lignin subunits. The major disadvantage of this technique is that only structures containing free phenolic groups are susceptible to detection and the assumption must be made that the frequency of linkages in these free phenolic structures is the same as the overall frequency of these linkages.

Gellerstedt has performed this analysis on residual and kraft lignins isolated from both batch and flow through cooks (9). Comparisons between residual and kraft lignins showed that throughout the cook the frequency of guaiacyl end groups was greater in the kraft lignins, while the frequency of 5-5 and 4-O-5 structures was greater in the residual lignins. In the residual lignins, the 5-5 and 4-O-5 structures accounted for about 25% and 18%, respectively, of the total amount of aromatic products analyzed. These structures are resistant to alkali and are difficult to dissolve from the pulp, which explains the greater frequency of such linkages in residual lignins. The content of C5-substituted aromatic units (which suggests the presence of β-5 and monophenolic biphenyl structures) in the kraft lignins was found to increase in frequency at the end of the cook, suggesting the possibility of condensation reactions occurring in the dissolved lignins (in addition to the lignin dissolved at the end of the cook being more condensed). The oxidative degradation analysis also allows for the quantification of catechol structures that are believed to be formed during pulping via demethylation reactions. The amount of catechol structures was found to increase in both the kraft and residual lignins. The effect was more pronounced in the kraft lignins, particularly at the end of the cook.

From the analysis, distinct changes in the chemical structure of residual and kraft lignins occurred at specific times during the cook; times that coincide with the transitions from the initial to bulk delignification phase and from the bulk to final delignification phase. This observation supports the view that chemical reactions during pulping influence the reactions necessary for the dissolution of lignin. This is an important observation because it suggests that the dissolution of lignin can be influenced by altering the chemistry of delignification, which is done during modified kraft pulping.

Argyropoulos et al. have found a similar result in their studies on kraft lignins by using ^{31}P-NMR spectroscopy (36,37). The analysis is capable of quantifying the content of C5 condensed aromatic phenolic groups (37). Kraft lignins were isolated at different stages of a conventional kraft cook, and the content of condensed structures was measured; such structures were found to increase with increasing levels of delignification.

The presence of a C5 condensed structure does not imply that the lignin has actually undergone a condensation reaction. Such structures are found in native wood lignin (β-5, 5-5, and β-1), as well as in residual lignin. C5 condensed structures are also believed to be formed during kraft pulping, as will be discussed in the next section.

Condensation Products

Model compound studies, along with various analyses of kraft lignins, indicate that condensation reactions occur in homogeneous solutions of lignin under alkaline pulping conditions (43-45). However, no direct evidence has been found to suggest that condensation reactions occur in the lignin that remains in the fiber.

Gellerstedt and Robert found indications that condensation products are formed during kraft pulping (11). A signal at δ 29.7 ppm in the ^{13}C-NMR spectra of kraft lignin could be assigned to the methylene carbon in a diarylmethane structure that is formed by the condensation of two phenolic groups with formaldehyde, as depicted in Figure 9. The quantity of this structure in kraft lignin was estimated to be 0.04 per aromatic ring. Using ^{13}C-NMR, Kringstad and Morck also suggested that this product was formed during kraft pulping (41). Gellerstedt and Robert provided further evidence for condensation using ^{13}C-NMR by quantifying methine carbons, which have chemical shifts from δ 55-0 ppm (11). The integration of this region was greater in kraft lignins compared to native wood lignin. Kringstad and Morck also found an increasing number and intensity of signals in this region of the ^{13}C-NMR spectra, which they too concluded to be due to the formation of methine carbons (41). The formation of these methine carbons in the kraft lignin may be explained by new linkages of the carbon-carbon type being formed, which can be indicative of condensation reactions. A similar ^{13}C-NMR analysis of residual lignin suggested that the content of condensation products was negligible, because the content of methine carbons was found to be similar to the content in native lignin (32). Further research is necessary before any definite conclusions can be made about whether or not condensation is occurring in the residual lignin.

Other Functional Groups

The content of stilbene structures in residual and dissolved lignins was measured by Yamasaki et al. who employed ultraviolet spectroscopy (33). Quantifying the differences in the absorption regions due to stilbene structures in spectra of milled wood lignin, residual lignin, and kraft lignin resulted in an estimate of the quantity of such structures in kraft and residual lignin. Kraft lignin was estimated to have 6-7 stilbenes structures per 100 C9 units, and residual lignin was estimated to have approximately 3 per 100 C9 units. Gellerstedt detected very small quantities of vinylic carbon atoms in kraft lignins (0.0-0.2 per aromatic ring) using quantitative ^{13}C-NMR (7). Kringstad and Morck suggested that unsaturated structures were formed during kraft pulping as evidenced by some signals observed in the ^{13}C-NMR spectra with chemical shifts similar to olefinic carbons in model compounds of the unsaturated type (41).

The ^{13}C-NMR technique is a powerful technique to quantify other carbon-containing functional groups in lignin, as has been demonstrated by many investigators (7,11,23,41,46-50). Quantitative ^{13}C-NMR analyses of milled wood lignin, residual lignin, and kraft lignin have provided data on various functional groups, as shown in Table 3, which was taken from work published by Gellerstedt and Robert (46).

Table 3. Number of functional groups per 100 carbon atoms in milled wood lignin from spruce (MWL) and in the residual and dissolved lignin after a kraft cook of pine. (The residual lignin was isolated after acid hydrolysis of the pulp) (46).

Type of Carbon	Native lignin (MWL)	Kraft cook to kappa number 30.5 Residual lignin	Dissolved lignin
Carbonyl	0.8	-	0.3
Carboxyl	-	2.1	1.5
Olefinic + Substituted Aromatic C	39	54	39
Aliphatic CH_x-OR	23.6	9.5	10.1
Methoxyl	11.2	9.1	8.9
Aliphatic CH_x	4.9	10.4	16.0
Phenolic OH*	1.5	3.0	8.3

*Data taken from references 7 and 8 and converted into C100 units assuming molecular weight of a C9 unit is 183.

One of the major changes in the wood lignin during kraft pulping is the apparent conversion of aliphatic carbons with oxygen substituents to hydrogen and carbon substituents. Residual lignin has a high content of substituted aromatic carbons, which is indicative of the increasing content of β-5, 5-5, 4-O-5, and condensed structures. The increasing content of β-5, 5-5, and 4-O-5 structures was suggested by the oxidative degradation analysis of residual lignin. Whether or not condensation products contribute to these high values has not been established. The decreasing content of methoxyl groups is likely due to demethylation reactions, which are believed to cause the increasing content of catechol structures in residual and dissolved lignins. Carboxylic acid groups have also been found in residual and kraft lignins (7,33,46). The content of such structures, however, is quite low.

Linkages to Carbohydrates

Residual lignin is believed to be attached to carbohydrates, which may influence its dissolution during pulping (23,33,47,51). Many studies have indeed found that residual lignin, isolated from kraft pulp by employing an enzymatic hydrolysis procedure, is incapable of being completely separated from carbohydrates. Treating this enzymatically isolated residual lignin with additional enzyme treatments and performing various solvent extractions have failed to separate the residual lignin from the carbohydrate (33,47,51). The data strongly suggest that residual lignin and carbohydrates are linked chemically in kraft pulps.

An analysis of the solubility of residual lignins isolated by enzymatic hydrolysis has shown that they are very soluble in dilute NaOH (33,51). The high solubility of this lignin implies that if the residual lignin was not attached to the carbohydrate in pulp it would be dissolved during pulping. This linkage may therefore contribute to the residual lignin's resistance to delignification during kraft pulping.

Additional evidence to support the hypothesis that residual lignin is attached to carbohydrates has come from Gellerstedt's flow-through studies, which found that, as the cook proceeds, the lignin being dissolved from the pulp becomes increasingly contaminated with carbohydrates (5,7,23). Figure 16 is a plot of the content of carbohydrates in kraft lignin versus the degree of delignification, revealing that the kraft lignin contains increasing amounts of carbohydrates as delignification is prolonged.

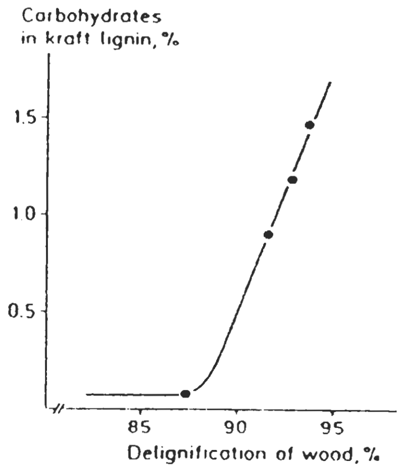


Figure 16. Amount of carbohydrates present in dissolved kraft lignin fractions from a laboratory cook of pine wood. Reprinted from reference (23) with permission from Prof. Gellerstedt.

ClO_2 DELIGNIFICATION

Chlorine dioxide is an important and versatile bleaching reagent for kraft pulp, as it can be used in two different stages during full-sequence bleaching to accomplish two distinct purposes. Chlorine dioxide has long been recognized to be an excellent brightening agent and is commonly used in the later stages of full-sequence bleaching to achieve the high brightness levels necessary for certain grades of paper. Chlorine dioxide is also a good delignifier of softwood kraft pulps and can be effectively used in the initial stages of full-sequence bleaching to achieve degrees of delignification comparable or better than Cl_2 alone and combinations of Cl_2 and ClO_2 (52,53). The need to better understand the chemistry of ClO_2 bleaching has become apparent, as this can lead to an enhanced and more efficient use of ClO_2 during delignification and guide new and innovative technological developments.

ClO_2 Delignification Chemistry

The chemistry of ClO_2 bleaching is quite complex and is the subject of a great deal of research. The inorganic reactions involving ClO_2 and its intermediates are very complex, not to mention, their reactions with lignin. Because ClO_2 bleaching is performed in aqueous medium, the most important chemical modification to lignin during a ClO_2 treatment is the introduction of hydrophilic carboxylic acid groups, making the lignin more water soluble thereby aiding in its dissolution during a bleaching stage. The reaction of ClO_2 with lignin is not limited to the formation of carboxylic acids as other products are created, some of which do not aid in its dissolution.

An overview of the major types of reactions occurring between lignin and ClO_2 and its reactive intermediates will be covered in this section. The section on the chemistry of ClO_2 delignification will be divided into two subsections, one dealing with lignin model compound studies on the fundamental chemistry of ClO_2 and the other dealing with the structural characterization of residual and dissolved lignins produced during ClO_2 bleaching. Lignin model compound studies have been the most informative studies on the fundamental chemistry of ClO_2 bleaching, although studies on the dissolved material and residual lignins remaining in the pulp after a treatment with ClO_2 are more informative on the actual chemistry occurring during bleaching.

Model compound studies

Many types of lignin models have been used in studying the fundamentals of ClO_2 chemistry. The typical models chosen range from simple guaiacyl structures, such as creosol, to more complex models that are more structurally similar to residual lignin. Such models include non-phenolic guaiacyl structures, C5 substituted dimers, and unsaturated structures, such as stilbenes. These studies, as will be discussed below, have found that ClO_2 reacts preferentially with free phenolic and unsaturated structures in lignins and that chlorinated species are evolved. The analyses are quite complex; even the reaction of simple models such as creosol results in a complex mixture of products that is difficult to characterize and quantify.

Phenolic structures

Model compound studies of chlorine dioxide chemistry with monomeric and dimeric non-etherified phenolic-type structures have been the subject of many investigations. These studies have found that free phenolic structures are quite reactive with ClO_2 and are believed to be the major site of attack of ClO_2, leading to the formation of a variety of oxidized and chlorinated products (54-62). Brage et al. and McKague et al. have each separately studied the reaction of creosol with ClO_2 in great detail and identified numerous products from this reaction (56,60). Quantitative yields of the products were difficult to ascertain from these studies; indeed, Brage et al. focused more on the identification of products rather than their yield. McKague et al., however, have come up with quantitative estimates of the products. Both studies found that there were two main reaction types occurring, chlorination and oxidation.

The pathway for the reaction between ClO_2 and free phenolic structures has been outlined by Brage et al. and reproduced in Figure 17 (60). The complex pathway shows that phenolic structures can undergo a variety of reactions, resulting in the formation of many oxidized products. Chlorine dioxide, itself being a radical, can abstract a hydrogen from a phenolic hydroxyl group to generate phenoxy and mesomeric cyclohexadienonyl radicals (structures 1A-1D). The mesomeric structures can then combine with ClO_2, creating reactive chlorite esters of ortho- and para-quinols (structures 2B, 2C, and 2D). These unstable chlorite esters further react to yield quinonoid structures (2B2 and 2C1), muconic acid-type structures (2B1), and an oxirane structure (2D1). Biphenyl products have also been found, suggesting that radical coupling reactions occur. The formation of carboxylic acid groups assists in delignification. Other products have the tendency to polymerize and are unreactive toward further degradation by ClO_2 thereby hindering delignification. Understanding which reactions are more prominent during ClO_2 bleaching is of great interest in comprehending the mechanisms that lead to delignification.

One of the more significant reactions that occurs with free phenolic structures and ClO_2 is the oxidative demethoxylation of the ortho-quinol chlorous ester intermediate, resulting in the formation of an ortho-quinone (2B2). Ortho-quinones are difficult to

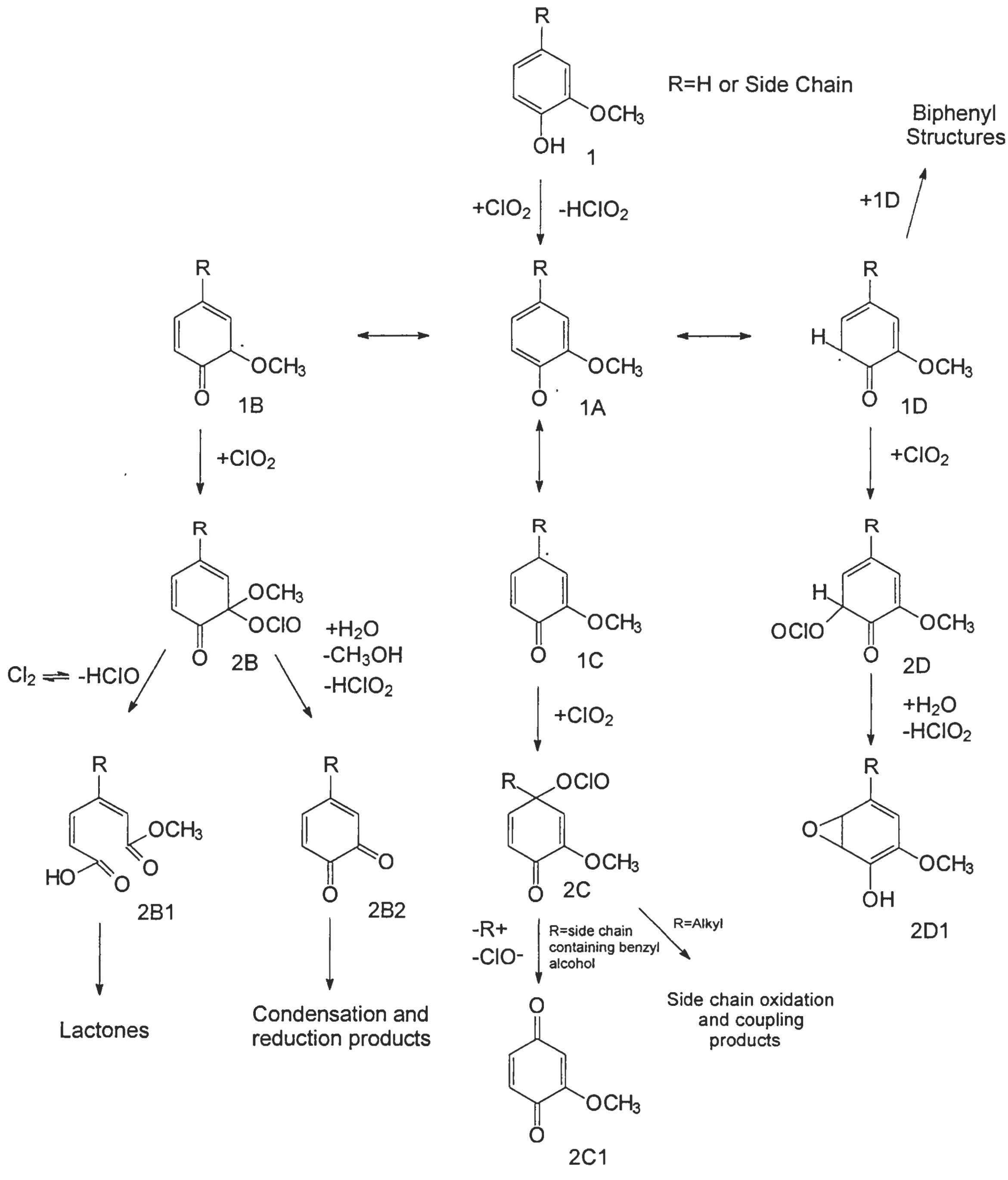


Figure 17. Oxidation of phenolic structures by chlorine dioxide (56,62).

isolate and quantify because they readily dimerize, polymerize, and/or are reduced to 4-methylcatechol (54,56). The release of methanol during these reactions has been found to be quite substantial, suggesting that oxidative demethoxylation is an important reaction pathway (61). Levels of methanol in ClO_2 bleaching effluents are quite high, which further indicates the relevancy of this reaction during pulp bleaching (63). One study estimated the quantity of ortho-quinone products from the reaction of creosol with ClO_2 to be 45% (54).

During ClO_2 delignification, the polymerization of the ortho-quinone product would certainly not be wanted. Because ortho-quinones formed in residual lignin have restricted mobility, polymerization would probably be less likely. If this were the case, residual lignin would be expected to contain a significant quantity of quinone structures, which has been confirmed by the FTIR analysis of lignin reacted with ClO_2 (64). Model compound studies have also shown that ortho-quinones are unreactive toward ClO_2. The formation of ortho-quinones from the ortho-quinol chlorous ester intermediate (2B) is, however, competing with a reaction that is more favorable for delignification.

The ortho-quinol chlorous ester intermediate (2B) can also undergo heterolytic fragmentation, causing the opening of the aromatic ring and the creation of a muconic acid structure (2B1) and its cyclicized lactone. This structure is difficult to isolate and quantify (in model compound studies). The formation of the carboxylic acid group greatly increases the water solubility of the product, which is very important for effective delignification during ClO_2 bleaching (23).

Another product isolated from the reaction of creosol with ClO_2 was biphenyl 5,5'-bis-creosol, which is formed by the oxidative coupling of ortho radicals of creosol. The phenolic groups in this structure would be prone to further oxidation by ClO_2. Formation of the chlorous ester intermediate at the para position results in either oxidation of the side chain (if the side chain contains an alkyl substitutent) or fragmentation of the side chain (if the side chain contains a benzyl alcohol group). The later reaction would assist in the fragmentation of lignin during ClO_2 bleaching, but the content of such structures in residual lignin may be quite low.

The chlorinated products identified during the reaction of ClO_2 with creosol in the study by Brage et al. are shown in Figure 18 (56). Careful procedures were employed during the experiments to prevent the addition of elemental chlorine to the system. The formation of the chlorinated products, therefore, must be attributed to the formation of elemental chlorine during the reaction. Chlorine is formed from its equilibrium partner, hypochlorous acid, which is formed when ClO_2 is reduced by lignin (65).

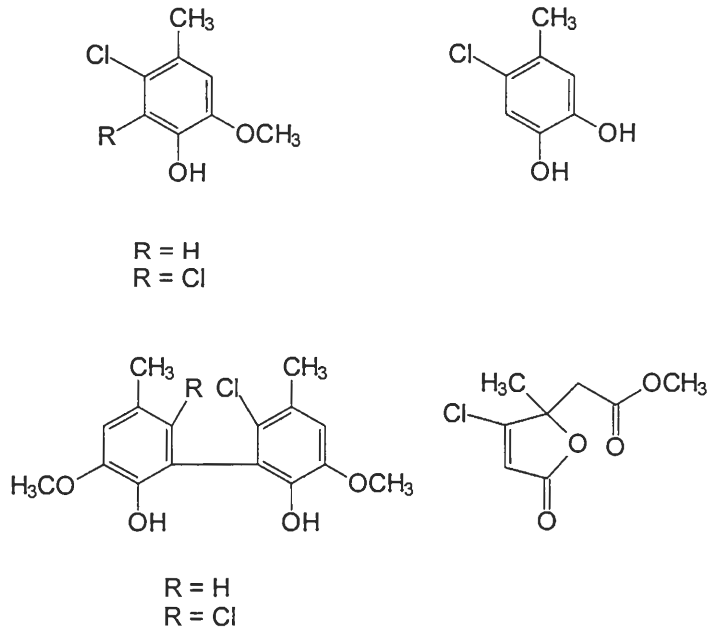


Figure 18. Identified chlorination products during the reaction of creosol with ClO_2 (56).

The study of McKague et al., involving the reaction of creosol with ClO_2, provided somewhat conflicting results (60). McKague was able to isolate and characterize other carboxylic acid-containing products that Brage did not find. The difference can most likely be attributed to the different solvents used in these studies. In the study by McKague, all reactions were done in water, while in the study by Brage, the solvents used were, in some cases, aqueous solutions of various alcohols (1:1, v/v). Pure water solvent systems are more representative of the reaction conditions used during pulp bleaching. The products identified in the reaction of creosol with ClO_2 by McKague are, therefore, more representative of the products formed during pulp bleaching. The products identified by McKague have been drawn and labeled in Figure 19. Of the six major products identified by McKague, only three were identified by Brage. Brage identified products 4, 5, and 7 but not 6, 8, and 9. Product 6 is another lactone structure that is chlorinated at a position that was not found by Brage. Products 8 and 9 are maleic acid derivatives.

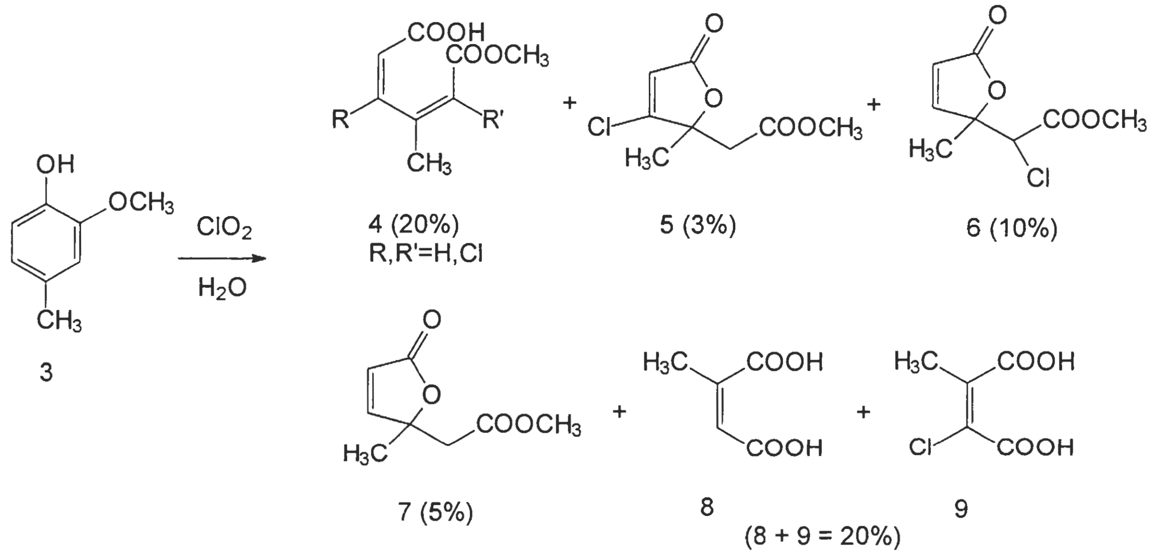


Figure 19. Products identified in the reaction of creosol with ClO_2. Estimated % yields are in parenthesis below the structures (60).

McKague quantified the products formed by the reaction between ClO_2 and creosol (60). The yield of products has been placed in parenthesis below the structures in Figure 19. The total yield of the reaction was 75%. The yield of the products in Figure 19, which are all formed via ring-opening reactions, was approximately 58%. The authors believe this estimate is low because the products were difficult to recover from the aqueous phase (as evidenced from the low total yield), suggesting that some of the more water-soluble acids were not recovered. Even still, a 58% yield of products derived from ring-opening reactions is quite high compared to what was suggested by Brage. The results imply that the competing reaction between the formation of orthro-quinones and muconic acids is favored by the formation of muconic acids in the aqueous system, which again is more representative of what occurs during pulp bleaching. McKague did note that when the reactions were done in aqueous methanol the products were more complicated and a negligible amount of maleic acid derivatives was formed (59). The formation of quinones is observed but not discussed in detail.

In addition to simple monomeric phenols, various dimeric phenolic lignin models have also been treated with ClO_2, and these products were identified by the same authors (57-59). The phenolic dimers used in these studies had structural features that are believed to be enriched in the residual lignins of unbleached pulps.

Both McKague and Brage studied the reaction of 5,5' bis-creosol, which has structural features that are present in both native and kraft pulp residual lignin. These types of structures can also be formed during ClO_2 bleaching (56). The biphenyl structures were found to undergo both chlorination and oxidation reactions, in a similar manner as their corresponding monomer (creosol) (Figure 18). Brage suggested that, from the products identified, both oxidative demethoxylation and ring-opening reactions occurred in this lignin model (57). McKague found that the total product was 20% 2-methylmaleic acid and 11% 2-chloro-3-methylmaleic acid. McKague also identified various dimeric products from this reaction, which contained one and two lactone functional groups. Some of the products characterized by McKague from the reaction of a 5-5-type lignin structure with ClO_2 are drawn in Figure 20. Although some of the products are complex, it is important to note that each has a carboxylic acid group or one or two lactone groups with a methyl ester.

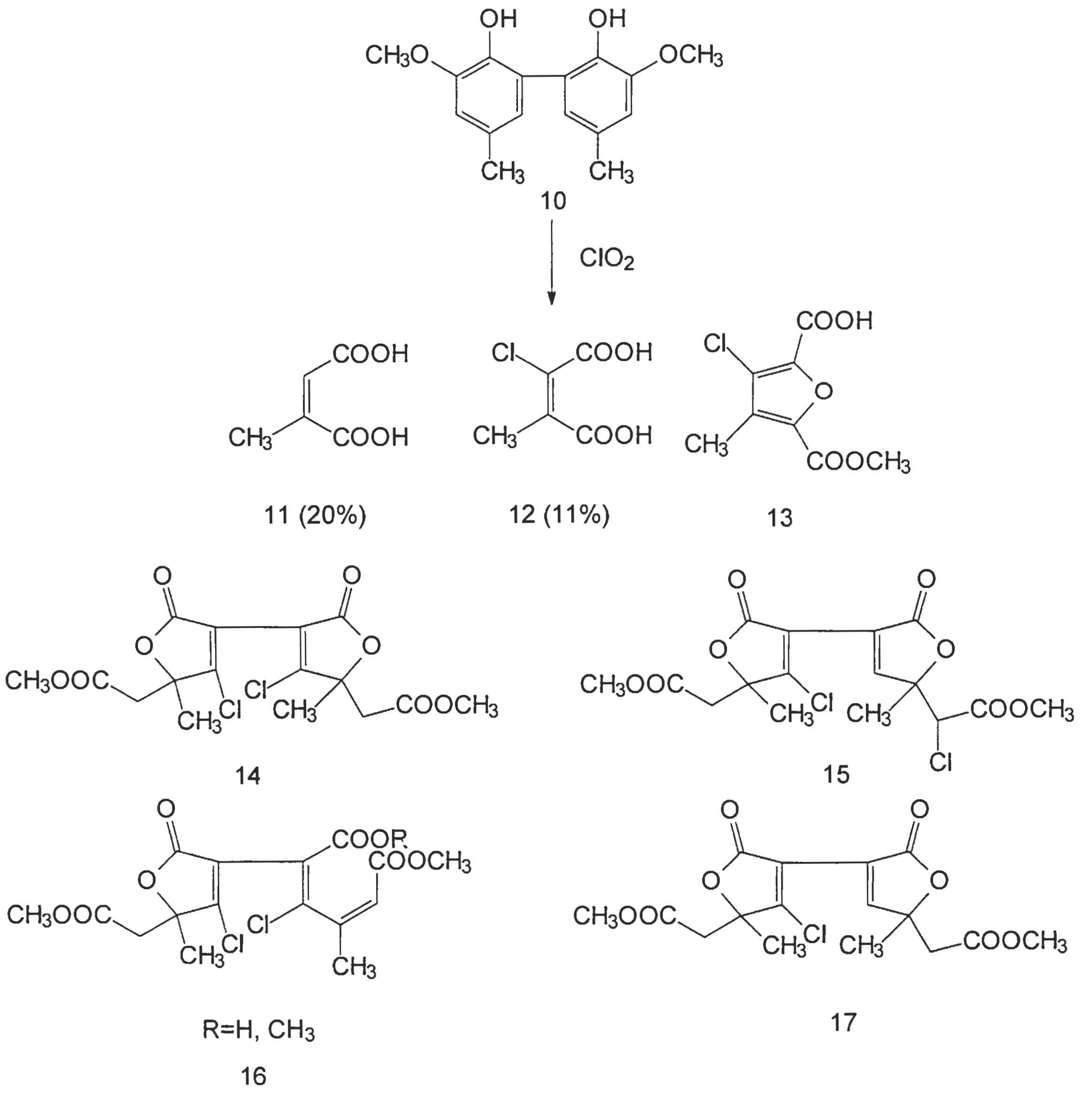
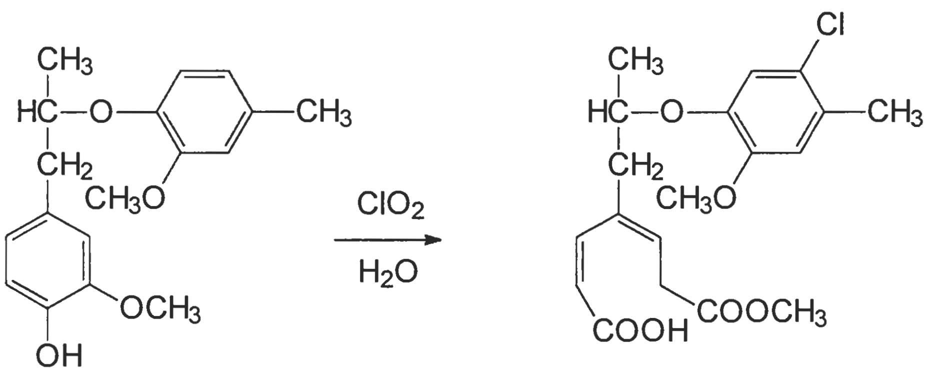


Figure 20. Reaction of a lignin model dimer similar to the 5-5 structure found in residual kraft lignin with ClO_2 (57,59).

Reactions of other dimeric phenolic lignin models with ClO_2 resulted in the creation of carboxylic acid and lactone groups with methyl esters (58,59). The products from these reactions were more complicated and structural assignments were difficult. One particular phenolic model compound dimer of interest was one that had a β-O-4 linkage and a methylene group at the alpha position (58). This type of reduced structure has been suggested to be present in the residual lignin of kraft pulp. The major product from its reaction with ClO_2 was a muconic acid derivative that resulted from the opening of the aromatic ring containing the phenolic group (Figure 21). The aromatic ring containing the non-phenolic group was observed to be difficult to oxidize under the conditions used. However, cleavage of these aryl ether linkages has been suggested to occur in the presence of elemental chlorine (66). Apparently, not enough elemental chlorine was generated during this reaction to cause the cleavage of this linkage.



18 19

Figure 21. Reaction of dihydroeugenol-β-4-methylguaiacyl ether with ClO_2 (58).

Non-phenolic structures

The reaction of ClO_2 with various non-etherified lignin models has also been studied (56,61). Such models react with ClO_2 to give both chlorinated and oxidized products (56). The rate of these reactions is significantly slower than phenolic lignin models, suggesting a clear preference for ClO_2 to react with phenolic substrates. Indeed, when phenolic (vanillyl alcohol) and non-phenolic (veratryl alcohol) model compounds were mixed together and reacted with ClO_2 in the presence of sulfamic acid to prevent the formation of chlorine, the non-phenolic model did not react, while 87% of the phenolic compound was consumed (61). Chlorine dioxide is believed to react with non-phenolic substrates by first abstracting an electron from the aromatic unit thereby creating a radical cation. These radicals can react again with ClO_2, creating reactive chlorous ester intermediates that proceed to muconic acids and quinones (56).

Ring-conjugated structures

Small quantities of olefinic structures are present in kraft residual lignins (10,33). Model compound studies have shown that ring-conjugated structures are quite reactive toward ClO_2 (56-58). Chlorine dioxide was shown to react with the electron-rich unsaturated olefinic carbons conjugated to an aromatic ring with a phenolic group. Oxidation reactions leading to ring-opened products could not be detected in the product mixture. This was explained by the high electron density at $C\beta$ in conjugated systems and by the deactivating effect of the conjugated double bonds on the aromatic nucleus. Fragmentation at the double bound was not observed, suggesting that the reaction does not assist delignification. Chlorination reactions were also found to be negligible. The products from these reactions included various ring-conjugated carbonyl compounds. The relative ease of the oxidative destruction of these potential chromophoric systems (ring conjugated olefinic structures) may partially explain the brightening effects of ClO_2 bleaching (67).

Reactions of products from ClO_2-treated lignin models with NaOH

Typically, a ClO_2 delignification stage is followed by an alkaline extraction stage in which a significant portion of residual lignin becomes solubilized and removed from the pulp. The chemistry of these two synergistic processes is of interest to the overall understanding of ClO_2 delignification. McKague et al. performed an interesting study in which the products from the reaction between phenolic lignin model compounds and ClO_2 were reacted with sodium hydroxide under simulated alkaline extraction stage conditions (60). The products from the ClO_2 reaction were discussed above. The reaction of lactones 5 and 6 (Figure 19) with sodium hydroxide resulted in the saponification of the methyl esters and ring opening to muconic acids as drawn in Figure 22. During the acidic work-up, some of these acids converted back into lactones, as evidenced by the product mixture containing the starting material and an isomer of the lactone. Other dimeric lactones structures, that were created during the reaction of ClO_2 with dimeric phenolic models, were also treated with NaOH. These lactones underwent saponification of their methyl esters, ring-opening reactions, and degradation into lower molecular weight products (60). The major products from these reactions were, however, the starting lactones, which were apparently recyclized back into the starting lactone during the acidic work-up. There was evidence for dechlorination reactions occurring during the alkaline treatment as 10% of the product yield was a structure containing a hydroxyl group where the compound had been chlorinated.

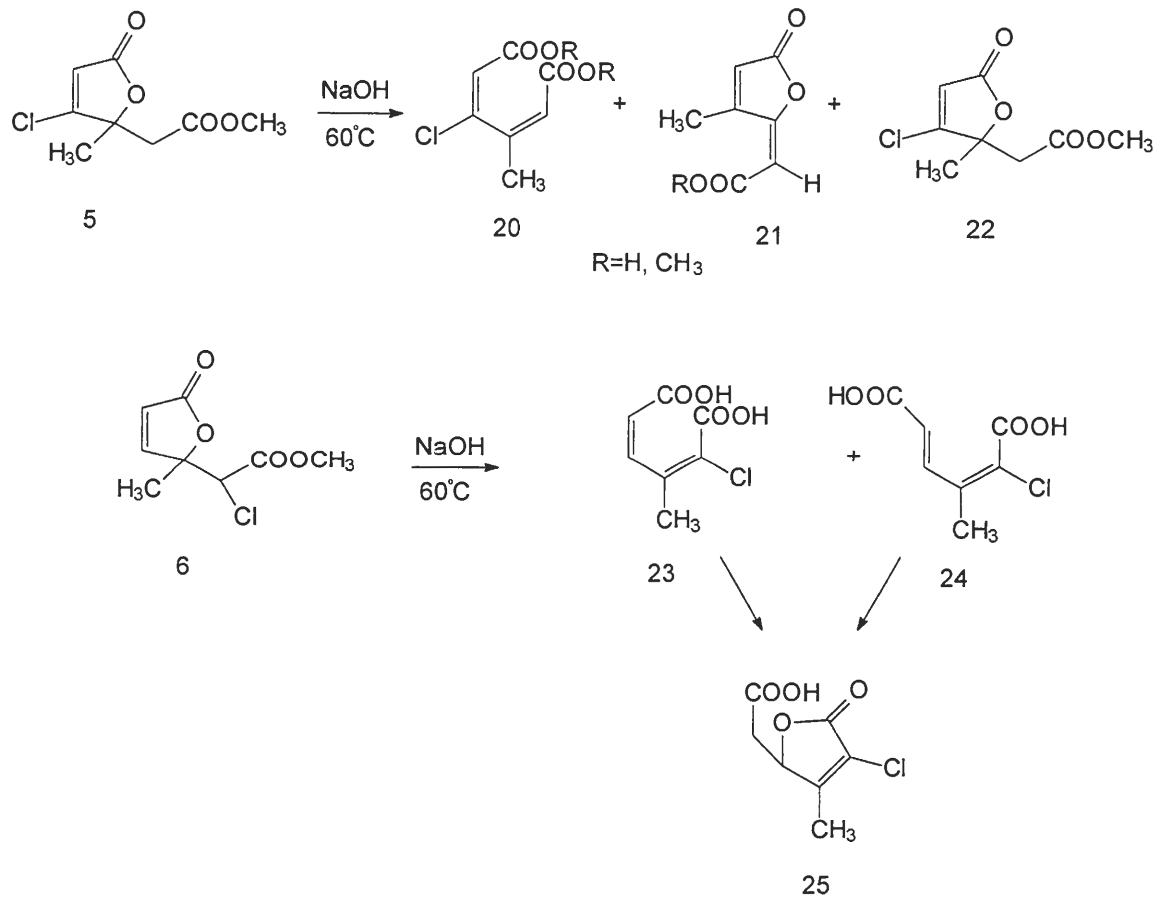


Figure 22. Reaction of monomeric lactones 7 and 8 with NaOH (60).

Interpretations of ClO_2 bleaching by model compound studies

Model compound studies on the chemistry of ClO_2 with lignin-like structures provide valuable insights into the chemical mechanisms causing delignification during ClO_2 bleaching. The studies can be used to assist in the interpretation of some interesting occurrences during ClO_2 bleaching. The difference in reactivity between phenolic and non-phenolic lignin structures serves as an example. An unbleached kraft pulp that is methylated to remove all free phenolic structures in the lignin is more difficult to bleach than the unbleached pulp that is not methylated (68,69). The methylated residual lignin is much less reactive toward the chlorine dioxide because it has such a low content of the highly reactive phenolic groups. This results in a poor delignification. Using a similar interpretation, an unbleached kraft pulp is easier to delignify with ClO_2 than an oxygen-delignified kraft pulp with a similar kappa number (68). Again, the oxygen-delignified kraft pulp has a residual lignin with a lower content of free phenolic groups causing the lignin to be less reactive toward ClO_2 and more difficult to oxidize.

Hypochlorous acid has been found to form during ClO_2 bleaching and participates in the reactions with lignin. Its reaction with lignin has been used to interpret some bleaching results. Dissolved and residual lignins contain organically bound chlorine, suggesting that elemental chlorine is formed and causes some of the lignin to be chlorinated (23,63,70,71,72). The presence of hypochlorous acid during ClO_2 bleaching has been suggested to be necessary for efficient delignification. Delignification is retarded when a scavenger of hypochlorous acid is added during ClO_2 bleaching, implying that hypochlorous acid and elemental chlorine are necessary for the efficient fragmentation, oxidation, and dissolution of the lignin during ClO_2 bleaching (66,73,74,75). Hypochlorous acid and elemental chlorine are capable of creating reactive phenolic groups by cleaving aryl ether linkages in the lignin, allowing for a more complete oxidation and removal of residual lignin (66).

The interpretation of many of the results in this dissertation will be made by employing the results from these informative model compound studies.

Summary

The results from these extensive model compound studies have illustrated that the reactions of ClO_2 with lignin structures are quite complex. Comparisons between phenolic and non-phenolic lignin models found that ClO_2 is much more reactive toward phenolic structures. Chlorination reactions were found to occur due to the presence of elemental chlorine formed during the reduction of ClO_2, by the substrate, to hypochlorous acid (an equilibrium partner of elemental chlorine). Although chlorination reactions may be unwanted, the presence of elemental chlorine during bleaching can assist in the dissolution of residual lignin (61,66,73).

Oxidation reactions are the most important and dominant reactions occurring during ClO_2 bleaching. Muconic and maleic acids are the main oxidation products from the reaction of ClO_2 with both monomeric and dimeric phenolic models in water. Under the acidic conditions, these muconic acid derivatives will cyclize to lactones. The formation of these carboxylic acid products aids in the dissolution of the lignin in both acidic and alkaline environments. During an alkaline treatment, methyl ester groups are saponified, creating additional carboxylic acid groups. Lactone rings are also opened into their hydrophilic carboxylic acid form, further assisting in the dissolution of lignin during an alkaline extraction.

Analysis of Residual and Dissolved Lignins

To truly comprehend the chemistry occurring during ClO_2 delignification of pulps, it is necessary to characterize the structure of the substrate and its products. The substrate is residual lignin, which is difficult to characterize, and its products are oxidized lignin, which is perhaps even more difficult to characterize. Attempts to characterize the lignin before and after bleaching with ClO_2 have been made with moderate success and have provided greater insights into the actual chemistry between ClO_2 and residual lignin.

Lindstrom and Osterberg performed an extensive study on the high molecular mass material in spent bleach liquors from a ClO_2 stage and from its subsequent alkaline extraction stage (63,71). The dissolved material in the acidic effluent of the ClO_2 stage was found, by elemental and methoxyl analysis, to have a C/Cl ratio of 45:1 and a methoxyl content of 2.3%. The corresponding values for the subsequent alkaline extraction stage material were 118:1 and 2.9%. The C/Cl ratio, although high, indicates that substitution reactions have occurred to a certain extent during the ClO_2 stage. Chlorination reactions during ClO_2 bleaching were predicted from model compound studies. Dechlorination reactions were also suggested under alkaline conditions and may explain the higher ratio in the spent alkaline effluent. The very low methoxyl content (a typical kraft and residual lignin has ~13-14% methoxyl) suggests that a high degree of demethoxylation occurred with these lignins. Model compound studies also predicted that a multitude of demethoxylation reactions will occur during ClO_2 delignification, resulting in the formation of ortho-quinones and polymerized products.

^{13}C-NMR analysis of these materials suggested the presence of both aliphatic and aromatic (conjugated) carboxylic acids. Signals in the region from δ 110-150 ppm were assigned to both aromatic and olefinic carbons. The presence of conjugated acids and olefinic structures in this material is believed to be due to muconic and maleic acid derivatives. ^{13}C-NMR spectra of various saturated and conjugated carboxylic acid model compounds confirmed these chemical shift assignments (71). Quinoniod structures could not be detected by the ^{13}C-NMR analysis. A weak aromatic signal in the ^{1}H-NMR spectrum of these materials suggested that they contained a low aromatic content. The spectra showed a broad peak in the region from δ 5.5-6.5 ppm, which was suggested to be due to olefinic protons.

Oxidative degradation analysis of the effluent material was used to determine the content of aromatic material and its substitution patterns. The aromatic content of the ClO_2 stage effluent was one eighth that of the alkaline extraction stage effluent. The oxidative degradation analysis suggested that the most abundant aromatic unit remaining in the E effluent material had a guaiacyl structure and was non-chlorinated.

Gellerstedt et al. have found that the residual lignin isolated from a OD(EOP) bleached softwood kraft pulp (4 kappa) had not undergone dramatic modifications (i.e., the ^{13}C-NMR spectra still contain aromatic and aliphatic regions characteristic of lignin) (23,70). The major differences between an unbleached residual lignin and a OD(EOP) residual lignin were a lower content of aromatic ring carbons, a lower content of methoxyl groups, and a higher content of carboxylic acid groups. Each of these observations is consistent with the model compound studies. Elemental and methoxyl analysis showed that the residual lignin has a content of organically bound chlorine equal to approximately one chlorine atom per 100 carbon atoms. An analysis of the residual lignin by oxidative degradation revealed that significant differences existed in the quantity of phenolic hydroxyl groups but not in their structures. There was a decrease in the quantity of phenolic hydroxyl groups compared to the unbleached and oxygen-delignified amount, although a fairly significant amount still remains. The ratio of C5 substituted to C5 unsubstituted guaiacyl structures remains the same, suggesting there is no selectivity toward a particular guaiacyl unit.

An investigation by Argyropoulos on determining the reactivity of ClO_2 toward kraft pulp residual lignins had some interesting results (72). A residual lignin isolated from a conventional kraft pulp (by acid hydrolysis) was treated with various charges of ClO_2 in a homogeneous solution. The reactivity of ClO_2 toward specific functional groups in the lignin was also measured by monitoring the changes in guaiacyl and condensed phenolic hydroxyl groups and carboxylic acid groups by quantitative ^{31}P-NMR. The guaiacyl phenolic hydroxyl groups were rapidly eliminated upon the treatment with ClO_2, demonstrating the reactivity of such structures toward ClO_2. The elimination of such groups leveled off at higher charges of ClO_2 (>1.6 mole %), which was interpreted as the possible formation of phenolic groups by the scission of aryl ether linkages by elemental chlorine.

The same effect on condensed phenolic groups was observed; initially there was a rapid decrease in the content of these structures and then a leveling off. The leveling off in this case was interpreted as such functional groups being unreactive toward ClO_2 and as the possible formation of condensed phenolic groups by radical coupling reactions. The formation of carboxylic acids was found to be quite prevalent, as the content of such groups increased dramatically in the lignin after their reaction with ClO_2. The reason for this increase was suggested to be due to the formation of muconic acid derivatives. Demethylation (as determined by the methoxyl analysis) of the lignins appeared to occur concurrently with the formation of carboxylic acids, which the authors interpreted as a relationship between ring-opening reactions and demethoxylation.

A recent study by Ni et al. has found evidence to suggest that phenolic groups are created during ClO_2 bleaching (66). A softwood kraft pulp was bleached with various charges of ClO_2 in the presence and absence of sulfamic acid, a scavenger of hypochlorous acid. The content of phenolic groups in the pulp was monitored. The number of phenolic groups was consistently higher in the pulps bleached in the absence of sulfamic acid, suggesting that when hypochlorous acid is allowed to form, additional phenolic groups are created. The creation of phenolic groups was interpreted as being a result of the cleavage of aryl ether linkages in the residual lignin.

All of these studies on the characterization of residual and dissolved lignins from a ClO_2 stage support the model compound studies. The ability of these studies to actually quantify the changes to the lignin structure occurring during ClO_2 bleaching provides a more informative analysis of the actual chemistry governing the reactions during ClO_2 bleaching.

NMR TECHNIQUES USED TO CHARACTERIZE LIGNINS

^{13}C-NMR and ^{1}H-NMR techniques are very valuable for elucidating the structural features of lignin. Additionally, a new technique using ^{31}P-NMR has also been demonstrated to quantitatively detect important hydroxyl-containing functional groups present in lignin. The following will be a review of the literature on using these techniques to characterize lignin.

Quantitative ^{13}C-NMR

^{13}C-NMR spectroscopy is a technique that is especially useful for the characterization of lignin (7,11,41,48-50,76-78). Due to the heterogeneous nature of the lignin, no other analytical technique is capable of providing as much structural information from one experiment. Quantitative information about specific functional groups and structures present in the lignins can be made by employing this technique, although the recording of the spectra can be time-consuming. Using lignin degradation techniques to characterize lignin structure is only semi-quantitative and sometimes does not result in an analysis of the entire lignin polymer. Quantitative ^{13}C-NMR therefore has the added benefit of being completely unbiased because it has the ability to analyze the structure completely, which makes the technique a most effective way to characterize residual and dissolved lignins.

A quantitative ^{13}C-NMR spectrum of spruce milled wood lignin (MWL) is shown in Figure 23. The signals arising from the various functional group carbon atoms in this spectra have been labeled, and the chemical shift assignments for the signals are given in

Table 4. The chemical shift assignments have been made based on numerous model compound studies (41,76,77). Carbonyl groups in aldehyde and carboxylic acid groups have chemical shifts in the region from δ 200-160 ppm; aromatic and olefinic carbons have chemical shifts in the region from δ 160-100 ppm; and aliphatic side chain carbons are found in the region from δ 20-90 ppm. When the ^{13}C-NMR spectra are recorded under quantitative conditions, the size of the peaks can be correlated to the amount of these specific carbon atoms present in lignin. Integrating the peaks therefore yields quantitative information about the quantity of the various structures. For this particular MWL sample, integration of the aromatic and olefinic region corresponds to 6.12 carbon atoms per aromatic ring because there are 3 coniferyl aldehyde and 3 coniferyl alcohol groups per 100 C_9-units, as determined from a separate analysis. The integrals and number of carbon atoms per aromatic ring for various regions of the spectrum are shown in Table 5. The NMR analysis shows that this sample contains 0.98 methoxyl groups per aromatic ring. An elemental analysis of this lignin sample found that there are 0.94 methoxyl groups per aromatic ring, demonstrating that this NMR analysis is quite an accurate technique to quantify various types of carbon atoms (49). Note that the limit of error allowed for the ^{13}C-NMR estimation is ± 5%.

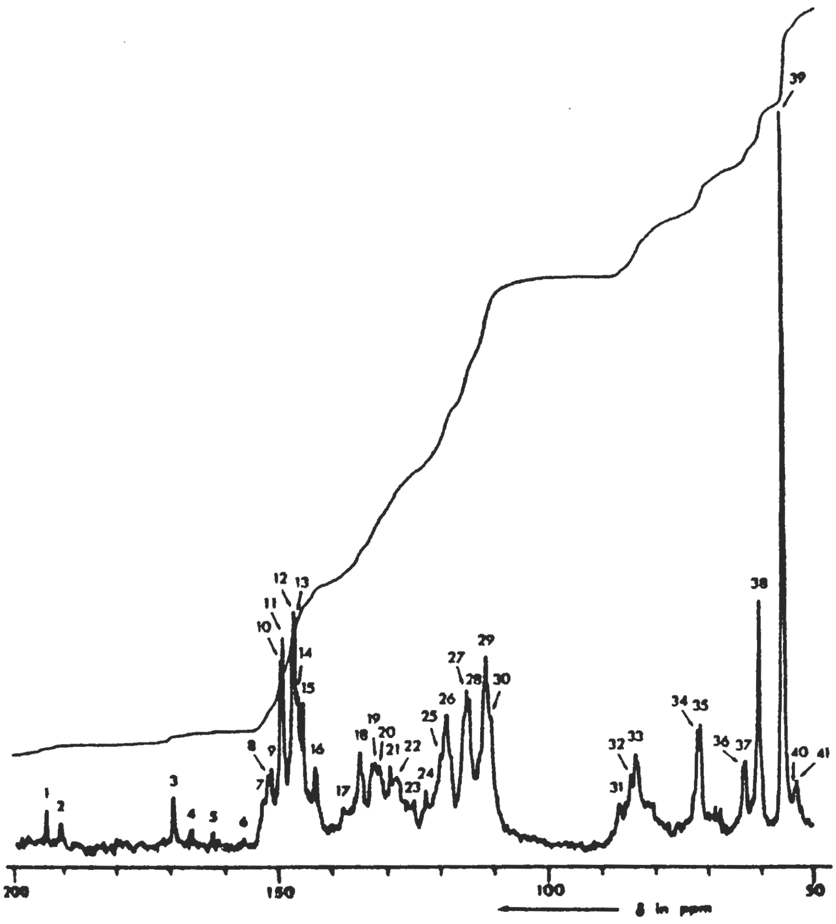


Figure 23. Quantitative [13]C-NMR spectrum of milled wood lignin (MWL) from spruce (*Picea glauca*) by Inverse Gated Decoupling (IGD) pulse sequence. Solvent: DMSO-d_6. Reprinted from reference (<u>49</u>) page 435 by courtesy of Marcel Dekker, Inc.

Table 4. ^{13}C-NMR chemical shifts and signal assignments for spruce milled wood lignin (MWL). solvent: DMSO-d_6 (49).

Signal Number	Chemical Shift (δ in ppm)	Assignment
1	193.4	C=O in Ar-CH=CH-CHO
		C=O in Ar-CO-CH(-OAr)-C-
2	191.6	C=O in Ar-CHO
3	169.4	Ester C=O in R'-O-CO-CH_3
4	166.2	C=O in Ar-COOH
		Ester C=O in Ar-CO-OR
5	162.2	Unknown
6	156.4	C-4 in H-units
7	152.9	C-3/C-3' in etherified 5-5 units
		C-α in Ar-CH=CH-CHO units
8	152.1	C-3/C-5 in etherified S units and B ring of 4-O-5 units
9	151.3	C-4 in etherified G units with α-C=O
10	149.4	C-3 in etherified G units
11	149.1	C-3 in etherified G type β-O-4 units
12	146.8	C-4 in etherified G units
13	146.6	C-3 in non-etherified G units (β-O-4 type)
14	145.8	C-4 in non-etherified G units
15	145.0	C-4/C-4' of etherified 5-5 units
16	143.3	C-4 in ring B of β-5 units
		C-4/C-4' of non-etherified 5-5 units
17	138.0	unknown
18	134.6	C-1 in etherified G units
19	132.4	C-5/C-5' in etherified 5-5 units
20	131.1	C-1 in non-etherified 5-5 units
21	129.3	C-β in Ar-CH=CH-CHO
22	128.0	C-α and C-β in Ar-CH=CH-CH_2OH
23	125.9	C-5/C-5' in non-etherified 5-5 units
24	122.6	C-1 and C-6 in Ar-CO-C-C units
25	119.9	C-6 in G units
26	118.4	C-6 in G units
27	115.1	C-5 in G units
28	114.7	C-5 in G units
29	111.1	C-2 in G units
30	110.4	C-2 in G units
31	86.6	C-α in G-type β-5 units
32	84.6	C-β in G-type β-O-4 units (threo)
33	83.8	C-β in G-type β-O-4 units (erythro)
34	71.8	C-α in G-type β-O-4 units (erythro)
35	71.2	C-α in G-type β-O-4 units (threo)
		C-γ in G-type β-β
36	63.2	C-γ in G-type β-O-4 units w/ a-C=O
37	62.8	C-γ in G-type β-5, β-1 units
38	60.2	C-γ in G-type β-O-4 units
39	55.6	C in Ar-OCH_3
40	53.9	C-β in β-β units
41	53.4	C-β in β-5 units
	40-15	CH_3 and CH_2 in saturated aliphatic chain

Table 5. Number of carbons in chemical shift range of the ^{13}C-NMR spectrum of spruce milled wood lignin (MWL) (49).

Chemical shift range (δ in ppm)	Integral[a]	Number of carbons per aromatic ring[b]
197-193	1.1	0.06
192-191	0.7	0.04
158-154	0.8	0.04
154-150	6.4	0.34
150-145	26.0	1.37
145-140	5.8	0.31
140-124	28.4	1.50
124-103	48.6	2.56
90-57	44.0	2.32
57-54	18.6	0.98
54-52	3.2	0.18

[a]Total integral for chemical shift range 160-100 ppm = 116. Thus, the integral for one aromatic carbon = 116/6.12 = 18.95, assuming that spruce MWL contains 3 Ar-CH=CH-CHO units and 3 Ar-CH=CH-CH_2OH units per 100 C9 units.
[b]See Table 4 for assignments.

^{1}H-NMR

Ludwig made the first attempts to characterize lignin using ^{1}H-NMR spectroscopy in 1964 (79,80). Since then, numerous other studies, mainly by Lundquist, have been devoted to characterizing lignin by using this technique with more powerful instruments yielding more refined data (81-88). These studies have led to an extensive database of ^{1}H-NMR chemical shift values for lignin functional groups. This information can be employed to analyze structural changes in lignin.

Although the proton chemical shift data of underivatized lignin are informative, as will be discussed later, acetylated lignin samples provide improved spectral resolution of key lignin functionality. Figure 24 is a ^{1}H-NMR spectrum of acetylated spruce milled wood lignin recorded with a 270-MHz instrument. Table 6 lists the structural assignments for the chemical shifts in this spectrum, which are based on extensive model compound studies. The small, broad peak at $\delta \sim 6.0$ ppm can be principally assigned to arylglycerol units with a β-aryl ether substituent; however, β-1 structures and arylglycerol units also have been shown to contribute to this peak (85). Additional types of β-aryl ether structures (e.g., derivatized arylglycerol β-aryl ethers with an ether group at the α position) do not contribute to the peak at $\delta \sim 6$ ppm. It is possible, however, to make semiquantitative estimates of the percentage of β-aryl ether linkages in the lignin by integrating this peak (85). The signals at δ 2.3 and 2.0 ppm are assigned to the phenolic and aliphatic acetate groups, respectively. However, it has been shown that phenolic acetate signals from biphenyl structures have a chemical shift at δ 2.08-2.11 ppm. Quantifying phenolic hydroxyl groups using this technique must be performed with the realization that some free phenolic groups are contributing to the aliphatic acetate signal, which will result in a slight underestimate of the total phenolic content and an overestimate of the aliphatic hydroxyl content (85). Other protons in lignins have chemical shifts in the δ 2.3-2.0 ppm range, which would also cause some minor errors in the quantitative analysis of hydroxyl groups.

More recently it has been demonstrated that ^{1}H-NMR spectroscopy of underivatized lignins offers another valuable way to analyze and quantify phenolic hydroxyl groups in lignins (88). Lundquist performed an extensive study on the use of

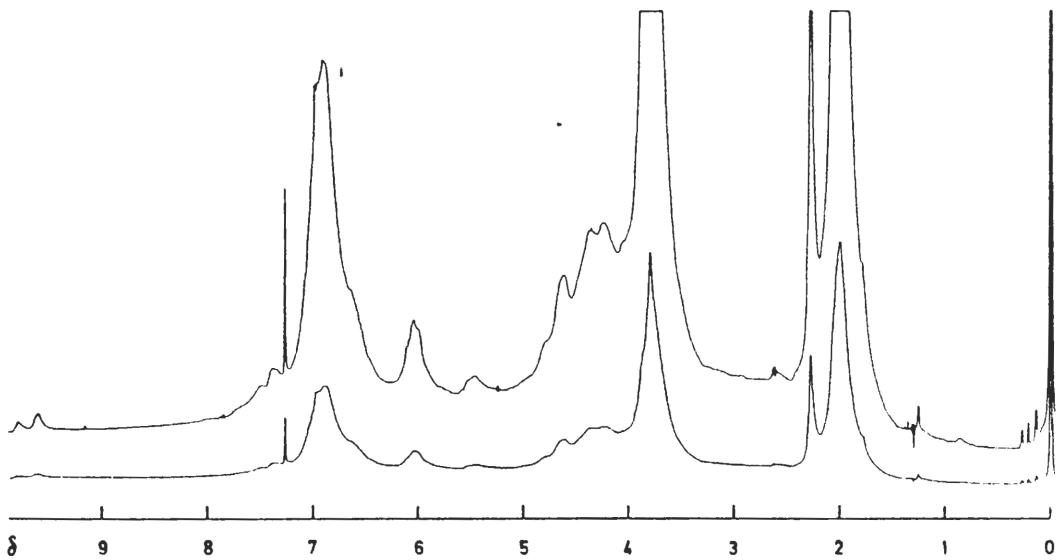


Figure 24. [1]H-NMR (270 MHz) spectrum of acetylated milled wood lignin from spruce. Reprinted from reference (87) with permission from Springer-Verlag.

Table 6. Assignments of signals in the [1]H-NMR spectrum of acetylated spruce lignin shown in Figure 24 (87).

δ ppm	Assignment
1.26	Hydrocarbon contaminant
2.01	Aliphatic acetate
2.28	Aromatic acetate
2.62	Benzylic protons in β-β structures
3.81	Protons in methoxyl groups
4.27	Hγ in several structures
4.39	Hγ in, primarily, β-O-4 structures and β-5 structures
4.65	Hβ in β-O-4 structures
~4.80	Inflection possibly due to Hα in pinoresinol units and Hβ in noncyclic benzyl aryl ethers
5.49	Hα in β-5 structures
6.06	Hα in β-O-4 structures (Hα in β-1 structures)
6.93	Aromatic protons (certain vinyl protons)
7.29	Chloroform (solvent)
7.41	Aromatic protons in benzaldehyde units and vinyl protons on the carbon atoms adjacent to aromatic rings in cinnamaldehyde units
7.53	Aromatic protons in benzaldehyde units
9.64	Formyl protons in cinnamaldehyde units
9.84	Formyl protons in benzaldehyde units

^{1}H-NMR spectroscopy to analyze phenolic groups in underivatized lignin samples, i.e., non-acetylated lignins (88). Model compounds were used to make signal assignments for the various types of phenolic groups present in lignins. Figure 25 is the spectral range from δ 8.0-10.5 ppm of milled wood lignin from spruce. The spectrum contains several resolved signals arising from protons on specific lignin structures. The peaks in the range of δ 9.4-10.0 ppm are mainly due to formyl groups, yet some phenolic hydroxyl groups may also be present in this region. Model compound studies found that phenolic groups with carbonyl groups conjugated with the aromatic ring had signals in this region. The more predominant phenolic groups, i.e., not conjugated with carbonyl groups, can be found in the δ 8.0-9.4 ppm range. The model compound study showed that the large signals at δ 8.99 and 8.76 ppm belong to phenolic groups in β-5 and arylgylcerol β-O-4 structures, respectively. Such structures are known to be predominant in wood lignin. Another region of interest is from δ 8.5-8.0 ppm in which C5 substituted or 'condensed'-type phenolic hydroxyl groups can be found, such as biphenyl structures.

The analysis of underivatized lignins also allows for the quantification of carboxylic acid groups, which have a well-separated signal at approximately δ 12 ppm. Integrating this signal has been found to yield valuable data on the quantity of carboxylic acid groups in lignins, as will be demonstrated in this dissertation. Employing this technique to quantify the carboxylic acid content of oxidized lignins (i.e., bleached lignins) is particularly useful because such lignins are not amenable for analysis by the ^{31}P-NMR technique, which requires that the lignin be derivatized. Phosphitylating (and acetylating) lignin with high carboxylic acid contents seems to be difficult, making the analysis of lignins with high contents of these functional groups impractical.

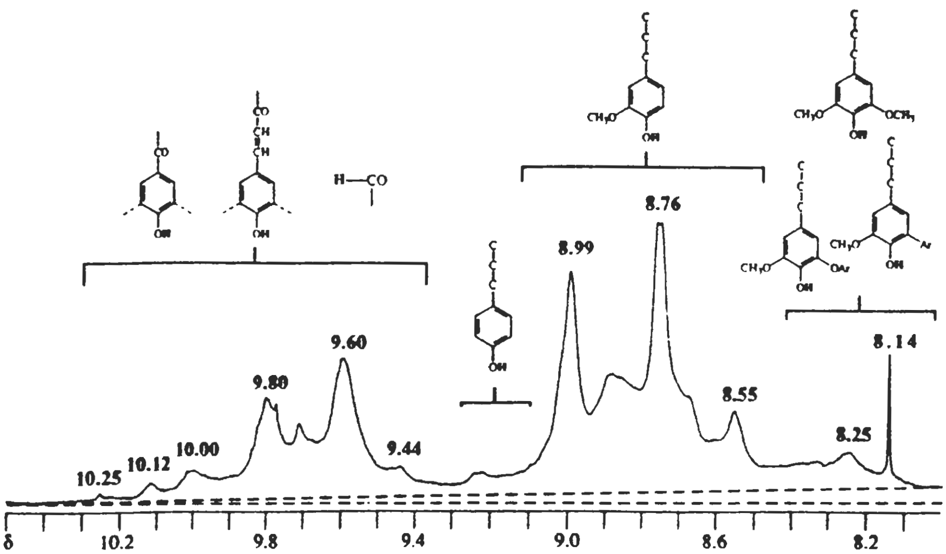


Figure 25. The spectral range δ 8.0-10.5 (400 MHz, solvent DMSO-d_6) of MWL from spruce. The assignments of the peaks are indicated in the figure (the peak at δ8.14 is due to an unidentified contaminant) (88).

^{31}P-NMR

The application of ^{31}P-NMR has been shown to be a very effective method of characterizing lignin. Initial studies performed by Lebo et al. have demonstrated the applicability of this technique to detect o-quinones in mechanical pulp (89). These studies have been further developed by Argyropoulos to determine quantitatively the amount of hydroxyl groups present in lignin (36,37,72,90,91). Aliphatic and phenolic (both guaiacyl and C5 substituted) hydroxyl groups, as well as carboxylic acids groups, can be quantitatively determined. The technique is straightforward and readily accomplished in the laboratory. Treating lignin with 2-chloro-4,4,5,5 tetramethyl-1,3,2-dioxaphospholane causes labile hydroxyl protons to be phosphoylated according to the reaction outlined in Figure 26.

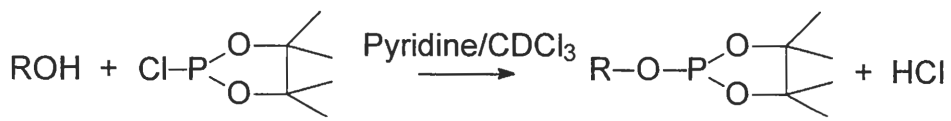


Figure 26. The reaction of labile protons present in lignins with 2-chloro-4,4,5,5 tetramethyl-1,3,2-dioxaphospholane (37).

The ^{31}P-NMR spectrum of this derivatized sample is then recorded with an internal standard, cyclohexanol. The spectrum contains well-separated peaks corresponding to the various types of hydroxyl groups present in the lignin. The fact that these peaks are well-separated is very important because this makes it possible to distinguish between the regions containing the various types of hydroxyl groups, allowing for their accurate integration. This is somewhat of a problem for the ^{1}H-NMR analysis of lignin acetates because the aliphatic and aromatic acetate peaks overlap and some structures have their aromatic acetate signal in the aliphatic acetate region. These are not of concern in the ^{31}P-NMR technique. Figure 27, which is a ^{31}P-NMR spectrum of kraft lignin derivatized with 2-chloro-4,4,5,5 tetramethyl-1,3,2-dioxaphospholane, illustrates that the signals arising from the various hydroxyl groups are indeed well-separated.

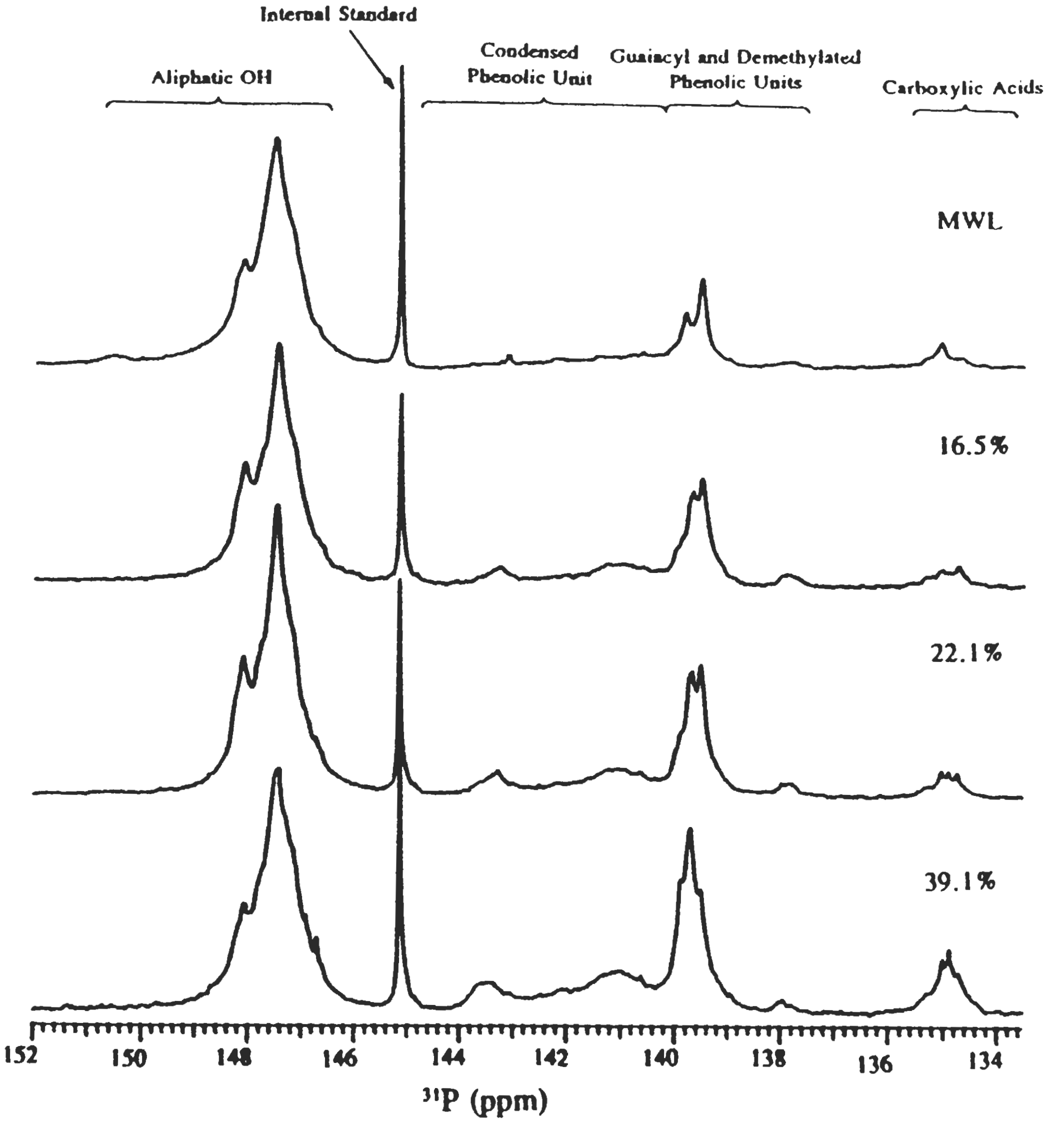


Figure 27. Quantitative ^{31}P-NMR spectra and signal assignment of a milled wood lignin obtained from black spruce and the three kraft lignins at various degrees of delignification. Reprinted with permission from (37), Copyright 1995, American Chemical Society.

THESIS OBJECTIVES AND EXPERIMENTAL APPROACH

THESIS OBJECTIVES

The overall objective of this research is to improve the fundamental chemical understanding of delignification during kraft pulping and chlorine dioxide bleaching by structurally characterizing residual and dissolved lignins produced during these two processes. Characterizing the changes in the lignin structure during these processes can provide valuable information about this chemistry. The structural characterization of lignins can be accomplished by using quantitative and qualitative NMR spectroscopic methods.

The following objectives were sought to provide new insights into the chemistry of kraft delignification and ClO_2 bleaching:

- Define the structural differences between high and low kappa residual lignins in both conventional and 'modified' kraft pulps produced at similar levels of delignification ranging from 30 to 13 kappa number.

- Define the structural features of kraft lignins isolated at various times during the cook and determine the structural differences between kraft lignin dissolved during conventional and modified kraft pulping with an emphasis on the kraft lignins found at the end of the cook in the 30 to 13 kappa number range.

- Define a relationship between unbleached residual lignin structure and reactivity toward chlorine dioxide to pulp bleachability in a D(EO) delignification sequence.

- Provide further insight into the chemistry of chlorine dioxide bleaching by structurally characterizing the residual and dissolved lignins produced from kraft pulps bleached with various charges of chlorine dioxide followed by an alkaline extraction, with and without oxygen reinforcement.

EXPERIMENTAL APPROACH

Kraft pulps were manufactured from a uniform chip source consisting of a sole 30-year-old loblolly pine tree that was cut in North Georgia, USA. The kraft pulping experiments were performed at Kamyr's research and development laboratory in Glens Falls, NY. The pulps and black liquor samples were collected, and the residual and kraft lignins were isolated. The lignins were then structurally characterized by employing advanced NMR spectroscopic techniques.

Three conventional (CK) and three 'modified' (EK) kraft pulps were employed for this detailed analysis. The three conventional kraft pulps had kappa numbers of 28, 18, and 13 and are designated throughout this thesis as C28, C18, and C13, respectively. The three EMCC kraft pulps had kappa numbers of 29, 18, and 14 and are designated as E29, E18, and E14, respectively. Black liquor samples were collected at the end of each of these cooks and at earlier times during these cooks.

The residual lignins from the pulps were isolated by an acid hydrolysis procedure in which the pulps were refluxed for 1 hour in a 0.05N HCl solution of 9:1 dioxane:water. The extract was collected and the residual lignin isolated as a precipitate after the dioxane was evaporated.

The kraft lignins were isolated from the black liquors by acidifying the black liquor to a pH of 3.0 with 2 M H_2SO_4 and collecting the precipitate. The precipitate was washed repeatedly with water and then dissolved in 9:1 dioxane:water. The solubilized material was collected by lyophilizing the filtered solution. As a final purification step, the lignin was extracted with pentane in a soxhlet extractor.

The isolated residual and kraft lignins were then structurally characterized by employing quantitative NMR spectroscopic techniques, including ^{13}C-NMR, ^{31}P-NMR, and ^{1}H-NMR analyses. These analyses allow for the quantification of various functional groups in lignin as described in the literature review.

The bleaching portion of this research was concerned with examining the delignification chemistry during a chlorine dioxide followed by an alkaline extraction delignification sequence. The kraft pulps produced during the pulping study were ideal to use because the residual lignins in these pulps had been well-characterized. The various pulps were bleached in a D(EO) delignification sequence, and the bleachability (or efficiency of delignification) was measured as the consumption of ClO_2 per unit kappa number drop. The bleachability was then related to the unbleached residual lignin structure. The isolated residual lignins were also reacted with ClO_2, and the changes in functional groups were measured. This analysis was also used for defining a relationship between residual lignin structure and pulp bleachability.

Residual and dissolved lignins produced during the ClO_2 stage and the alkaline extraction stage (with and without oxygen reinforcement) were also isolated and structurally characterized by the NMR techniques. The residual lignins were isolated from the ClO_2-bleached and alkaline-extracted pulps by the same acid hydrolysis technique as was used for the unbleached residual lignins. The dissolved lignins from the extraction stage effluents were collected by first concentrating the effluent, acidifying to a pH of 2.5, and collecting the lignin precipitate. The precipitate was washed repeatedly with water and dissolved in 9:1 dioxane:water. The solubilized lignin was collected by lyophilizing this solution after filtering. The freeze-dried lignin was then used for the NMR analysis.

Various NMR analyses were used to characterize the structure of these lignins. These analyses allowed for such structural features as aliphatic hydroxyl groups, phenolic hydroxyl groups (both guaiacyl and C5 substituted), carboxylic acid groups, β-O-4 structures, methoxyl groups, and condensed structures to be quantified. Changes in the contents of these structures in the residual and dissolved lignins during kraft pulping and ClO_2 bleaching were then used to interpret the chemistry of these processes.

MATERIALS AND METHODS

CHEMICALS

All chemicals used in this research were purchased from Aldrich, JT Baker, Isotec, and EM Science. Except for the dioxane, which was purified by distilling in the presence of $NaBH_4$ prior to use, all chemicals were used without further purification. Acetylation and phosphitlation were performed with anhydrous solvents and reagents. All NMR solvents were anhydrous and purchased from either Isotec or Aldrich. Filtered Nanopure deionized (DI) water was used in all instances when water was required. Chlorine dioxide was prepared by reducing $NaClO_3$ by acidification in the presence of oxalic acid. The chlorine dioxide solution was prepared, so elemental chlorine was not present.

WOOD SOURCE AND CHIP PROCESSING

The chips used for the pulping experiments were obtained from a loblolly pine (*Pinus taeda*) tree that was cut in North Georgia, USA. The tree was cut into four-foot logs that were debarked and spilt in two. The split logs were then chipped in IPST's chipper. The chips produced from all the logs were then mixed thoroughly and carefully screened. The chips were screened by first collecting the fraction that passed through a 6-mm bar screen. The accepts were then screened on a ¼″ mesh screen to remove all the small debris. The total wet weight of the chips was 195 kg (93 kg dry). The chips were then frozen at 0°C and stored until needed.

PULPING AND BLEACHING

Kraft Pulping

Chips were sent to the pulping facilities of Ahlstrom Machinery in Glens Falls, NY, where the simulated EMCC® (EK) and conventional kraft (CK) pulping experiments were performed. Conventional pulping was performed by charging all the white liquor at the beginning of the cook. Simulated EK pulping was performed following literature-established procedures involving various additions of white liquor (3). EK pulping was started by adding white liquor and impregnating the chips for 30 minutes at 110°C and ~1000 kPa. The co-current cooking stage began after this impregnation stage by adding another charge of white liquor and raising the temperature to the maximum cooking temperature. Counter-current cooking was simulated by adding weak white liquor while simultaneously extracting black liquor at a flow rate that maintained a desired profile of alkali and dissolved lignin concentration.

A series of EK and CK pulps were produced with various kappa numbers ranging from 33 to 13. Table 7 highlights some of the conditions used for the pulping experiments and some of the final properties of the pulps. The pulps have been assigned an ID, which is designated by the first letter of the cook type followed by the kappa number.

During the cook, black liquor samples were extracted at various times. A sample was collected at the end of each cook that will be referred to as the end of cook (eoc) kraft lignins. Additionally, black liquor samples were extracted after the impregnation stage of the C18 and E14 cook. These lignins will be referred to as after impregnation (ai) kraft lignins. One additional black liquor sample was collected after the co-current stage of the E14 cook. This lignin will be referred to as the after co-current (eo1) kraft lignin.

Table 7. Relevant pulping conditions and pulp properties from the conventional and EMCC kraft pulps.

	CK pulps				EK pulps		
Pulp ID	**C33**	**C28**	**C18**	**C13**	**E29**	**E18**	**E14**
WL sulfidity, %AA	27.4	27.4	27.4	27.4	27.4	27.4	27.4
Initial EA, % NaOH	19.7	19.7	19.7	22.0	12.0	12.0	12.0
Co-Current EA, %	-	-	-	-	5.0	5.0	5.0
Counter-current EA, %	-	-	-	-	4.4	4.2	5.0
L/W ratio	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Max. Temp, °C	170	170	170	170	158	161	169
H-factor	1600	1715	2601	4238	1651	2229	4238
Kappa Number	33.0	28.0	18.5	13.0	29.1	18.5	14.5
Viscosity, mPa.s	35.6	33.6	17.5	10.9	51.8	35.4	18.1
V/K ratio	1.08	1.20	0.95	0.84	1.78	1.91	1.25
Screened Yield, %	46.7	45.9	42.8	41.0	45.6	43.8	40.9

Upon receiving the pulps and black liquors from Ahlstrom Machinery, they were placed in a cold room at 10°C until needed.

ASAQ Pulping

An alkaline sulfite anthraquinone (ASAQ) pulp was also prepared so that comparisons could be made with the kraft pulp residual lignin. The pulping conditions used can be found in Table 8.

Table 8. Pulping conditions used for the manufacture of the ASAQ pulp.

Pulp ID	A26
Cooking schedule	preheat chips to 100°C 90 min rise to 173°C hold at 173°C for 3 hours
L/W ratio	4.0
NaOH charge	9.6% as Na_2O
Na_2SO_3 charge	14.4% as Na_2O
AQ charge	0.1 %
H-factor	3800
Kappa number	25.6

ClO_2 Bleaching

The kraft pulps were bleached with chlorine dioxide (D stage) followed by an alkaline extraction with and without oxygen reinforcement (EO and E stages, respectively). The chlorine dioxide stages were all performed in a Quantum Technologies mixer. A variety of ClO_2 charges were employed. For the bleachability study, a kappa factor (KF, defined as total active chlorine charge/kappa number) of 0.20 was used, but for the residual and dissolved lignins study, kappa factors of 0.05 and 0.10 were also used. The pulps bleached for the residual and dissolved lignins study were first extracted with acetone to remove any residual extractives that could contaminate the isolated lignins. The pulps, at 10% consistency and ~5 pH, were preheated to 45°C in the mixer, and an aqueous solution of ClO_2 was added to the pulp, the amount of which depended on the kappa factor of the particular experiment being performed. The pulps were mixed every 5 minutes for 30 minutes and then removed from the mixer. They were then washed following a standardized procedure that began by filtering the pulp on a buchner funnel under a water aspirator until all the effluent that could be removed was removed. Then the pulps were washed with DI water twice (15L of water for every 200 o.d. grams of pulp) and filtered, resulting in a fully washed ClO_2-bleached pulp. For the bleachability study, this pulp was immediately extracted with alkali. For the residual and dissolved lignins study, the pulp was split and one portion extracted with alkali and the other portion saved for residual lignin isolation.

The alkaline extraction was performed in a peg mixer. The peg mixer was preheated to 70°C and the washed pulp added. Sodium hydroxide was added at a charge corresponding to 50% of the total active chlorine (TAC) charge in the preceding ClO_2 stage. The cover of the mixer was sealed, the mixer turned on, and for the alkaline extraction stages, reinforced with oxygen, oxygen pressure was applied at an initial pressure of 60 psig. In order to simulate a pre-retention tube in a commercial EO stage, the oxygen pressure was decreased 12 psi every 5 minutes. After 60 minutes at 70°C, the pulp was removed from the mixer and a portion of the effluent collected so that a final pH could be measured. The bulk of the effluent was collected by filtering the pulp on a Buchner funnel. The effluent was saved for the isolation of the dissolved lignin. The pulp was then thoroughly washed with DI water and the kappa number measured. For the residual and dissolved lignins study, the residual lignin from this pulp was isolated. Appendix I contains the results from all the bleaching experiments.

Table 9 is a list of all the bleaching experiments that were performed. Included in the table are the charges of ClO_2 used in the D stage, whether or not the extraction stage was reinforced with oxygen, and identifications of the pulps both before and after each bleaching stage.

Table 9. A description of all the bleaching experiments performed along with the pulp ID's that will be used throughout this dissertation.

Unbleached pulp ID	**ClO_2 Stage**		**Extraction Stage**	
	Kappa factor	ID	Oxygen reinforcement	ID
C28	0.05	C28 D (0.05)	no	C28 DE (0.05)
	0.20	C28 D (0.20)	no	C28 DE (0.20)
			yes	C28 D(EO) (0.20)
C18	0.20	C18 D (0.20)	yes	C18 D(EO) (0.20)
E29	0.10	E29 D (0.10)	no	E29 DE (0.10)
			yes	E29 D(EO) (0.10)
	0.20	E29 D (0.20)	yes	E29 D(EO) (0.20)
E18	0.20	E18 D (0.20)	yes	E18 D(EO) (0.20)
E14	0.20	E14 D (0.20)	yes	E14 D(EO) (0.20)

RESIDUAL LIGNIN ISOLATION

Unbleached Pulps

The residual lignins from the kraft and the ASAQ pulps were isolated by employing an acid hydrolysis technique that has been commonly used to isolate lignin from wood and kraft pulps (23,36,92,93). The procedure was optimized here by using a lower concentration of acid and a shorter refluxing period, as is discussed in greater detail in Appendix II.

The pulps were extracted with acetone for 24 hours in a Soxhlet extractor, washed thoroughly with deionized water, and air dried prior to isolating the residual lignin. The air-dried pulp was placed in a 5-L three neck round-bottom flask. A solution of 0.05 N HCl 9:1 dioxane:water was added to the pulp, making the consistency 4%. The flask was sealed, purged with argon, and heated to the solution's reflux temperature. The mixture was then refluxed for 1 hour with a continuous purge of argon.

After refluxing, the slurry was allowed to cool and then filtered on a Bukner funnel. The filtrate was neutralized with sodium bicarbonate to a pH of ~6 and then filtered through celite on a medium sintered glass funnel. The celite was washed with water to collect any water-soluble material remaining on the celite. The solution was then rotary evaporated under vacuum at 45°C until only residual water remained. The solution was acidified to a pH of 2.5 with 1.0 N HCl (which precipitates the lignin) and frozen at -20°C. The solution was thawed, centrifuged, washed with water, acidified to a pH of 2.5, and frozen again. The washing step was repeated twice more and the precipitate collected by freeze drying from a water suspension and analyzed by the NMR techniques as discussed in Chapter 1 of the Results and Discussion section. Table 10 is a list of all the unbleached pulps and residual lignins used in these experiments. Residual lignin E29 r.l.' was a replicated isolation from the E29 pulp and was used throughout the dissertation for reproducibility purposes.

Table 10. A list of the residual lignins isolated from unbleached pulps and their corresponding residual lignin ID's.

Pulp ID	Residual lignin ID
C33	C33 r.l.
C28	C28 r.l.
C18	C18 r.l.
C13	C13 r.l.
E29	E29 r.l.
E29	E29 r.l.'
E18	E18 r.l.
E14	E14 r.l.
A26	A26 r.l.

ClO_2-Bleached and Alkaline-Extracted Pulps

A somewhat modified acid hydrolysis technique was used to isolate the residual lignins from the ClO_2-bleached and alkaline-extracted pulps. The acid concentration was kept the same at 0.05 N HCl, but the refluxing time was increased to 2 hours, the dioxane:water ratio decreased to 6.5:1, and the consistency decreased to 3.5%. A longer time was used because the bleached pulps contained less lignin and increasing the time improves the isolation yield. The lower ratio of dioxane:water and lower consistency were used because the pulps were not dried after bleaching and therefore contained a significant amount of water, causing the water concentration to be high.

Table 11 is a list of all the residual lignins that were isolated from the ClO_2-bleached and alkaline-extracted pulps. The results from the NMR analysis of these lignins are discussed in Chapter 4 of the Results and Discussion section.

Table 11. A list of the bleached residual lignins that were isolated from the ClO_2-bleached and alkaline-extracted pulps.

	Pulp ID	Residual lignin ID
D	C28 D (0.05)	C28 D r.l. (0.05)
	C28 D (0.20)	C28 D r.l. (0.20)
s	C18 D (0.20)	C18 D r.l. (0.20)
t	E29 D (0.10)	E29 D r.l.(0.10)
a	E29 D (0.20)	E29 D r.l.(0.20)
g	E18 D (0.20)	E18 D r.l.(0.20)
e	E14 D (0.20)	E14 D r.l.(0.20)
E	C28 DE (0.05)	C28 DE r.l. (0.05)
	C28 DE (0.20)	C28 DE r.l.(0.20)
s	C28 D(EO) (0.20)	C28 D(EO) r.l.(0.20)
t	C18 D(EO) (0.20)	C18 D(EO) r.l.(0.20)
a	E29 DE (0.10)	E29 DE r.l.(0.10)
g	E29 D(EO) (0.10)	E29 D(EO) r.l.(0.10)
e	E29 D(EO) (0.20)	E29 D(EO) r.l.(0.20)
	E18 D(EO) (0.20)	E18 D(EO) r.l.(0.20)
	E14 D(EO) (0.20)	E14 D(EO) r.l.(0.20)

Comments on the Isolation of Residual Lignin

The strong acidic conditions used during the isolation of residual lignin were of concern because structural modifications to the lignin during isolation are unwanted. The technique is, however, quite useful because the procedure is quick and the product is free of carbohydrates. Under the acidic conditions, it can be expected that any residual α-aryl and/or α-alkyl ether linkages could be cleaved. In addition, residual β-O-4 structures with benzyl alcohol groups could also be cleaved. The content of such linkages in the residual lignin of kraft pulp, however, should be quite low because these structures are sensitive to kraft pulping conditions, as discussed in the Literature Review. Compared to other studies employing this technique, the milder conditions used in this research can be expected to result in less modifications to the residual lignin during isolation (see Appendix II). Condensation reactions may also be expected to occur under the acid conditions; however, such reactions were suggested not to be of great significance during the isolation of residual lignin by the acid hydrolysis technique (93).

DISSOLVED LIGNIN ISOLATION

Kraft Lignins

The black liquors extracted at the end of each cook and at other times during the cooks were isolated by precipitating the lignin from solution by acidification. The black liquors were first filtered through a Whatman #4 filter paper on a Bukner funnel. Approximately 0.5 gram of EDTA-2Na^{+} was added for every 100 ml of black liquor. The liquors were neutralized with 2 M H_2SO_4 until a pH of approximately 6.0 was reached. The solutions were then stirred vigorously for 1 hour. The liquors were further acidified to a pH of 3.0 and frozen at -20°C. After thawing the solutions, the precipitates were collected on a medium sintered glass funnel and washed twice with cold water by suspending the precipitates in the water and stirring vigorously at 0°C. The precipitates were collected, air dried, and extracted with pentane for 8 hours in a Soxhlet extractor to remove sulfur and other impurities.

The kraft lignin precipitates were further purified by suspending them in a 9:1 dioxane:water solution and stirring for 1 hour. The solutions were centrifuged and the supernatants collected. The precipitates were washed again with 9:1 dioxane:water and centrifuged. The supernatants were combined and filtered over celite on a medium sintered glass funnel. The dioxane was removed by rotary evaporation and the purified kraft lignins freeze dried. These purified kraft lignins were then used for the subsequent NMR analyses.

Table 12 is a list of the kraft lignins that have been isolated and their ID's. The results from the NMR analyses of these lignins are discussed in Chapter 2 of the Results and Discussion section.

Table 12. A list of the kraft lignins that were isolated and their corresponding ID's.

Pulp ID	Black liquor extraction point	Kraft lignin ID
E14	after impregnation	E14-ai
C18	after impregnation	C18-ai
E14	after co-current	E14-eo1
C28	end of cook	C28-eoc
C18	end of cook	C18-eoc
C13	end of cook	C13-eoc
E29	end of cook	E29-eoc
E18	end of cook	E18-eoc
E14	end of cook	E14-eoc

Extraction Stage Dissolved Lignins

The dissolved lignins from the alkaline extraction effluents were also isolated by precipitating the lignin from solution by acidification. Before the lignins could be precipitated, however, the effluents had to be concentrated. Failing to concentrate the dilute effluents yielded a minimal precipitate upon acidification to pH 2.0. The effluents were sometimes in excess of 4 liters, making the lignin solutions quite dilute. The effluents were filtered through celite on a medium sintered glass funnel and neutralized to a pH of 7.0 with 1.0 N HCl and concentrated on the rotary evaporator to a volume of approximately 50-100 ml. The concentrated effluents were then further acidified to a pH of 2.5 with 1.0 N HCl, which resulted in the formation of a thick, light brown precipitate. The combined solution and precipitate was frozen at -20°C. After thawing, the solutions were centrifuged, the supernatants discarded, and the precipitates washed with pH 2.5 DI water. The washing procedure was repeated two additional times, and after the third wash, the precipitates were suspended in DI water and freeze dried.

After freeze drying, the lignins were further purified by suspending them in a 9:1 dioxane:water solution and stirring for approximately 1 hour. The solubilized lignins were collected by centrifuging the solution and filtering the supernatant through a bed of celite on a medium sintered glass funnel. The dioxane was removed by rotary evaporation, and the purified extraction stage dissolved lignins were freeze dried. These lignins were then used for the subsequent NMR analyses.

Table 13 is a list of the alkaline extraction dissolved lignins that have been isolated. The results from the NMR analyses of these lignins are discussed in Chapter 4 of the Results and Discussion section.

REACTION PROCEDURES

Acetylation

Acetylation was performed on the residual and kraft lignins for ^{1}H-NMR analysis. The lignins (dried under vacuum at 40°C for 8-16 hours) were acetylated with acetic

Table 13. A list of the extraction stage dissolved lignins that were isolated and their corresponding ID's.

Alkaline extracted pulp ID	Alkaline extraction dissolved lignin ID
C28 DE (0.05) C28 DE (0.20) C28 D(EO) (0.20)	C28 DE d.l. (0.05) C28 DE d.l. (0.20) C28 D(EO) d.l. (0.20)
C18 D(EO) (0.20)	C18 D(EO) d.l. (0.20)
E29 DE (0.10) E29 D(EO) (0.10) E29 D(EO) (0.20)	E29 DE d.l. (0.10) E29 D(EO) d.l. (0.10) E29 D(EO) d.l. (0.20)
E18 D(EO) (0.20)	E18 D(EO) d.l. (0.20)
E14 D(EO) (0.20)	E14 D(EO) d.l. (0.20)

anhydride/pyridine (1/1, v/v) at room temperature for 24 hours in a 50-ml round-bottom flask. The concentration of the lignin in this solution was approximately 50 mg/ml. After 24 hours, the solution was diluted with ~30 ml of ethanol and stirred for an additional 30 minutes, after which the solvents were removed with a rotary evaporator. Repeated addition and removal of ethanol allowed for the removal of acetic acid and pyridine from the sample. The residue was then dissolved in chloroform, washed twice with filtered deionized water in a separatory funnel, and dried with anhydrous sodium sulfate. The chloroform solution (~10 ml) was added drop-wise to approximately 150 ml of anhydrous ether and the product collected as a precipitate. The precipitate was washed twice with ether, each time being collected by centrifugation. The precipitate was dried under high vacuum at 40°C for 24 hours.

Kraft Treatment of Lignins

Residual lignins C28 r.l and E14 r.l. and kraft lignin E14-ai were treated under kraft pulping conditions and analyzed by ^{31}P-NMR and ^{13}C-NMR. The lignins were dried and carefully weighed out into 4-cm^3 steel bombs. A predetermined amount of water, aqueous NaOH, and aqueous Na_2S were added and the reaction bomb sealed. The concentrations of alkali and sodium sulfide were equivalent to an effective alkali concentration of 20 g/l as NaOH and a sulfidity of 36%. The bombs were placed in a sand bath at 170°C and kept there for an extended period of time (either 15 or 120 minutes), as shown in Table 14. A replicate was performed for C28 r.l treated for 120 minutes.

After the reaction, the lignin solution was filtered through celite on a fine sintered glass funnel. The filtered solution was acidified to a pH of 2.0 with 1.0 N HCl. The precipitate was collected by centrifugation and washed five times with 15 ml of pH 2.0 water. The lignin was collected by freeze drying from a suspension of water. The results from the NMR analyses of these lignins are discussed in Chapters 1 and 2 of the Results and Discussion section.

Table 14. Lignins and reaction times used during the kraft pulping treatment of various lignins.

Lignin ID	Time at 170°C (min)	Kraft-treated lignin ID
C28 r.l.	15	C28 r.l.-15
	120	C28 r.l.-120
	120	C28 r.l.-120'
E14 r.l.	15	E14 r.l.-15
	120	E14 r.l.-120
E14-ai	120	E14-ai-120

ClO_2 Treatment of Residual Lignins

Various unbleached residual lignins were treated with chlorine dioxide and analyzed by ^{31}P-NMR, ^{1}H-NMR, and ^{13}C-NMR. For the ^{31}P-NMR and ^{1}H-NMR experiments, 80.0 mg of the dried residual lignin sample were dissolved into 25.0 ml of 9:1 dioxane:water (the dioxane was first distilled). A charge of chlorine dioxide was added equivalent to either a 0.05, 0.10, or 0.20 kappa factor (0.127 g ClO_2/g lignin, 0.253 g ClO_2/g lignin, or 0.507 g ClO_2/g lignin, respectively). The reaction was done at room temperature and the solution stirred every 5 minutes. After 30 minutes, a 1.0-ml aliquot of the solution was taken and the reaction terminated by adding a vacuum to the solution and bubbling argon through the system to remove any residual ClO_2. The solution was then lyophilized, dried under vacuum, and analyzed by NMR. Table 15 is a list of the lignins reacted with ClO_2 and the ID's of the reacted lignins. The results from the NMR analyses of these lignins are given and discussed in Chapters 3 and 4 in the Results and Discussion section.

The consumption of ClO_2 after these experiments was monitored by performing an iodimetric titration on the 1.0-ml aliquot of the solution. The results from this titration are presented in Table 16. This titration was not done on the 0.05 KF experiments because of the low residual ClO_2.

Table 15. A list of the residual lignins used for the ClO_2 reactivity experiments along with the charges of ClO_2 used (expressed as kappa factors) and the corresponding ID of the ClO_2-reacted residual lignins.

Residual lignin ID	Charge of ClO_2 (expressed as kappa factor)	ClO_2-treated residual lignin ID
C33 r.l.	0.05 0.20	C33 r.l.-0.05 C33 r.l.-0.20
C28 r.l.	0.05 0.10 0.20	C28 r.l.-0.05 C28 r.l.-0.10 C28 r.l.-0.20
C18 r.l.	0.05 0.10 0.20	C18 r.l.-0.05 C18 r.l.-0.10 C18 r.l.-0.20
C13 r.l.	0.05 0.10 0.20	C13 r.l.-0.05 C13 r.l.-0.10 C13 r.l.-0.20
E29 r.l.	0.05 0.10 0.20	E29 r.l.-0.05 E29 r.l.-0.10 E29 r.l.-0.20
E18 r.l.	0.05 0.10 0.20	E18 r.l.-0.05 E18 r.l.-0.10 E18 r.l.-0.20
E14 r.l.	0.05 0.10 0.20	E14 r.l.-0.05 E14 r.l.-0.10 E14 r.l.-0.20
A26 r.l.	0.05 0.10 0.20	A26 r.l.-0.05 A26 r.l.-0.10 A26 r.l.-0.20

For the ^{13}C-NMR analysis, two flasks containing 450 mg of dried C33 r.l. and 140.6 ml of dioxane:water (9:1) were treated with ClO_2 corresponding to kappa factors of 0.05 and 0.20. The lignins were isolated in a similar manner as above. The ID's used for these lignins were C33 r.l.-0.05 and C33 r.l.-0.20, respectively. The lignins were analyzed by ^{13}C-NMR, as discussed in Chapter 4 of the Results and Discussion section, and used in some alkaline extraction experiments that are described below and also discussed in Chapter 4 of the Results and Discussion section.

Table 16. Consumption of ClO_2 of various residual lignins upon the treatment of residual lignin with various charges of ClO_2.

Kappa Factor	Lignin ID	ml 0.001N Thio	ClO_2 applied (as g/l Cl_2)	Residual Cl_2 (as g/l Cl_2)	Consumed Cl_2 (as g/l Cl_2)
0.05	C28 r.l.	-	1.00	0.0	1.00
	C18 r.l.	-	1.00	0.0	1.00
	C13 r.l.	-	1.00	0.0	1.00
	E29 r.l.	-	1.00	0.0	1.00
	E18 r.l.	-	1.00	0.0	1.00
	E14 r.l.	-	1.00	0.0	1.00
	A26 r.l.	-	1.00	0.0	1.00
0.10	C28 r.l.	0.8	1.87	0.028	1.84
	C18 r.l.	0.75	1.87	0.027	1.84
	C13 r.l.	0.85	1.87	0.030	1.84
	E29 r.l.	0.70	1.87	0.025	1.85
	E18 r.l.	0.65	1.87	0.023	1.85
	E14 r.l.	0.4	1.87	0.014	1.86
	A26 r.l.	0.80	1.87	0.028	1.84
0.20	C28 r.l.	28.4	3.34	1.01	2.33
	C18 r.l.	24	3.34	0.85	2.49
	C13 r.l.	23.5	3.34	0.83	2.51
	E29 r.l.	31.5	3.34	1.12	2.22
	E18 r.l.	30.8	3.34	1.09	2.25
	E14 r.l.	22.5	3.34	0.80	2.54
	A26 r.l.	30	3.34	1.07	2.27

Alkaline Treatment of ClO_2-Bleached Residual Lignin

Residual lignin C28 D r.l. (0.20) was treated under alkaline extraction stage conditions with and without oxygen reinforcement and with the total exclusion of oxygen. The residual lignin was treated with a 160% charge of NaOH with and without an initial O_2 pressure of 60 psig. In the case of the lignin treated in the absence of oxygen, the oxygen was removed from the solution by freeze-thawing the solution under argon prior to the reaction and performing the reaction under argon. The charge of NaOH on lignin was equivalent to that frequently used in an alkaline extraction stage (i.e., 2.6% NaOH charge on pulp for a 28 kappa pulp bleached with a 0.20 KF of ClO_2). The concentration of lignin was 1.8 g/l, again a typical value for the dissolved lignin concentration in an alkaline extraction stage. The reaction with O_2 pressure was performed in a sealed bomb; the reaction in air was performed in the same bomb without being sealed, and the reaction in argon was done inside a three neck round-bottom flask. Each reaction was performed at 70°C for 60 minutes. For the reaction with O_2, an initial pressure of 60 psig was used and decreased 12 psi every 5 minutes. These were the same conditions used for the EO stages during the pulp bleaching experiments. The pH was monitored for the reactions done under O_2 pressure and under air and was found to remain constant at 12.1. A blank was performed in which the lignin was treated at 70°C for 60 minutes without NaOH. The pH of this reaction was acidic, approximately 5.0. Table 17 illustrates the conditions used for the four lignins analyzed during this experiment.

Table 17. Conditions used for the treatment of C28 D r.l. (0.20) under various conditions simulating an alkaline extraction.

Lignin ID	Charge of NaOH (% on lignin)	O_2 pressure (psig)	Time at 70°C (min)
Blank	0.0	-	60
E	160	-	60
EO	160	60[‡]	60
E w/o O_2[†]	160	-	60

[†]An E stage in the absence of O_2; [‡]O_2 pressure initially 60 psig and decreased 12 psi every 5 minutes.

After the reaction, the lignin was precipitated from the solution by acidifying to a pH of 2.0 with 1.0 N HCl. The precipitate was washed three times with pH 2.0 water and centrifuged. The centrifuged precipitate was freeze dried and analyzed by NMR, as discussed in Chapter 4 of the Results and Discussion Section.

Alkaline Treatment of ClO_2-Reacted Residual Lignin

A similar experiment to the alkaline extraction treatment of ClO_2-bleached residual lignin was also performed. The experiment utilized the unbleached residual lignins that had been treated with two different charges of ClO_2, namely C33 r.l.-0.05 and C33 r.l.-0.20. The two lignins (100 mg were used for each treatment) were treated under alkaline extraction stage conditions in a similar manner as previously described above for the E stage (70°C, 60 minutes). The C33 r.l.-0.05 sample was treated with one charge of NaOH corresponding to a charge of 2.6% on pulp. The pH of this solution at 70°C before the lignins were added was 11.2. The C33 r.l.-0.20 sample was treated with two charges of NaOH corresponding to a charge of 2.6% on pulp and one much lower than that. The pH's of these solutions at 70°C were 11.2 and 9.6, respectively. The pH of the former solution remained constant during the alkaline treatment, while the pH of the later solution dropped to 7.6 after 1 hour at 70°C (Table 18).

The lignins were collected after these treatments by acidifying the solutions to a pH of 2.0 and washing the precipitates three times with DI water before freeze drying. These lignins were then analyzed by ^1H-NMR, and the results are discussed in Chapter 4 of the Results and Discussion section.

Table 18. Conditions used for the alkaline extraction treatment of the ClO_2 treated C33 r.l.

Lignin ID	Alkaline Extraction Treatment			Lignin ID after treatment
	Charge NaOH†	Initial pH‡	Final pH‡	
C33 r.l.-0.05	2.6	11.2	11.2	C33 r.l.-0.05-pH 11
C33 r.l.-0.20	2.6	11.2	11.2	C33 r.l.-0.20-pH 11
C33 r.l.-0.20	-	9.6	7.6	C33 r.l.-0.20-pH 9

† % on pulp; ‡ pH measured at 70°C

Residual Lignin Permanganate Consumption

The permanganate consumption experiments were performed in a similar fashion as the kappa number test. The isolated residual lignin samples were dried under vacuum at 40°C for 24 hours. Approximately 21 milligrams of the lignins were accurately weighed out and placed in a beaker with 200 ml of DI water. Then, 25.0 ml of 0.10 N $KMnO_4$ and 25 ml of 4 N H_2SO_4 were added to each solution. After stirring this solution for 60 minutes, the reactions were terminated by adding 5 ml of 1 N KI, and the solutions were titrated to their starch end point with 0.10 N sodium thiosulfate. A blank was also run in the absence of lignin. The milliliters of permanganate consumed per milligram of lignin were then calculated from the following equation:

$$K=(B-T)/W \qquad \text{Equation (1)}$$

where K is the ml of 0.10 N $KMnO_4$ consumed per mg of lignin; B is the ml of 0.10 N sodium thiosulfate consumed by the blank; T is the ml of 0.10 N sodium thiosulfate consumed in the presence of the lignin; and W is the weight of lignin sample in milligrams. Duplicates were run for each sample.

The lignins used in these experiments can be found in Table 19 and included four unbleached residual lignins with kappa numbers ranging from 29 to 14, three ClO_2 bleached residual lignins that were bleached with three different kappa factors, one DE and one D(EO) residual lignin bleached with the same kappa factor, and one dissolved lignin from the corresponding EO stage. The results from these experiments are presented in Appendix VI.

Table 19. A list of the residual and dissolved lignins used in the potassium permanganate consumption experiments.

Lignin ID
E29 r.l.
C28 r.l.
C18 r.l.
E14 r.l.
C28 D r.l. (0.05)
C28 D r.l. (0.20)
E29 DE r.l. (0.10)
E29 D(EO) r.l. (0.10)
E29 D(EO) d.l. (0.10)

NMR SPECTROSCOPY

Several NMR spectroscopic techniques were used to elucidate structural features about the numerous lignins studied in this research. The NMR experiments included ^{13}C, ^{1}H, and ^{31}P-NMR. This section describes in detail the experimental protocol used for each technique. All NMR spectra were recorded on a Bruker 400-MHz DMX NMR spectrometer.

^{13}C-NMR Spectroscopy

All ^{13}C-NMR spectra, unless otherwise stated, were recorded under quantitative conditions, which were accomplished by using a pulse sequence (inverse-gated) that eliminated the nuclear overhauser effect (NOE) and had a sufficiently long pulse delay, allowing for all nuclei to be fully relaxed before the next pulse. The pulse delay commonly used for lignin, which had been established in the literature and verified in some unpublished work, was 10 seconds (78).

The solvent used for all lignin samples was DMSO-d_6. The samples were made as concentrated as possible, typically about 300-400 mg/ml for residual lignins and 550-650 mg/ml for dissolved lignins. All samples were placed in a 5-mm NMR tube (sample volume 0.45-0.50 ml) and heated to 50°C in the Bruker QNP probe.

Some of the acquisition parameters used during the recording of the spectra included 9-15 k number of acquisitions, 90° pulse width (p1 = 8 usec, pl1 = 1.00 db), 222 ppm sweep width, and a 10-second pulse delay. The total acquisition time for recording each spectrum was typically quite long, ranging from 24 to 36 hours. Samples with lower lignin concentrations required longer acquisition times than samples with higher lignin concentrations to obtain suitable signal-to-noise ratios. During processing, a line broadening of 10.0 Hz was used to obtain acceptable line widths. Phasing and baseline corrections were necessary and completed with care because these processes can influence the integration data. Both phasing and baseline corrections were done manually prior to integrating. The regions chosen to be integrated were based on literature references. An integration file was created on the computer, allowing the same integration regions to be used for each spectrum. The integration regions used are found in Table 20.

Table 20. Functional group frequency and integration regions used for the quantitative analysis of the ^{13}C-NMR spectra of lignin.

Region	Structure or Functional Group	Integration region (ppm)
1	COOH	180-165
2	Aromatic-O-R (C3, C4)	154-140
3	Aromatic-C-C (C1)	140-127
4	Aromatic-C-C (C5)	127-123
5	Aromatic-CH (C6)	123-117
6	Aromatic-CH (C5)	117-114
7	Aromatic-CH (C2)	114-106
2-7	Aromatic C total	160-106
2-4	Aromatic-C-R (substituted)	160-123
5-7	Aromatic-CH (unsubstituted)	123-106
8	Aliphatic C-O (Cβ in β-O-4; Cα in β-5 and β-β)	90-78
9	Aliphatic C-O (Cα in β-O-4)	78-67
10	Aliphatic COR	67-61
11	Aliphatic C-O (Cγ in β-O-4)	61-57
12	Methoxyl OCH_3	57-54
13	Cβ in β-β and Cβ in β-5	54-51

The integration regions allow for the quantification of various structures and/or functional groups in lignin. Interpretation of the integration was made by taking advantage of the distinct separation of aromatic carbons from other types of carbon functional groups. The aromatic region was integrated and assigned a value of 6; for the six carbons in an aromatic group, other integration regions can be integrated relative to this value. Therefore, integration regions can be quantified as number of carbon atoms per aromatic unit. This technique has been used in the literature to quantify functional groups in lignin and has been found to be quite a viable quantitative analytical technique for lignin (78). The procedure differs from the ^{1}H-NMR and ^{31}P-NMR techniques, which rely on the addition of an internal standard for the quantitative analysis of functional groups.

The quantitative results from all ^{13}C-NMR experiments can be found in Appendix III.

^{1}H-NMR Spectroscopy

Two ^{1}H-NMR techniques were used to quantify various functional groups in lignin. Both techniques used pentafluorobenzaldehyde (PFB) as an internal standard and TMS as a chemical shift reference. The PFB has a sharp singlet at 10.1, out of range of other signals from lignin, allowing it to be easily integrated. This signal, along with the TMS signal (0.0 ppm), is also used for assisting in the phasing of the spectra. One technique involves acetylating the lignin and recording the ^{1}H-NMR spectrum in $CDCl_3$. The other technique requires no derivatization, and the spectra are recorded in DMSO-d_6. The procedure used for each technique will be discussed separately.

Lignin acetates

By far the most popular method to characterize lignin by ^{1}H-NMR is to first derivatize the lignin by acetylation and record the spectrum in chloroform solutions. The various residual and kraft lignins were acetylated following the procedure outlined above, and their ^{1}H-NMR spectra were recorded as described below. After being acetylated, the lignins were dried under vacuum for 24 hours at 40°C and accurately weighed out into a 2-ml vial (~22 mg). A standard solution containing PFB and TMS in "100%" $CDCl_3$ was made and added to the lignin. The standard solution was made by first carefully weighing out the PFB (1.3189 g) and diluting to 10.0 ml with 100% $CDCl_3$. An aliquot of this solution (1.25 ml) was diluted to 25.0 ml, TMS added, and 0.50 ml added to the lignin. The solution of lignin and internal standard in $CDCl_3$ was stirred vigorously and transferred into a 5-mm NMR tube and the ^{1}H-NMR spectrum recorded.

The ^{1}H-NMR spectra were recorded under quantitative conditions using a 30° pulse and 4-second pulse delay. For each spectrum, 800 acquisitions were recorded, and a 17 ppm sweep width was used. Manual phasing and baseline corrections were done, and an integration file was created so the same integration regions were used for each spectrum. Table 21 is a list of the regions integrated for each spectrum.

Quantitative estimates of the various proton-containing functional groups were made by performing the following calculation. The signal area of the PFB signal, which was due to the 0.003297 g of PFB, was integrated and calibrated to 1.0. Because this molecule contains one proton and has a molecular weight of 196.07 g/mol,

Table 21. Functional group frequency and integration regions used for the quantitative ^{1}H-NMR spectra of lignin acetates.

Structure or Functional Group	Integration region (ppm)
PFB	10.4-10.2
Aromatic H	8.0-6.2
Ha in β-O-4 structures	6.2-5.8
$-OCH_3$	4.2-3.6
Aromatic acetate	2.6-2.2
Aliphatic acetate	2.2-1.6
TMS	0.0

0.003297/196.07=1.682x10-5 was the number of moles of H present in the internal standard in the sample. Because the integration region of the internal standard was calibrated to 1.0, each unit area in the spectrum is equal to 1.682x10-5 moles of H. For each spectrum, this value (or factor) is multiplied by the integration region of interest and divided by the weight of the lignin sample. For example, if the lignin sample weighed 22.03 mg and the integration of the aromatic region equaled 12.437, then: (12.437x1.682x10-5)/.02203=0.0095 mol aromatic H /g lignin are present in the lignin sample. This number was multiplied by 1000 to convert the value into mmol/g lignin.

The quantitative results from all ^{1}H-NMR experiments of lignin acetates can be found in Appendix IV.

Underivatized lignins

Lignin samples can also be analyzed by ^{1}H-NMR in their underivatized form. This technique has the advantage of precluding any unwanted chemical modification to the lignin during acetylation or other derivatization techniques and was very helpful for the analysis of the highly oxidized lignins. Such lignins were incapable of being acetylated and were not amenable for the ^{31}P-NMR technique. The underivatized lignin was first dried under vacuum for 24 hours at 40°C and accurately weighed out into a 2-ml vial (~22 mg). A standard solution containing PFB and TMS in DMSO-d_6 was made and added to the lignin. The standard solution was made by first carefully weighing out the PFB (0.1881 g) and diluting to 10.0 ml with DMSO-d_6. An aliquot of this solution (0.250 ml) was then added to the lignin. An additional 0.25 ml of DMSO-d_6 was added to the sample and stirred vigorously. The solution was then transferred into a 5-mm NMR tube and the ^{1}H-NMR spectrum recorded.

The ^{1}H-NMR spectra were recorded under quantitative conditions using a 30° pulse and 7-second pulse delay. For each spectra, 750 acquisitions were recorded, and a 17 ppm sweep width was used. In some cases only 128 acquisitions were recorded because it was much quicker, and although the signal-to-noise ratio was a little poorer, the integration values were the same as with 750 scans. Manual phasing and baseline corrections were done, and an integration file was created so the same integration regions were used for each spectrum. Table 22 is a list of the regions integrated for each spectrum.

Table 22. Functional group frequency and integration regions used for the quantitative ^{1}H-NMR spectra of underivatized lignins.

Structure or Functional Group	Integration region (ppm)
PFB	10.2-10.0
COOH	13.5-12.6
Phenolic OH	9.3-8.0
Aromatic H	7.7-6.3
TMS	0.0

The quantitative analysis was performed in a similar manner as for the lignin acetates with PFB; the results can be found in Appendix IV.

^{31}P-NMR Spectroscopy

The ^{31}P-NMR technique is a relatively new technique developed by Argyropoulos and co-workers to quantify hydroxyl functional groups in lignin, as has been extensively described in the Literature Review section (37). The phosphitlating reagent employed here was 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). TMDP was prepared by following a procedure developed by Zwierzak (94).

The lignin samples were dried under vacuum at 40°C for 24 hours and accurately weighed into a 2-ml vial. In most cases, approximately 25 milligrams were used. A solvent mixture of pyridine:$CDCl_3$ (1.6/1 v/v) (Aldrich) was prepared and 400 μl added to the lignin. A solution of chromium (III) acetylacetonate (3.6 mg/ml) and cyclohexanol (4.0 mg/ml) in pyridine/$CDCl_3$ was prepared and 150 μl added to the lignin solution. The chromium (III) acetylacetonate served as a relaxation reagent and the cyclohexanol as the internal standard. The lignin solution was then vigorously stirred until completely dissolved. Minutes before starting the NMR experiment, approximately 50 μl of TMDP were added to the vial and the solution transferred into a 5-mm NMR tube.

The ^{31}P-NMR spectra were recorded with the following acquisition parameters, inverse-gated pulse sequence (allowing for quantitative spectra), 25-second pulse delay, 200 acquisitions, 61.7 ppm sweep width, and a 30° pulse width (p1 = 6.5 usec, pl1 = -2.0 db). A 4-Hz line broadening was employed, which gave acceptable line widths for the spectra. The spectra were manually phased using the signals due to the internal standard and water as aids, and baseline correction was accomplished using the computer. All chemical shifts were reported from the signal due to the internal standard (145.1 ppm). An integration file was saved on the computer and used for each spectra. The integration regions used for the ^{31}P-NMR spectra are listed below in Table 23.

Table 23. Functional group frequency and integration regions used for the quantitative ^{31}P-NMR spectra of lignins phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

Structure or Functional Group	Integration region (ppm)
Cyclohexanol (internal standard)	145.3-139.8
Aliphatic OH	150.0-145.3
Condensed phenolic OH	144.0-141.0
Guaiacyl phenolic OH	141.0-137.0
COOH	136.2-134.0

Quantitative estimates of the various hydroxyl functional groups were made by performing the calculation outlined below. The signal area of the cyclohexanol derivatized with TMDP, which was due to 6.01x10-4 g of cyclohexanol, was integrated and calibrated to 1.0. Because this molecule contains one hydroxyl group and has a molecular weight of 100.16 g/mol, 6.01x10-4/100.16=5.9994x10-6 was the number of moles of hydroxyl groups present in the internal standard in the sample. Because the integration region of the internal standard was calibrated to 1.0, each unit area in the spectrum is equal to 5.9994x10-6 moles of hydroxyl groups. For each spectrum this value (or factor) is multiplied by the integration region of interest and divided by the weight of the lignin sample. For example, if the lignin sample weighed 25.28 mg and the integration of the carboxylic acid region equaled 1.859, then: (1.859x5.9994x10-6)/.02528=0.00044 mol /g lignin are present in the lignin sample. The number was then multiplied by 1000 to convert the value into mmol/g lignin.

The quantitative results from all ^{31}P-NMR experiments employing 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane can be found in Appendix V.

Comments on the ^{31}P-NMR and ^{1}H-NMR Analyses

A few concerns about the quantification of functional groups employing the ^{31}P-NMR and ^{1}H-NMR techniques should be addressed. As discussed, functional groups were quantified by adding an internal standard to the sample, which gave a clear signal in the spectrum that was capable of being integrated. The integration of this signal was then used as a reference to the integration of other regions in the NMR spectra. The internal standard was added to the sample from a pre-made stock solution of the internal standard. The exact concentration of this internal standard solution was difficult to determine precisely, even though a very accurate balance was employed. To minimize experimental errors due to the concentration effect of the internal standard, groups of lignin samples were analyzed from the same stock solution. For example, the internal standard was added to all the unbleached residual lignin samples at the same time and the spectra recorded as soon as possible. Reproducibility of the data was good after performing the analysis in this manner, as will be shown throughout this dissertation. The exact content of the functional groups, that are graphed in all the figures throughout this dissertation, should be considered as relative amounts of functional groups, even though the numbers in the graphs suggest otherwise.

RESULTS AND DISCUSSION

The results and discussion section of this dissertation will be divided into four chapters. The first and second chapters will be concerned with understanding the structural changes in lignin during kraft delignification. Specifically, the first chapter will be an analysis of unbleached residual lignins isolated from CK and EK pulps with kappa numbers ranging from 29 to 13. The second chapter will be an analysis of the kraft lignins isolated from black liquors extracted at various times during both CK and EK pulping. These first two chapters will provide new insights into kraft delignification chemistry and help to interpret the improved selectivity of EK pulping compared to conventional kraft pulping.

The third and fourth chapters deal with the chemistry of chlorine dioxide and alkaline extraction bleaching. Specifically, the third chapter compares the bleachability of CK versus EK pulps and high versus low kappa kraft pulps in a D(EO) delignification sequence. In addition, this chapter considers the relationship of the unbleached residual lignin structure and residual lignin reactivity toward ClO_2 to the bleachability. The fourth chapter analyzes the chemical mechanisms leading to delignification during ClO_2 bleaching by monitoring the structural changes to the lignin. This was accomplished by structurally comparing residual and dissolved lignins isolated from various ClO_2 bleaching sequences.

CHAPTER 1. ANALYSIS OF RESIDUAL LIGNIN DURING KRAFT PULPING

INTRODUCTION

The various residual lignins isolated from unbleached kraft pulps (as listed in Table 10 in the Materials and Methods section, page 76) were subjected to four different NMR analyses. Each NMR analysis was capable of quantifying some functional group or structural feature about the lignin.

The yield of lignin from the various pulps ranged from 30 - 45% depending on both the pulp type and kappa number of the pulp. The yields are given in Figure AII.1 on page 238. While the yields may be low, the isolated lignin will be considered as representative of the total lignin present in the pulp. This is probably a good assumption but should be the subject of further study.

The Results and Discussion section below has been divided into five subsections, presenting the results from the analysis and quantification of aliphatic hydroxyl groups, phenolic hydroxyl groups, carboxylic acid groups, β-O-4 structures, and condensed structures. Included in each section is an analysis of the particular functional group and the changes it undergoes during a treatment under kraft pulping conditions. The changes observed for each functional group in the residual lignins and the changes it undergoes after being treated under pulping conditions are then discussed in terms of their importance to understanding kraft delignification chemistry.

Analysis Overview

An example of how a section will be analyzed and discussed is presented here. The results from the NMR analysis of a particular functional group and/or structural feature of the residual lignins will be presented first and use graphs of the content of the functional group or structural feature of the lignin versus the kappa number of the pulp from which the residual lignin was isolated. Next, the results from the kraft treatment of residual lignins C28 r.l. and E14 r.l. are presented as graphs of the content of the particular functional group and/or structural feature versus the time of the kraft treatment. Finally, a discussion will follow concerning the relevance of the results (from both the analysis of the residual lignins and the kraft treatments) in terms of the chemistry of kraft delignification.

RESULTS AND DISCUSSION

<u>Aliphatic Hydroxyl Content</u>

The ^{31}P-NMR analysis is capable of quantifying the aliphatic hydroxyl content of the lignins. Figure 1.1 is a plot of the aliphatic hydroxyl content determined by ^{31}P-NMR of the residual lignins plotted against the kappa number of the pulp from which the lignin was isolated. Most residual lignins were only analyzed once by ^{31}P-NMR, with the exception of C28 r.l., which was replicated four times, and E29 r.l., which was isolated from the E29 pulp twice and both lignins analyzed once. These replicates were done to show the reproducibility of the analysis. The results in Figure 1.1 clearly indicate that the residual lignins of both CK and EK pulps are significantly reduced in aliphatic hydroxyl content as delignification proceeds. The excellent reproducibility of the analysis is observed in the four replicates of C28 r.l. and in the replicated residual lignin isolation of E29 r.l.'. The results also showed that CK residual lignins had lower contents of aliphatic hydroxyl groups than EK residual lignin at 28 and 18 kappa numbers. The ASAQ residual lignin had an aliphatic hydroxyl content that was more similar to the EK residual lignin.

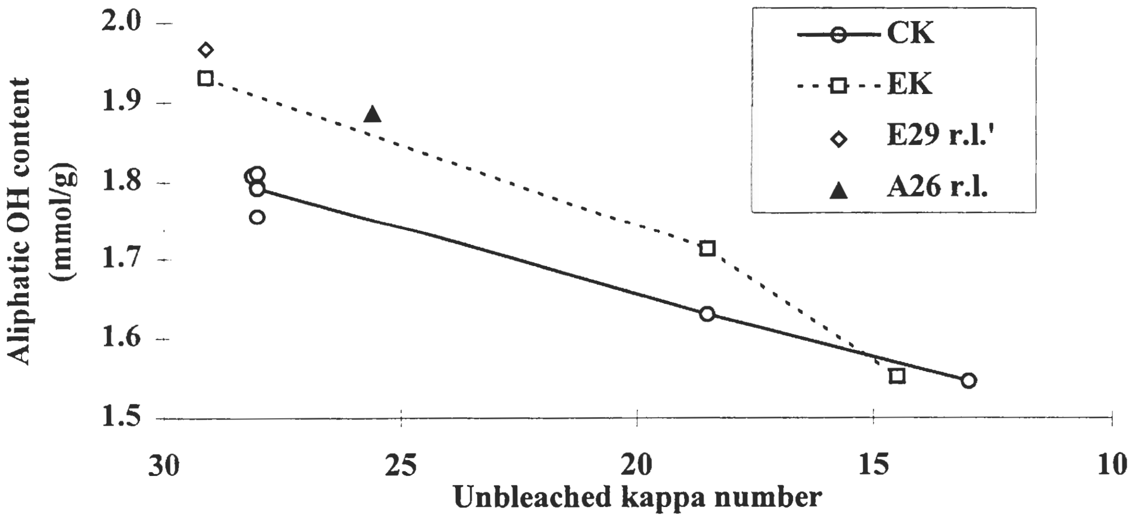


Figure 1.1. Aliphatic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l.

Kraft-treated residual lignins

The aliphatic hydroxyl contents of kraft-treated residual lignins were monitored by ^{31}P-NMR. Figure 1.2 contains the results from this analysis and indicates that an additional kraft treatment of residual lignin resulted in an additional loss of aliphatic hydroxyl groups. The C28 r.l. sample, which had a greater content of aliphatic hydroxyl groups, showed a greater loss of such groups during the kraft treatment in comparison to E14 r.l. Both lignins, after the 120-minute treatment, contained a similar amount of aliphatic hydroxyl groups, suggesting that there is a limit to the loss of aliphatic hydroxyl groups the residual lignins can undergo during kraft pulping. The replicate of the 120-minute treatment of C28 r.l. showed that the experiment was reproducible.

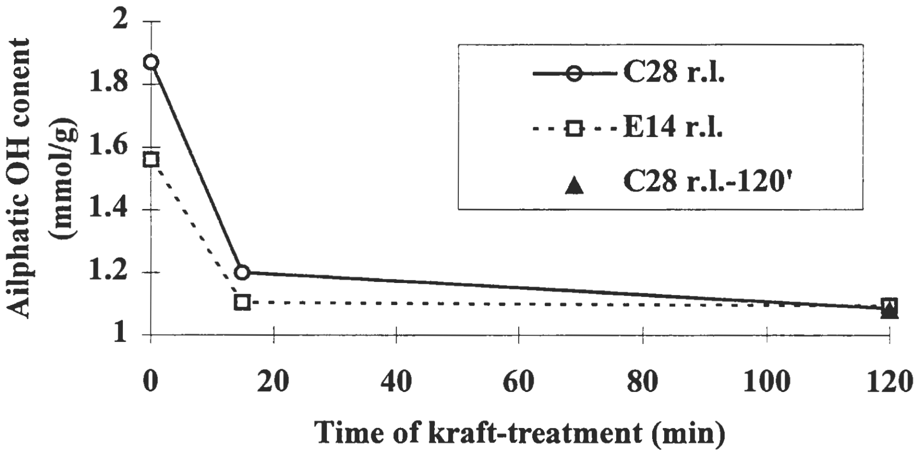


Figure 1.2. Aliphatic hydroxyl content of residual lignins treated under kraft pulping conditions for different lengths of time. The aliphatic hydroxyl content was determined by ^{31}P-NMR. Duplicates of each sample were performed and the averages graphed. C28 r.l.-120' is a replicate of C28 r.l. treated for 120 minutes.

Discussion of results

The aliphatic hydroxyl content of lignin is mainly comprised of primary and secondary hydroxyl groups located on the gamma (terminal) and alpha carbon atom on the phenylpropane side chain of lignin, respectively. The loss in aliphatic hydroxyl groups observed here may be due to a loss of primary hydroxyl groups on the gamma carbons as formaldehyde, as shown in Figure 10 (page 19).

The ^{31}P-NMR analysis showed that the aliphatic hydroxyl content of the EK residual lignins was greater than the CK residual lignins at 28 and 18 kappa numbers. If the degree to which lignin is modified during kraft pulping can be related to the content of aliphatic hydroxyl groups, the CK residual lignin has undergone a more severe modification at a given kappa number. This may be due to the different process conditions employed during these pulping processes, which will be discussed further later in this chapter.

The kraft treatment of the residual lignins yielded some interesting results on the fate of aliphatic hydroxyl groups during kraft pulping. The aliphatic hydroxyl groups in residual lignin are still reactive under pulping conditions as they are significantly decreased during the treatment. The content of aliphatic hydroxyl groups decreases significantly after 15 minutes for both lignins but then appears to approach a floor level of aliphatic hydroxyl content as both lignins have a similar content after a 2-hour treatment. The floor level of aliphatic hydroxyl groups indicates that these aliphatic hydroxyl groups are unreactive under pulping conditions.

Phenolic Hydroxyl Content

The phenolic hydroxyl group is another important functional group in lignin. Native wood lignin contains quite a low content of such groups. During kraft delignification, the cleavage of aryl ether linkages creates new phenolic groups. Phenolic groups assist in the dissolution of the lignin during pulping by aiding in the lignin's solubility in alkaline medium and are involved in the formation of reactive quinone methide intermediates. As a result, dissolved (kraft) lignin has a high content of phenolic groups, while residual lignin has a substantially lower content, although greater than native wood lignin (8).

The techniques used to quantify the phenolic hydroxyl content included ^{31}P-NMR and both ^{1}H-NMR (acetylated and underivatized lignins) analyses. The ^{31}P-NMR technique has the added ability to distinguish between guaiacyl and C5 substituted ('condensed') phenolic groups. Figures 1.3, 1.4, and 1.5 are plots of the total phenolic content, guaiacyl phenolic content, and condensed phenolic content versus the unbleached kappa number for various residual lignins, respectively.

A clear trend is observed in all three figures; the phenolic hydroxyl content of CK lignins increases as the kappa number is decreased from 29 to 18. Further delignification does not increase the phenolic content of these CK lignins, rather the phenolic content appears to level off. Under EK pulping conditions, a relatively minor increase in phenolic content is observed as the kappa number is lowered from 28 to 18, but a dramatic increase is observed from 18 to 14. Similar trends were observed in all three graphs in terms of the phenolic hydroxyl content, whether it be the total phenolic, guaiacyl phenolic, or condensed phenolic.

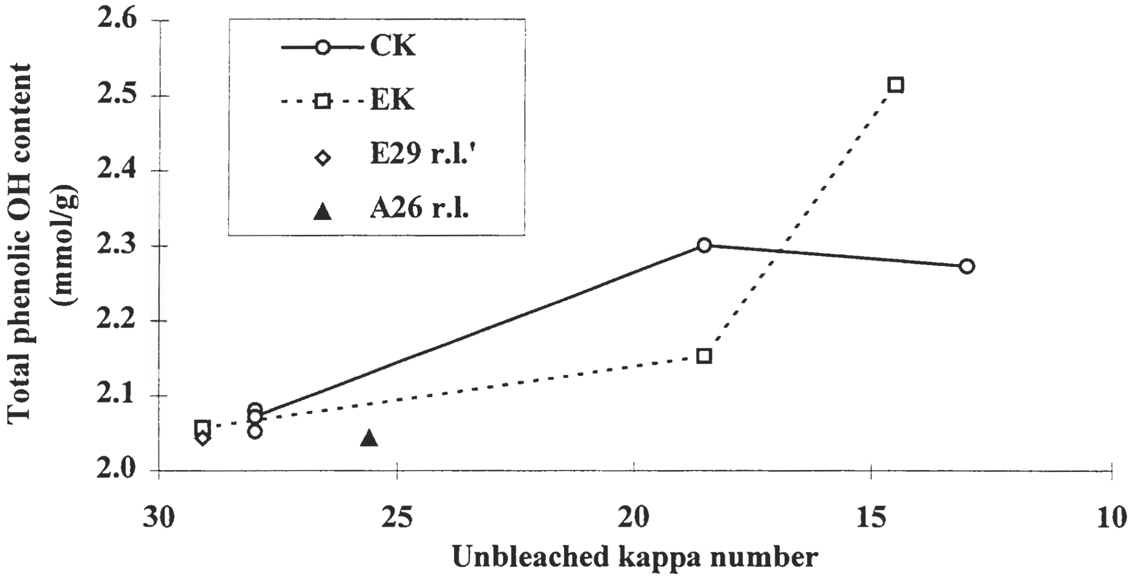


Figure 1.3. Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.' and four replicates of C28 r.l.

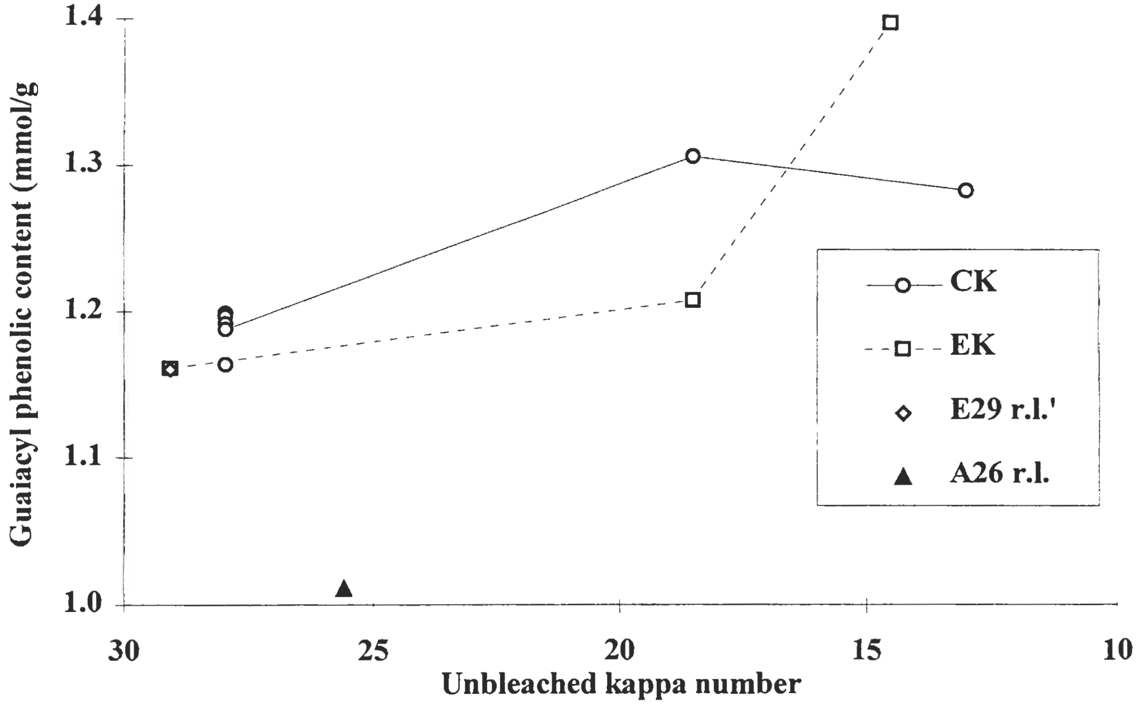


Figure 1.4. Guaiacyl phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l.

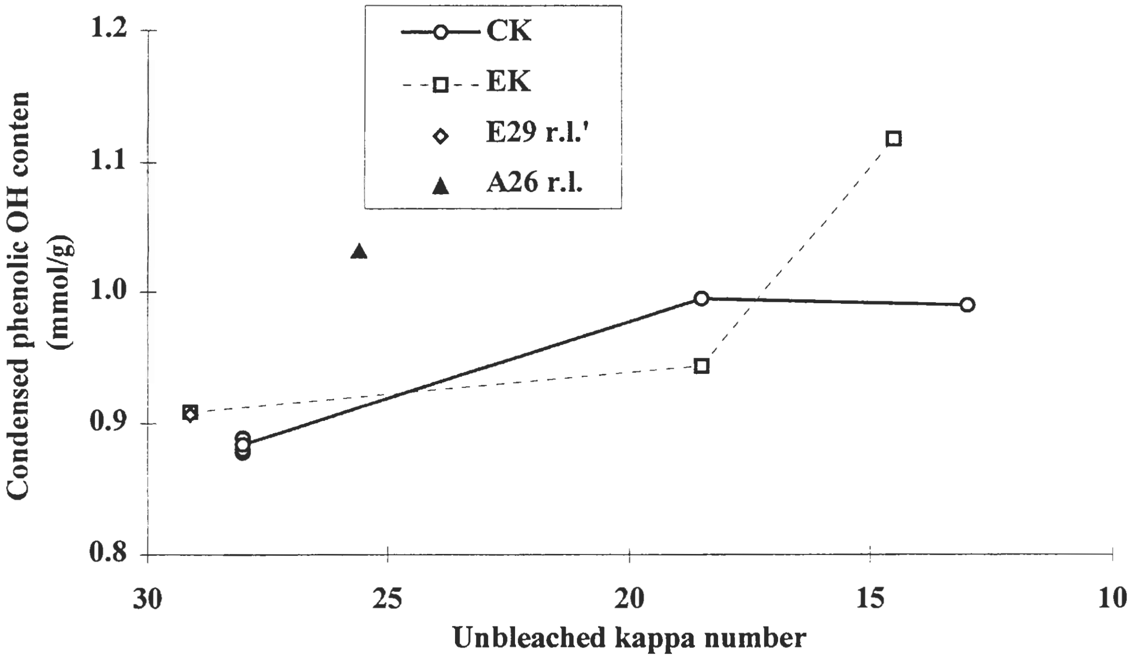


Figure 1.5. Condensed phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l.

ASAQ residual lignin had a similar total phenolic hydroxyl content compared to kraft residual lignins at a 26 kappa number; however, the contents of guaiacyl and condensed phenolic groups were quite different. ASAQ residual lignin had a greater content of condensed phenolic groups and a lower content of guaiacyl phenolic groups compared to kraft residual lignins.

^{1}H-NMR of lignin acetates also allows for the quantification of phenolic hydroxyl groups. Figure 1.6 is a plot of the phenolic hydroxyl content versus unbleached kappa number of residual lignin. Again, similar trends as observed by ^{31}P-NMR analysis were found. For CK lignins, there was an increase in phenolic content from 28 to 18 kappa and then a leveling off to 13 kappa. For the EK lignins, there was no increase from 29 to

18 but a substantial increase from 18 to 14 kappa. ASAQ residual lignin again had a similar content of phenolic groups as kraft residual lignins at comparable kappa numbers.

^{1}H-NMR analysis of underivatized residual lignins was also performed to quantify the content of phenolic hydroxyl groups. Figure 1.7 is a plot of the total phenolic content versus unbleached kappa number of residual lignin. Once again similar trends were found in this analysis as the phenolic content was shown to increase, although in this analysis, differences between CK and EK lignins were suggested.

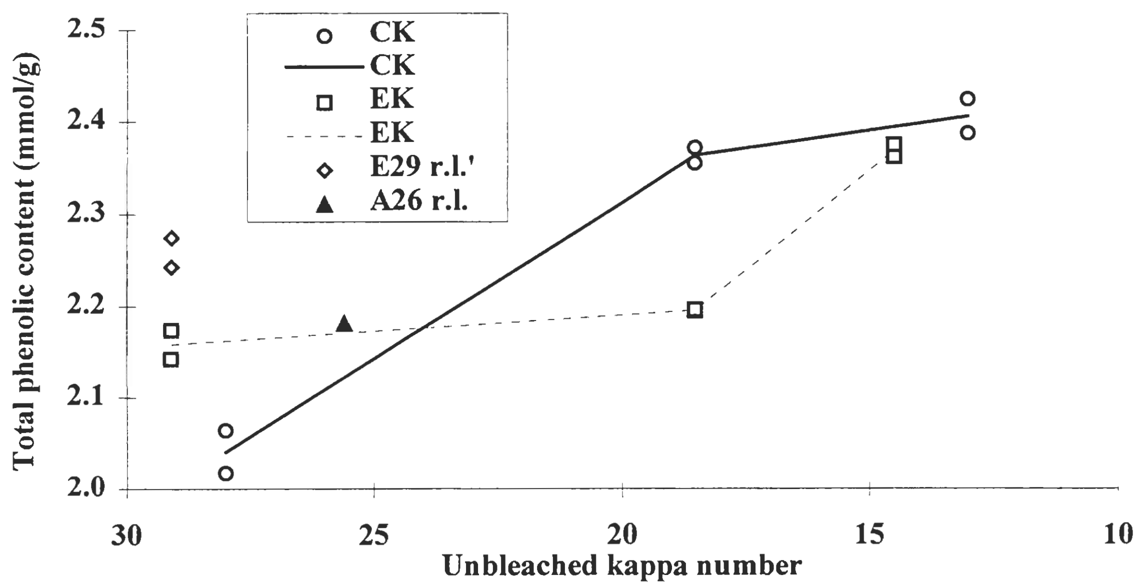


Figure 1.6. Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates. Also included are A26 r.l. and E29 r.l.'.

Kraft-treated residual lignins

The phenolic hydroxyl content of the kraft-treated residual lignins was monitored by ^{31}P-NMR (Figures 1.8, 1.9, and 1.10). The analyses show that a further treatment of residual lignin under kraft pulping conditions results in a further increase in the content of phenolic hydroxyl groups. For each lignin, there was a greater increase in the condensed phenolic groups compared to the guaiacyl phenolic groups, as shown for C28 r.l. in Figure 1.9 and E14 r.l. in Figure 1.10.

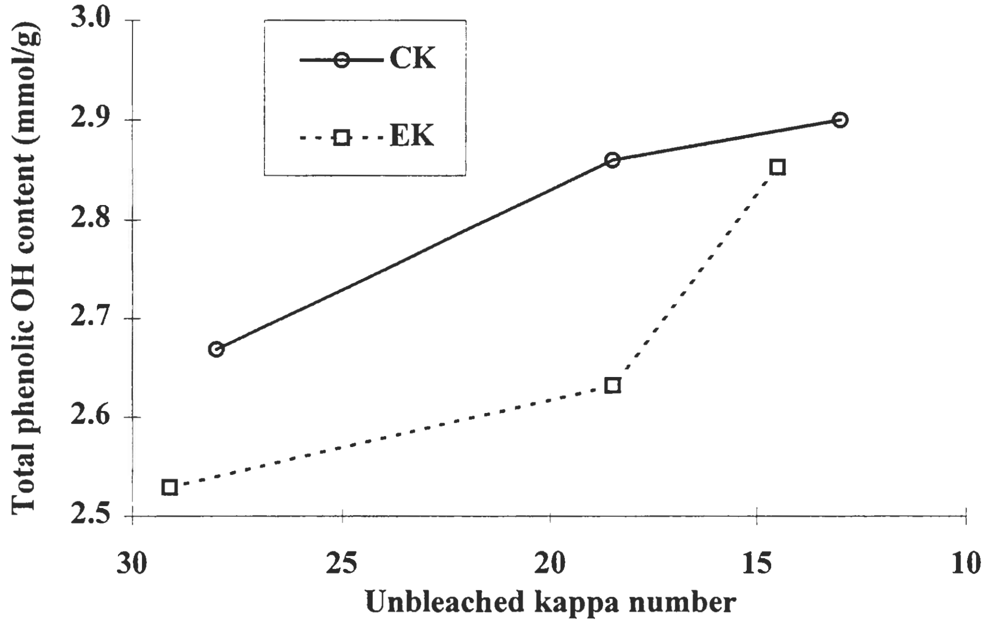


Figure 1.7. Total phenolic hydroxyl content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of underivatized lignins.

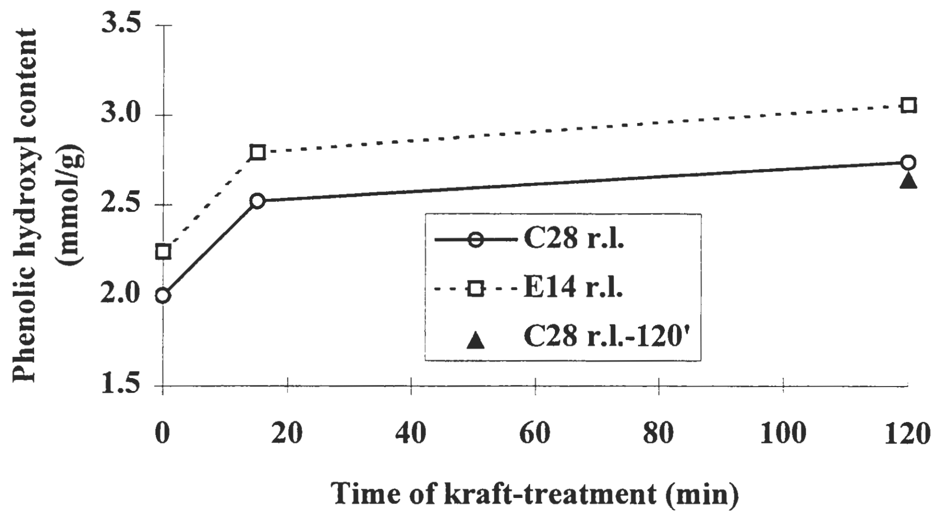


Figure 1.8. Total phenolic hydroxyl content of residual lignins treated under kraft pulping conditions for different lengths of time as determined by ^{31}P-NMR. Duplicates of each sample were performed and the averages graphed. C28 r.l.-120' is a replicate of C28 r.l. treated for 120 minutes.

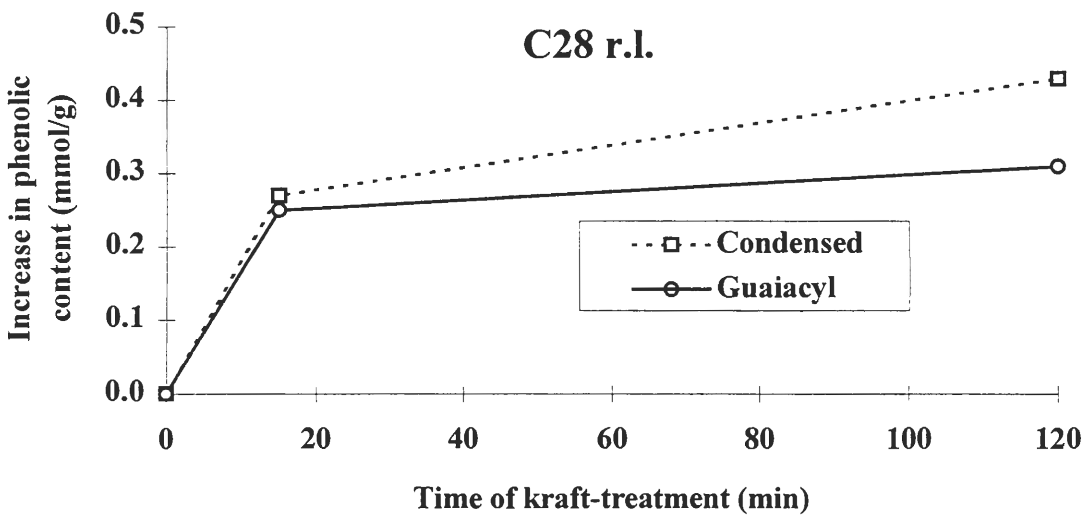


Figure 1.9. Change in the guaiacyl and condensed phenolic hydroxyl content of C28 r.l. during the kraft treatment.

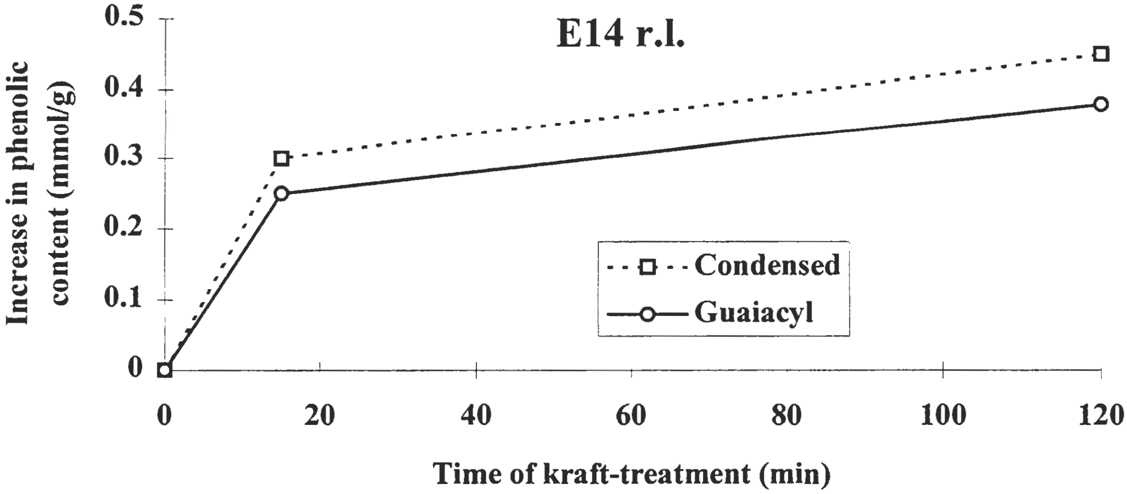


Figure 1.10. Change in the guaiacyl and condensed phenolic hydroxyl content of E14 r.l. during the kraft treatment.

Discussion of results

The analysis of phenolic hydroxyl contents in various residual lignins can provide some insightful information about kraft delignification chemistry. The observation that the content of phenolic hydroxyl groups is increasing with decreasing kappa number implies that the residual lignin is still undergoing cleavage of remaining aryl ether linkages. The presence and decreasing quantity of aryl ether linkages in residual lignin will be shown later. The leveling off of the phenolic content in the CK residual lignins suggests that additional aryl ether cleavage is minimal, while the increase in the EK residual lignins indicates that additional aryl ether cleavage is still occurring.

The fact that residual lignin undergoes additional aryl ether cleavage was further substantiated from results on the kraft treatment of residual lignins, which also showed an increase in the phenolic hydroxyl content. The kraft treatment was performed on both a high and low kappa residual lignin, both of which showed an increase in the phenolic hydroxyl content as a result of the treatment. Interestingly a greater increase in the phenolic hydroxyl content was observed in E14 r.l. compared to C28 r.l., even though the content of aryl ether linkages was lower in E14 r.l. (as will be shown later). In addition, there was a greater increase in the condensed phenolic content compared to the guaiacyl phenolic content. The greater increase in condensed phenolic groups suggests that the majority of new phenolic groups being created are of the C5 condensed type, and/or some of the phenolic structures have undergone condensation reactions. If the greater increase in the condensed phenolic content is coming from the cleavage of condensed aryl ether linkages, then the results would seem to suggest that a significant portion of the non-phenolic structures in residual lignin is of the condensed (C5 substituted) type.

<u>Carboxylic Acid Content</u>

The carboxylic acid content of the residual lignins was determined by ^{31}P-NMR. Figure 1.11 shows that residual lignin contains an increasing amount of carboxylic acid groups as delignification proceeds. Interestingly both EK and CK residual lignins appear to undergo a similar increase in the carboxylic acid content.

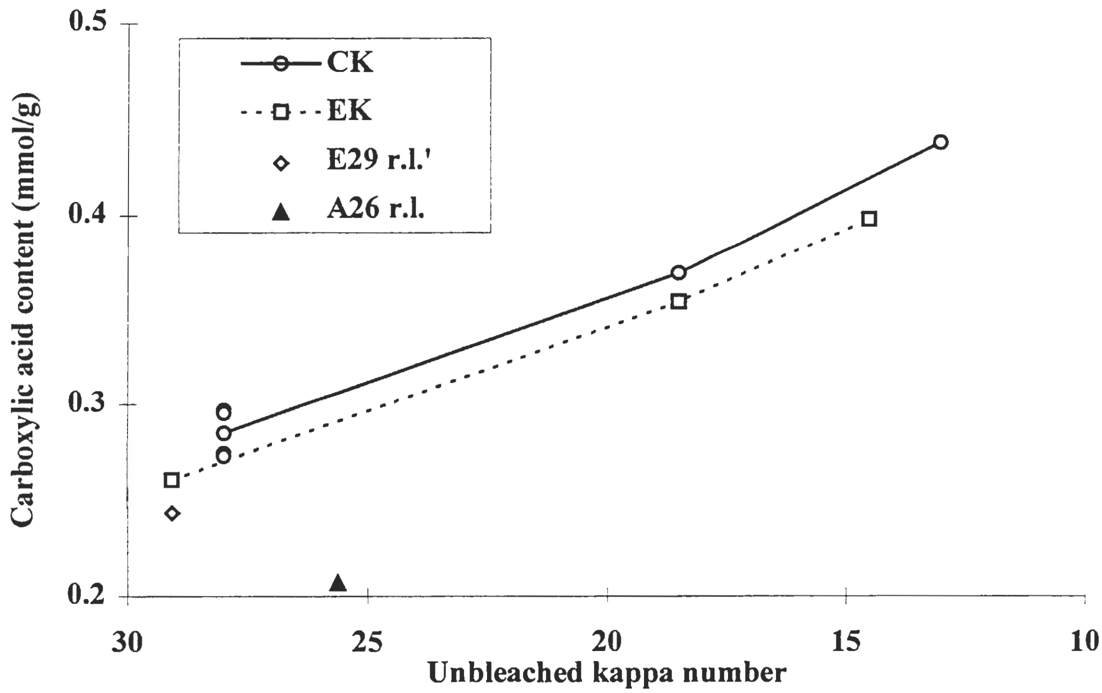


Figure 1.11. Carboxylic acid content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{31}P-NMR. Also included are A26 r.l., E29 r.l.', and four replicates of C28 r.l.

Kraft-treated residual lignins

The carboxylic acid content of the kraft-treated residual lignins was also monitored by ^{31}P-NMR analysis (Figure 1.12). The additional treatment of the residual lignins under kraft pulping conditions results in a further increase in the carboxylic acid content for both C28 r.l and E14 r.l. The increase was about the same for each lignin.

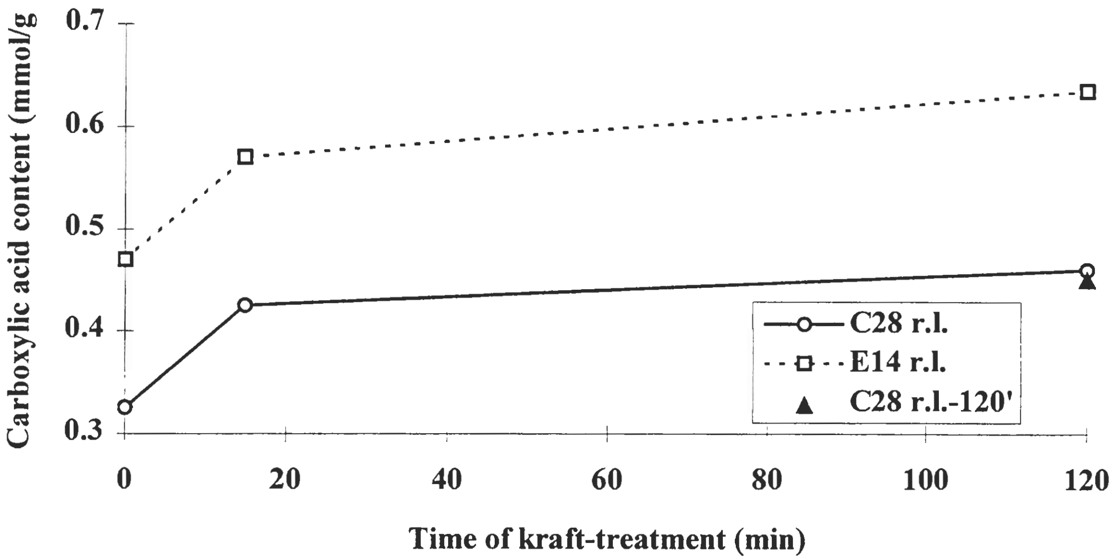


Figure 1.12. Carboxylic acid content of residual lignins treated under kraft pulping conditions for different lengths of time as determined by ^{31}P-NMR. Duplicates of each sample were performed and the averages graphed. C28 r.l.-120' is a replicate of C28 r.l. treated for 120 minutes.

Discussion of results

The results from the analyses of residual lignins and lignins treated under kraft pulping conditions show that carboxylic acid groups in lignin are formed during kraft pulping. Other studies have shown similar results (33,46,95). The ^{13}C-NMR spectra suggest that these carboxylic acids are aliphatic.

β-O-4 Structures

The contents of β-O-4 structures in the residual lignins have been conveniently measured by ^{1}H-NMR of lignin acetates and ^{13}C-NMR. Acetylating the lignin causes the chemical shift of the Hα proton in β-O-4 arylglycerol structures to be sufficiently separated from other signals arising from lignin, allowing for the signal to be integrated and the content of β-O-4 structures quantified. Figure 1.13 is a plot of the β-O-4 content versus the unbleached kappa number of the isolated residual lignin. There is clearly a decreasing content of β-O-4 structures in residual lignins as delignification proceeds from 29 to 13 kappa during both CK and EK pulping. The graph also shows that at a given kappa number the EK residual lignins have a higher content of β-O-4 structures than the CK residual lignins.

The ^{13}C-NMR analysis also allows for qualitative comparisons and quantitative estimates to be made on the content of β-O-4 structures. The quantitative ^{13}C-NMR spectra of E29 r.l. and E14 r.l. are presented in Figure 1.14. The signals arising from the β-O-4 structures are clearly much less intense in the E14 r.l. sample (signals 8, 9, 11; see Table 20, page 91, for signal assignments). The signal arising from aromatic C3 carbon atoms in etherified guaiacyl structures is highlighted in the spectra and shown to be relatively weak in the lower kappa residual lignin. Because most of the etherified guaiacyl structures are of the β-O-4 type, the almost nonexistence of this signal in the E14 r.l. spectrum implies that only a few of these structures remain.

Results from the quantitative ^{13}C-NMR analysis of the β-O-4 content in residual lignins have been plotted in Figures 1.15 and 1.16. Figure 1.15 is a plot of integration region 8 (Table 20, page 91, in the Material and Methods section). The signals in this region are mainly due to Cβ in β-O-4 structures and other aliphatic carbons linked to oxygen. Figure 1.16 is a plot of integration region 11, which is the chemical shift area for the well-resolved signal arising from Cγ in β-O-4 aryl glycerol structures.

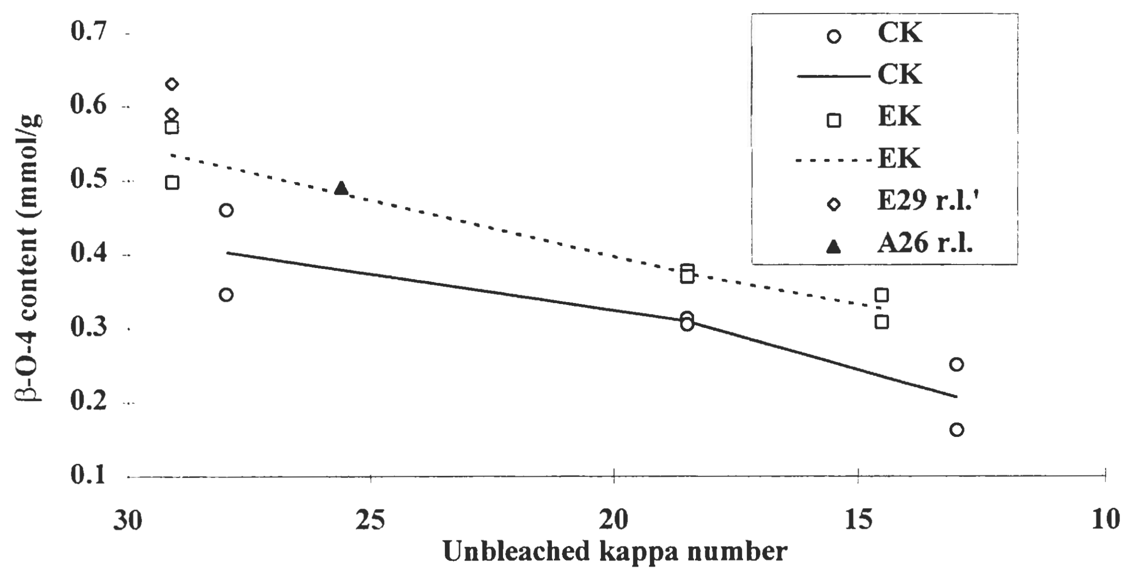


Figure 1.13. β-O-4 content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates. Also included are A26 r.l. and E29 r.l.'.

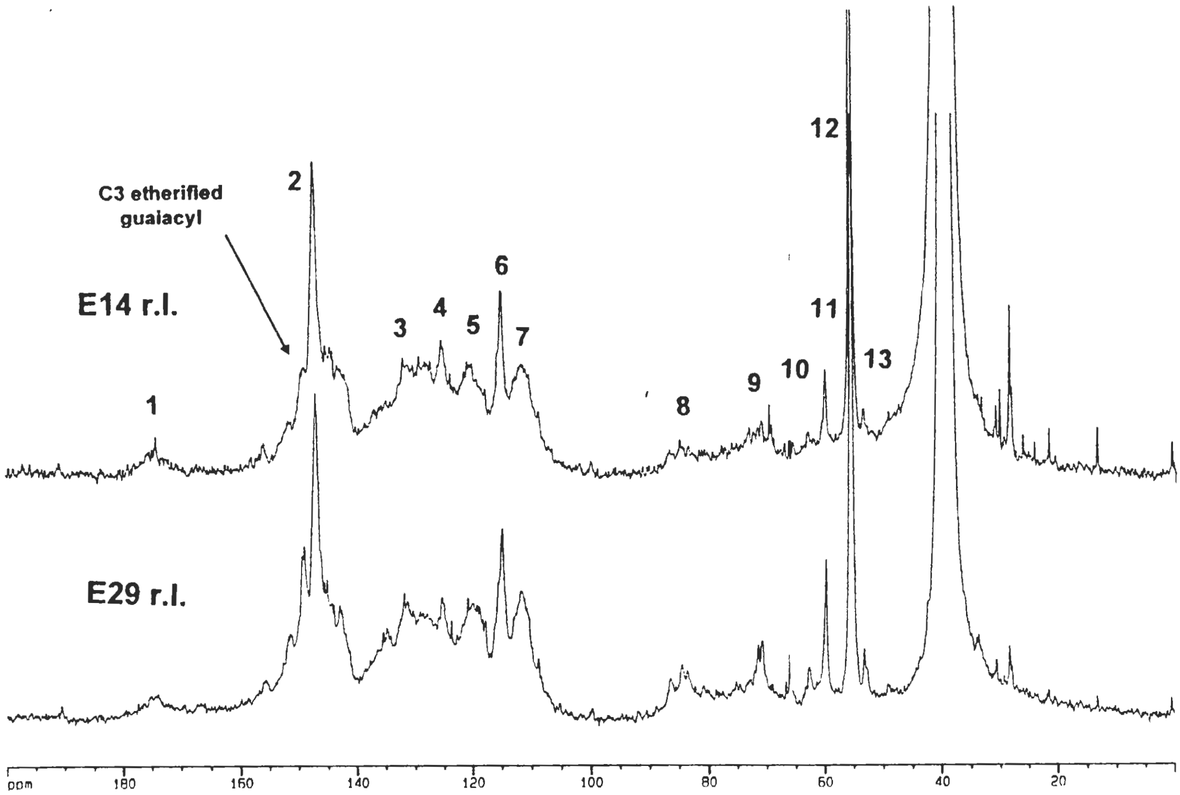


Figure 1.14. Quantitative ^{13}C-NMR spectra of residual lignins E29 r.l. and E14 r.l. Signal assignments are presented in Table 20 on page 91.

The ^{13}C-NMR analysis agreed with the ^{1}H-NMR analysis. The content of β-O-4 structures diminishes in both CK and EK residual lignins as the unbleached kappa number is decreased and EK residual lignins had a greater content of β-O-4 structures than CK residual lignins at comparable kappa numbers.

Kraft-treated residual lignins

Kraft-treated residual lignins were also analyzed for β-O-4 structures by quantitative ^{13}C-NMR. The ^{13}C-NMR spectra of C28 r.l. and C28 r.l.-120 are compared in Figure 1.17. Significant structural changes have occurred, particularly in the chemical shift region of the spectra where aliphatic carbons are linked to oxygen (signals 8-11; see Table 20, page 91, for signal assignments). There is a significant decrease in the intensity of the signals due to β-O-4 structures (signals 8, 9, 11, and C3 in etherified guaiacyl structures), showing that further fragmentation of such linkages has occurred.

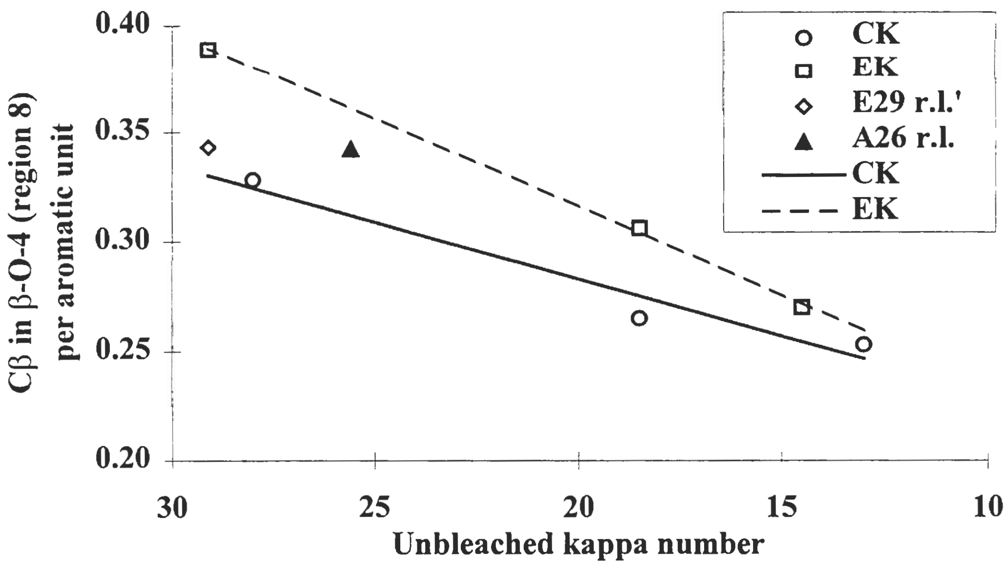


Figure 1.15. Content of Cβ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK residual lignins as determined by the integration of region 8 in the quantitative ^{13}C-NMR spectra. Also included are A26 r.l. and E29 r.l.'.

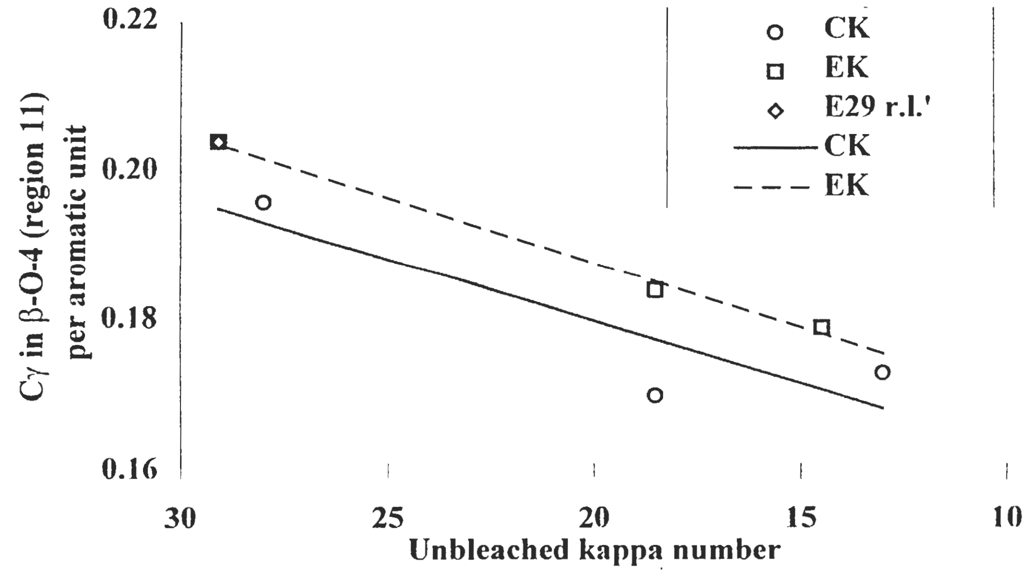


Figure 1.16. Content of $C\gamma$ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK residual lignins as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra. Also included are A26 r.l. and E29 r.l.'.

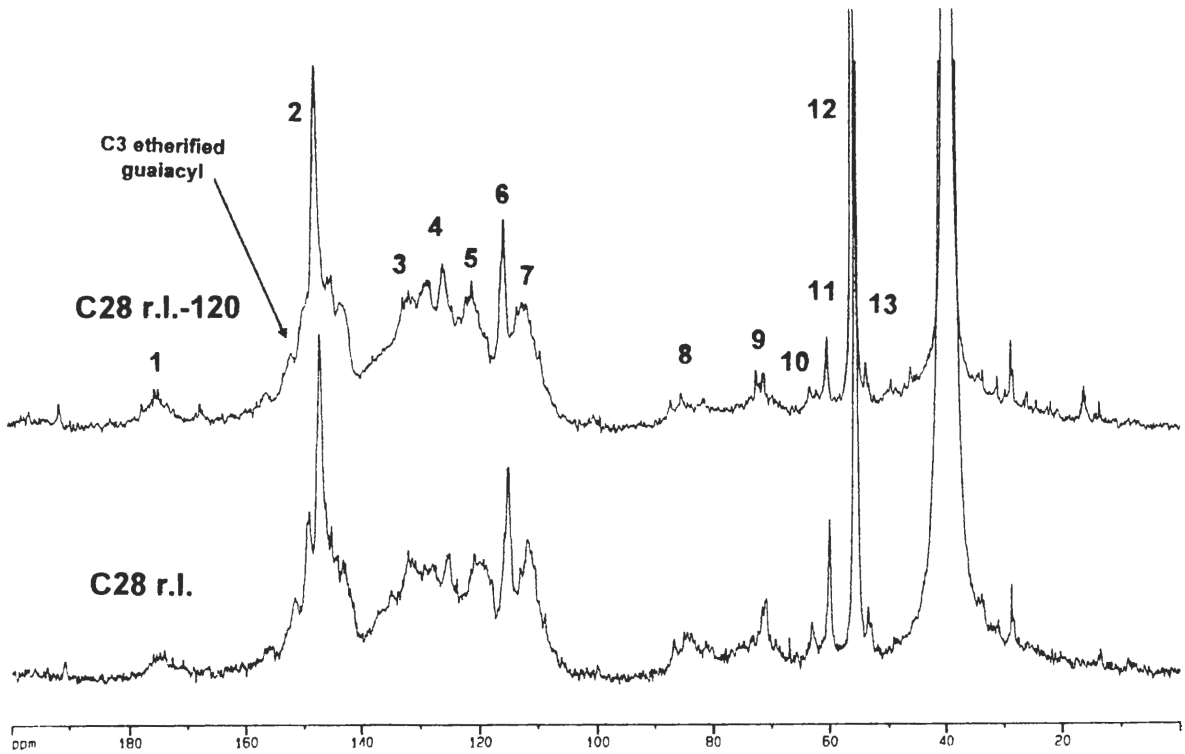


Figure 1.17. Quantitative ^{13}C-NMR spectra of residual lignin C28 before and after a two-hour treatment under kraft pulping conditions. Signal assignments are presented in Table 20 on page 91.

Figures 1.18 and 1.19 are bar graphs displaying the content of β-O-4 structures for the untreated and kraft-treated C28 r.l. and E14 r.l. The graphs show the dramatic loss in β-O-4 structures after the 15-minute treatment. After the 120-minute treatment, minimal additional fragmentation has occurred, indicating that during the first 15 minutes most of the reactive β-O-4 structures are fragmented.

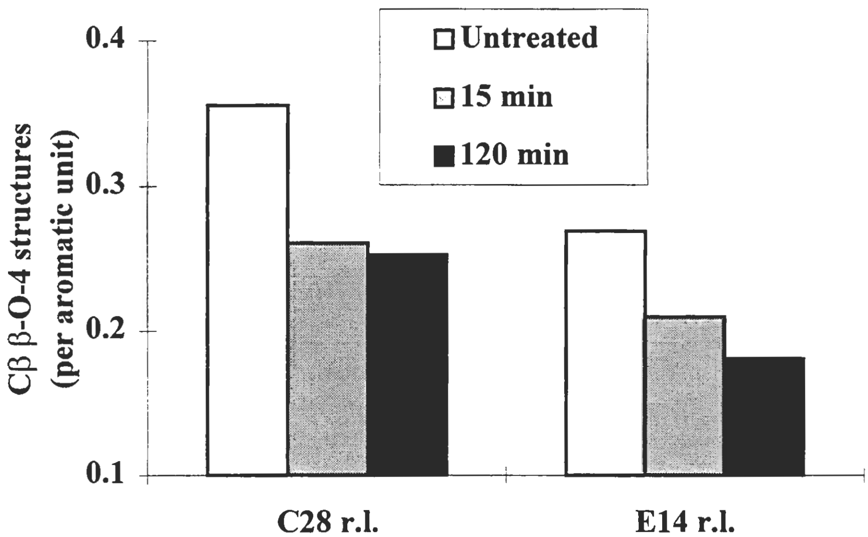


Figure 1.18. Content of Cβ in β-O-4 structures (expressed as number of C atoms per aromatic unit) in untreated and kraft-treated residual lignins C28 r.l. and E14 r.l. as determined by the integration of region 8 in the quantitative ^{13}C-NMR spectra.

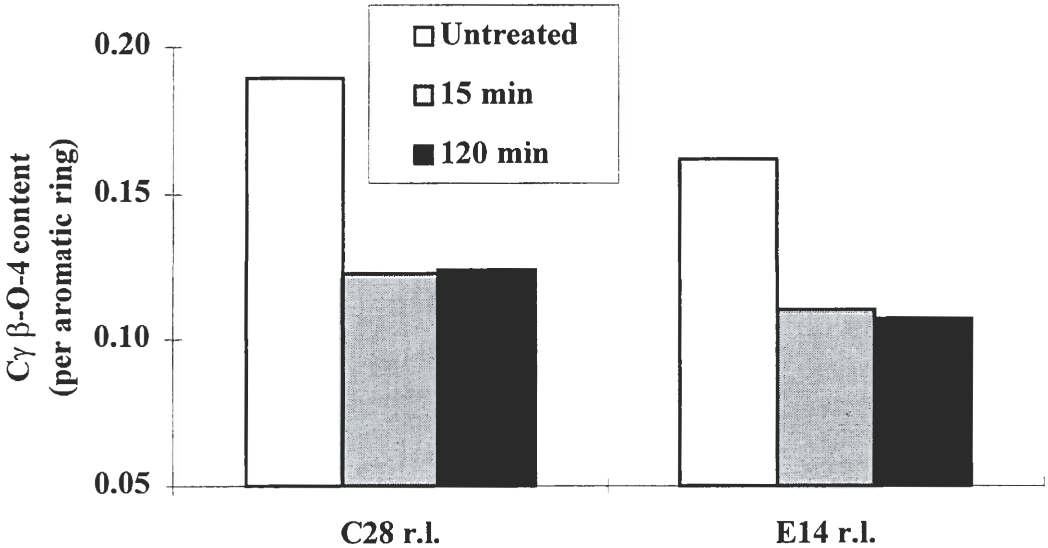


Figure 1.19. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) in untreated and kraft-treated residual lignins C28 r.l. and E14 r.l. as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra.

Discussion of results

The cleavage of β-O-4 structures degrades lignin into smaller more soluble fragments and also creates phenolic hydroxyl groups that increase the lignin's solubility and reactivity. During kraft delignification, the content of β-O-4 structures is greatly reduced as seen from our data and that of others (6). The decreasing content of β-O-4 structures gives additional credence to the increasing phenolic content being a result of additional β-O-4 cleavage.

The observation that there remains a detectable amount of β-O-4 structures even in the very low kappa residual lignin, after such a prolonged high temperature alkaline treatment, is somewhat surprising. The data from Figures 1.13, 1.15, and 1.16 do not seem to approach a minimal level of β-O-4 structures, as would be expected if some β-O-4 structures were resistant to cleavage. There is a continual, steady decrease in the content of these structures; cleavable β-O-4 linkages remain even in the 13 kappa residual lignin.

The kraft treatment experiments on the residual lignins indicated that some of the β-O-4 structures are cleavable while others are resistant. After a 15-minute treatment, there was a significant decrease in the content of such linkages. However, an additional 105 minutes resulted in minimal further fragmentation.

The residual lignins, even in the 13 kappa pulp, contain some β-O-4 structures that are still cleavable during kraft pulping, but there does seem to exist a definite quantity of structures that are resistant under pulping conditions. Delignification even at 13 kappa should still be possible because the fragmentation of this linkage can assist in the fragmentation and dissolution of the lignin. However, the very low content of these structures makes the residual lignin quite unreactive toward the pulping chemicals and no doubt assists in the poor selectivity of kraft pulping after prolonged cooking. Improving the selectivity of kraft pulping would therefore seem possible if a relatively high concentration of β-O-4 structures is maintained in the residual lignin during pulping. The results presented in Figures 1.14, 1.16, and 1.17 show that EK residual lignins have a higher concentration of β-O-4 structures at a given kappa number compared to CK residual lignins. A residual lignin that has a higher concentration of β-O-4 structures would seemingly be more reactive under pulping conditions. This is what has been observed in the EK and CK residual lignins and may partially explain the improved selectively of 'modified' kraft pulping.

Condensed Structures

Condensed structures is the term used to describe lignin that has an aryl or alkyl substituent at the C5, C6, and/or C1 position of the aromatic ring. Native wood lignin has some condensed-type structures such as the 5-5, β-5, β-1, and 4-O-5 structures, as depicted in Figure 1 in the Literature Review (page 5). Evidence for the formation of additional condensed structures during kraft pulping has also been suggested (11,41,43). Condensed structures are stable under kraft delignification conditions and are believed to be enriched in the residual lignin of kraft pulp.

The content of condensed structures in residual lignins has been estimated by employing two NMR techniques. ^{1}H-NMR is capable of quantifying the amount of aromatic protons in lignin, which is indicative of the degree of aromatic ring substitution and thus the degree of condensation. ^{13}C-NMR can quantify the amount of substituted aromatic carbon atoms, which is also indicative of the degree of aromatic ring substitution. All of these analyses and their results will be discussed below.

Aromatic proton content

Aromatic protons have a distinct, broad signal at approximately δ 7.0 ppm in the ^{1}H-NMR spectrum. The content of aromatic protons can be quantified by integrating this signal, although certain vinyl protons also contribute to the signal (see Table 6, page 60). The estimate of aromatic proton content made by integrating this signal will therefore be considered as an apparent aromatic proton content because most of this signal is due to aromatic protons, although a minor contribution is likely coming from vinyl protons (33).

Figure 1.20 is a plot of the apparent aromatic proton content versus the unbleached kappa number for various residual lignin acetates. Figure 1.21 is a similar plot of the corresponding underivatized residual lignins. Both figures clearly show the decrease in aromatic proton content of the residual lignins with decreasing kappa numbers.

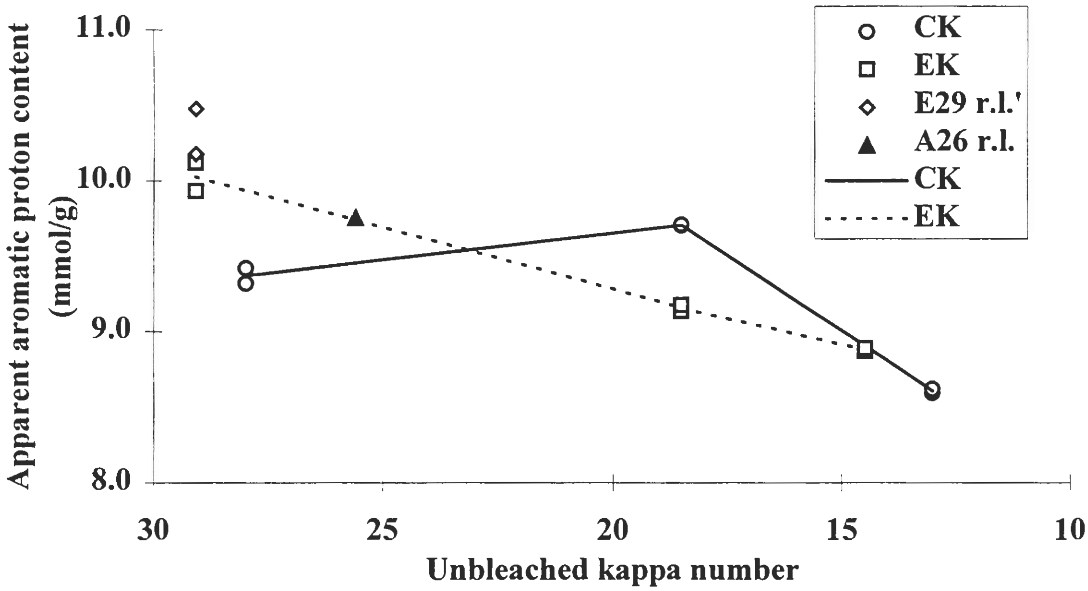


Figure 1.20. Apparent aromatic proton content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of lignin acetates. Also included are A26 r.l. and E29 r.l.'.

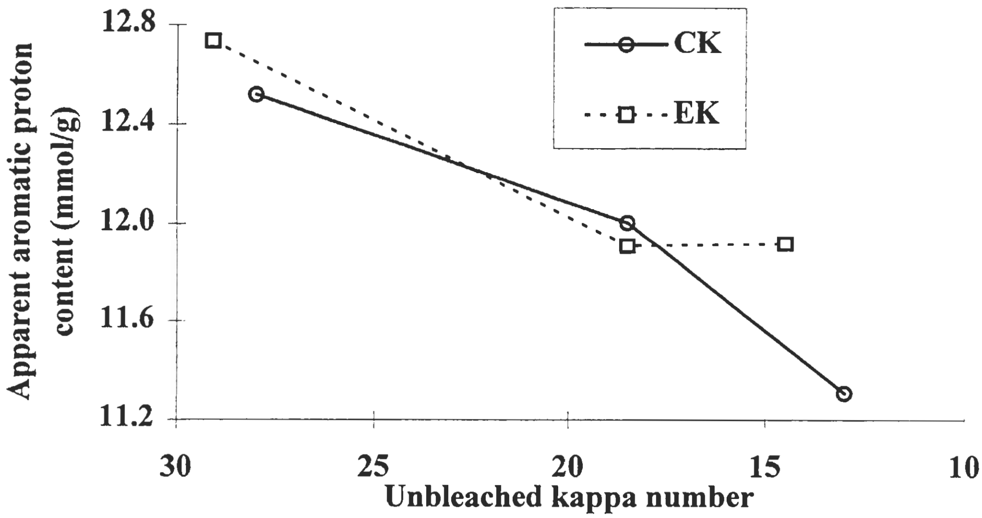


Figure 1.21. Apparent aromatic proton content versus unbleached kappa number for various CK and EK residual lignins as determined by ^{1}H-NMR of underivatized lignins.

Substituted aromatic carbons

Substituted aromatic carbons have ^{13}C-NMR chemical shifts in the range of δ 160 to 123 ppm (regions 2-4 in Table 21 page 94). Integrating this region in the ^{13}C-NMR spectra of residual lignin allows for the quantitative determination of substituted aromatic carbon atoms. Figure 1.22 is a plot of the substituted aromatic content versus the unbleached kappa number for EK and CK residual lignins. The graph shows that as the kappa number is decreased the residual lignins contain more substituted aromatic rings. The figure also shows that the EK residual lignins have less substituted aromatic rings than CK residual lignins at comparable kappa numbers.

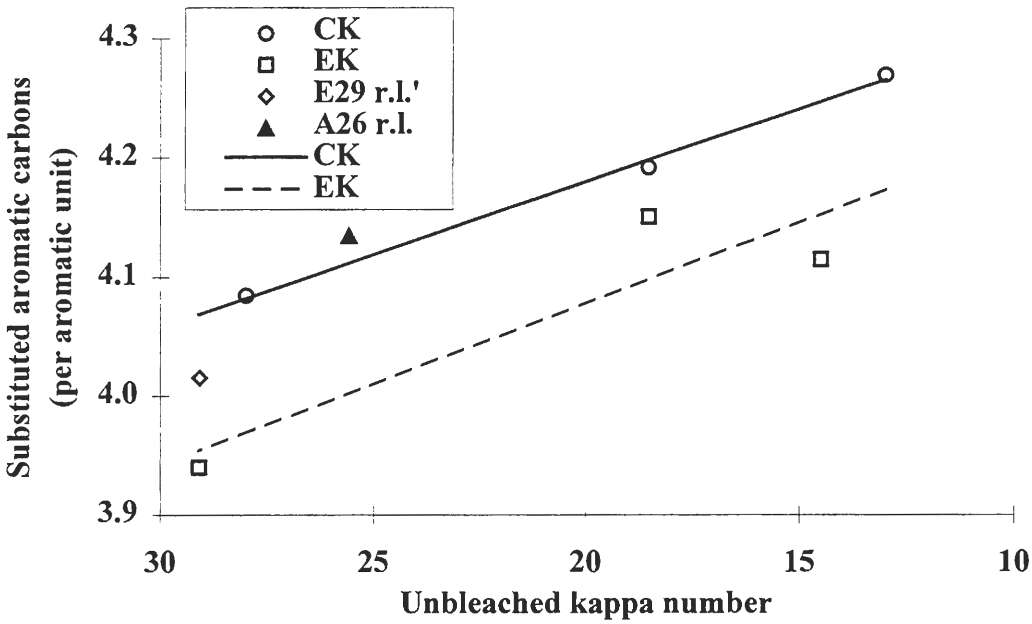


Figure 1.22. Content of substituted aromatic carbon atoms (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for CK and EK residual lignins as determined by ^{13}C-NMR. Also included are A26 r.l. and E29 r.l.'.

Kraft-treated residual lignins

The residual lignins treated under kraft pulping conditions were analyzed for the presence of condensed structures by the underivatized ^{1}H-NMR and ^{13}C-NMR techniques. The apparent aromatic proton content of the these treated residual lignins is presented in Figure 1.23. The bar graph shows that, for both residual lignins, there was an initial increase in the aromatic proton content after the 15-minute treatment, then a decrease after the additional 105 minutes.

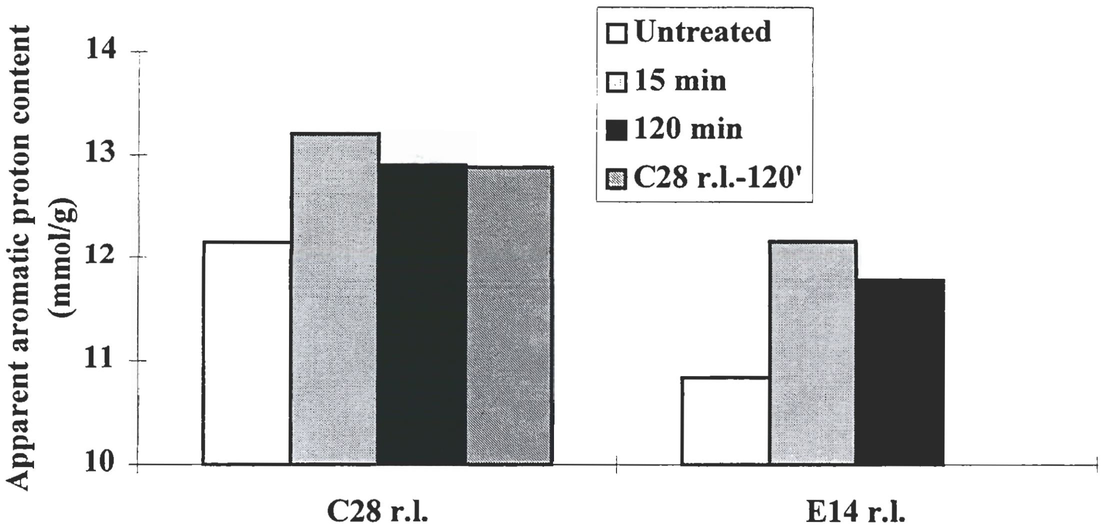


Figure 1.23. Apparent aromatic proton content in untreated and kraft treated residual lignins C28 r.l. and E14 r.l. as determined by ^{1}H-NMR analysis of underivatized lignins.

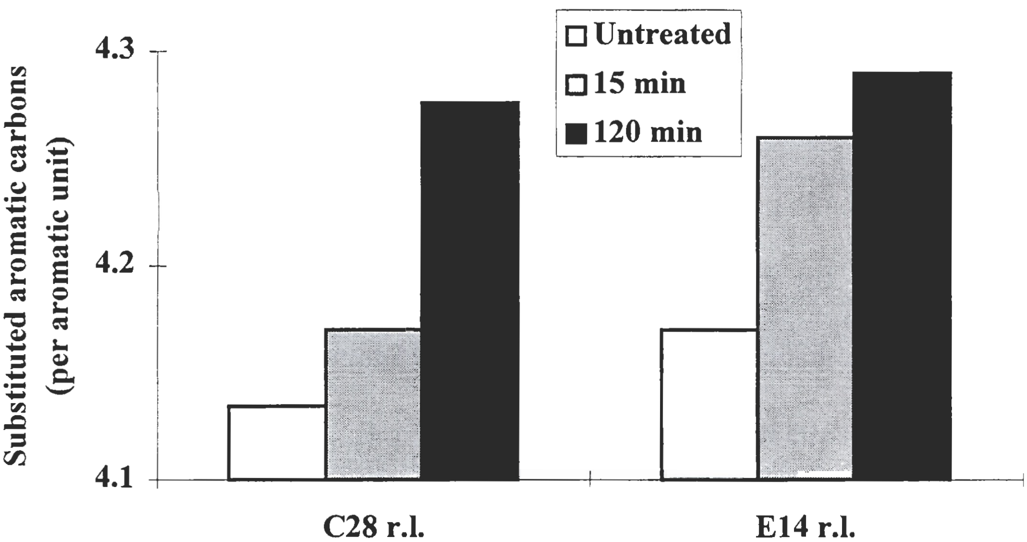


Figure 1.24. Content of substituted aromatic carbon atoms (expressed as number of carbon atoms per aromatic unit) in untreated and kraft treated residual lignins C28 r.l. and E14 r.l. as determined by quantitative ^{13}C-NMR analysis.

The ^{13}C-NMR analysis of the same kraft-treated residual lignins indicated a significant increase in the content of substituted aromatic carbons indicative of the formation of condensed structures (Figure 1.24).

Discussion of results

The results from the analysis of residual lignin for condensed structures by ^{1}H-NMR and ^{13}C-NMR proved to be very informative. The ^{1}H-NMR analysis showed that the apparent content of aromatic protons decreased as delignification proceeded, indicating an increase in the amount of condensed structures. This result was supported by the ^{13}C-NMR analysis, which indicated an increase in the amount of condensed structures, as it showed the content of substituted aromatic carbons increased. Whether these condensed structures are formed during pulping or are enriched in the residual lignin by the selective dissolution of uncondensed lignin during pulping cannot be elucidated from this analysis. Gellerstedt has found in his flow-through studies of kraft pulping that the lignin going into solution at the end of the cook is more condensed than the lignin being dissolved early during the cook, suggesting that there is a selective dissolution of uncondensed lignin (9). The selective dissolution of uncondensed lignin may be causing the residual lignin to become more condensed as pulping is prolonged.

The results from the ^{1}H-NMR analysis of kraft-treated residual lignins found that when residual lignin was dissolved into the pulping liquor and heated at 170°C for 15 minutes there was an increase in the apparent aromatic proton content. The increase can be explained by the formation of unsaturated structures containing vinyl protons, which also have chemical shifts in the region integrated for the aromatic protons. Unsaturated structures such as stilbenes are known to be created during kraft delignification and could certainly be created during the kraft treatment. An additional 105 minutes at temperature caused a decrease in the aromatic proton content, suggesting that condensation reactions had occurred. The ^{13}C-NMR analysis found that the content of substituted aromatic carbons increased after the 15- and 120- minute kraft treatments, which is indicative of condensation reactions occurring under homogeneous conditions.

The analysis of the kraft-treated residual lignins showed that residual lignin can undergo condensation reactions when reacted under homogenous conditions. Whether or not condensation reactions occur in the residual lignin during pulping cannot be resolved from this analysis; however, the data do show that condensation reactions may be taking place in the dissolved lignin during pulping. This will be discussed in more detail in Chapter 2 on kraft lignin.

CONCLUSIONS

A structural analysis of CK and EK residual lignins isolated from pulps with different kappa numbers has revealed some significant differences in the structure of these residual lignins. As delignification proceeds, there is a decrease in aliphatic hydroxyl groups, an increase in phenolic hydroxyl groups, an increase in carboxylic acid groups, a decrease in β-O-4 structures, and an increase in condensed structures. The differences were quite significant, considering that the difference in kappa number between these pulps was approximately 15 units. The significant changes occurring as delignification is prolonged, such as the diminishing content of β-O-4 structures and increasing content of condensed structures, would seemingly aid in the unreactive nature of the residual lignin toward pulping chemicals. The low content of cleavable β-O-4 structures and the presence of alkali-stable condensed aromatic structures in lower kappa number pulp hinder the ability of the lignin to be fragmented and dissolved. The poor selectivity of kraft pulping can therefore be partly attributed to the unreactive nature of residual lignin.

Structural differences between the CK and EK residual lignins at comparable kappa numbers were found that may, in part, explain the improved delignification selectivity of EK pulping. At comparable kappa numbers, the EK residual lignins had a higher content of β-O-4 structures and a lower content of condensed aromatic structures, which would indicate that EK residual lignins are in a more reactive form than the CK residual lignins perhaps allowing for a greater degree of delignification to occur during EK pulping. It may be that under the EK conditions the residual lignin did not react to the same extent as the CK residual lignin. The harsher conditions used during CK pulping resulted in a more modified structure; i.e. a lower content of β-O-4 structures and a higher content of condensed structures. The higher content of condensed structures may be a result of more condensation reactions occurring during CK pulping. These condensed products may then be enriched in the residual lignin.

Lignins that were isolated from the unbleached pulps and treated under kraft pulping conditions were fairly reactive, particularly during the first 15 minutes of the reaction. During this time, the residual lignins showed dramatic losses in β-O-4 structures and increases in the phenolic hydroxyl groups and condensed structures. After an additional 105 minutes, the lignin appears to approach a structure that is no longer reactive with the pulping chemicals. Because some of the β-O-4 linkages are quite resistant to kraft pulping conditions, additional fragmentation and dissolution of this lignin would be difficult.

Although residual lignin is still somewhat reactive under pulping conditions, it seems to be unreactive enough to cause the poor selectivity. Improving the selectivity seems to be possible by modifying the pulping conditions such that a reactive lignin structure is maintained in the fiber, which can allow the cook to be extended to greater levels of delignification. EK pulping produces pulps with a residual lignin that has retained a more reactive structure at a given kappa number compared to CK pulping. The process conditions of EK pulping that may be influencing the reactivity of the lignin include a more leveled out alkali profile, lower cooking temperature, and lower dissolved lignin concentration during the final stage of the cook. These conditions may be causing a more efficient dissolution of lignin. The results from this study suggest that by further optimizing the conditions an even greater delignification selectivity during kraft pulping is possible.

CHAPTER 2. ANALYSIS OF DISSOLVED LIGNIN DURING KRAFT PULPING

INTRODUCTION

An alternative method of characterizing the reaction mechanisms involved in kraft pulping is to characterize dissolved (kraft) lignins. Kraft lignins have been the subject of many investigations, as described in the Literature Review. An analysis of the structural changes occurring to the CK and EK kraft lignins during the cook provides further insight into the chemistry of kraft delignification and on the differences between CK and EK pulping.

The kraft lignins isolated from the black liquors (listed in Table 14 in the Materials and Methods section page 83) were subjected to various NMR analyses in a similar manner as the residual lignins. The kraft lignins analyzed included two after impregnation (ai) kraft lignins (C18-ai and E14-ai), one after co-current (eo1) kraft lignin (E14-eo1), and seven end of cook (eoc) kraft lignins (C28-eoc, C18-eoc, C13-eoc, C13-eoc' (a replicated isolation of C13-eoc), E29-eoc, E18-eoc, and E14-eoc). The eoc lignins for the CK cooks are a composite of all the lignin dissolved during the cook. The eoc lignin for the EK cooks is not a composite of all the lignin dissolved during the cook because the counter-current stage extracts black liquor during the cook. The eoc lignin from the EK cooks is therefore more representative of the lignin dissolved later in the cook.

The Results and Discussion section of this chapter will be divided into sub-sections dealing with a specific functional group and/or structural feature, as was done in the previous chapter on residual lignins. The structural features of the kraft lignins that were monitored were phenolic groups, β-O-4 structures, and condensed structures. The results from an experiment in which an ai kraft lignin was treated under kraft pulping conditions will also be presented. The purpose of this experiment was to determine how the structure of a lignin that is dissolved early during the cook is altered during pulping. The differences observed between CK and EK kraft lignin will then be discussed and interpreted in terms of the different pulping conditions used. Finally, a comparison between kraft and residual lignins will be made, providing further insights into the chemical changes of lignin during kraft delignification.

RESULTS AND DISCUSSION

Phenolic Hydroxyl Content

The phenolic hydroxyl contents of the kraft lignins were determined by ^{1}H-NMR analysis of lignin acetates (Figure 2.1). Table 2.1 contains the results for the ai and eo1 kraft lignins (these data were not placed on the graph because the kappa numbers at this stage of the cook were unknown). Replicate spectra were recorded for each kraft lignin, as shown in Figure 2.1.

Table 2.1. Phenolic hydroxyl content of the ai and eo1 kraft lignins as determined by ^{1}H-NMR of kraft lignin acetates.

Kraft lignin ID	Phenolic hydroxyl content (mmol/g)†
C18-ai	2.34
E14-ai	2.31
E14-eo1	2.70

†Average of two samples

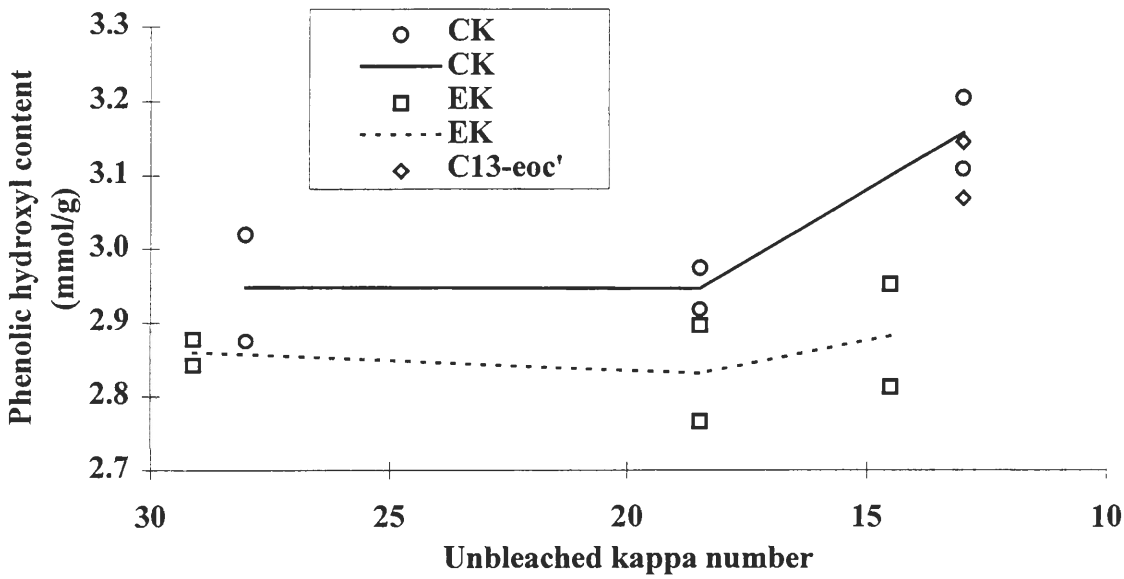


Figure 2.1. Phenolic hydroxyl content for various CK and EK end of cook kraft lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR. Also included in the analysis is C13-eoc'.

The ai kraft lignins have a low phenolic content, probably similar to the native wood lignin because this lignin is extracted from the wood during the initial part of the cook. As the cook proceeds, there is an increase in the phenolic hydroxyl content, as seen by the fact that the eoc kraft lignins have a content that is significantly higher than the ai lignins. Some differences exist between the CK and EK eoc kraft lignins. The EK kraft lignins have a lower phenolic hydroxyl content than the CK kraft lignins at comparable extents of delignification. Also, the CK kraft lignins undergo an increase in the phenolic hydroxyl content as delignification is extended from 18 to 13. The EK kraft lignins, on the other hand, do not show the same effect, as the phenolic content stays relatively constant as delignification proceeds. The different phenolic contents indicate that the different process conditions of EK pulping are influencing the phenolic content of the kraft lignins. This question will be addressed further after other structural features of the lignin have been analyzed.

β-O-4 Structures

^{1}H-NMR analysis

The content of β-O-4 structures in the kraft lignins has been estimated by the ^{1}H-NMR analysis of lignin acetates (Figure 2.2). Table 2.2 is a similar analysis of the ai and eo1 kraft lignins.

Table 2.2. Content of β-O-4 structures in the ai and eo1 kraft lignins as determined by ^{1}H-NMR of kraft lignin acetates.

Kraft lignin ID	β-O-4 content (mmol/g)†
C18-ai	1.01
E14-ai	0.90
E14-eo1	0.73

†Average of two samples

Not surprisingly, the content of β-O-4 structures is shown to significantly decrease from a relatively high value in the ai kraft lignins to a very low value in the eoc lignins of low kappa pulps. There is a continual decrease in the content of these structures except from the C18 to the C13, which were found to be quite similar. A detectable amount of β-O-4 structures remains in the low kappa kraft lignins, suggesting that some β-O-4 structures are stable under prolonged pulping conditions. The stability of such linkages can be considered detrimental to kraft pulping because the linkage represents a site of possible fragmentation, which is a major goal of any delignification process. Chapter 1 also suggested that resistant β-O-4 structures exist in lignin.

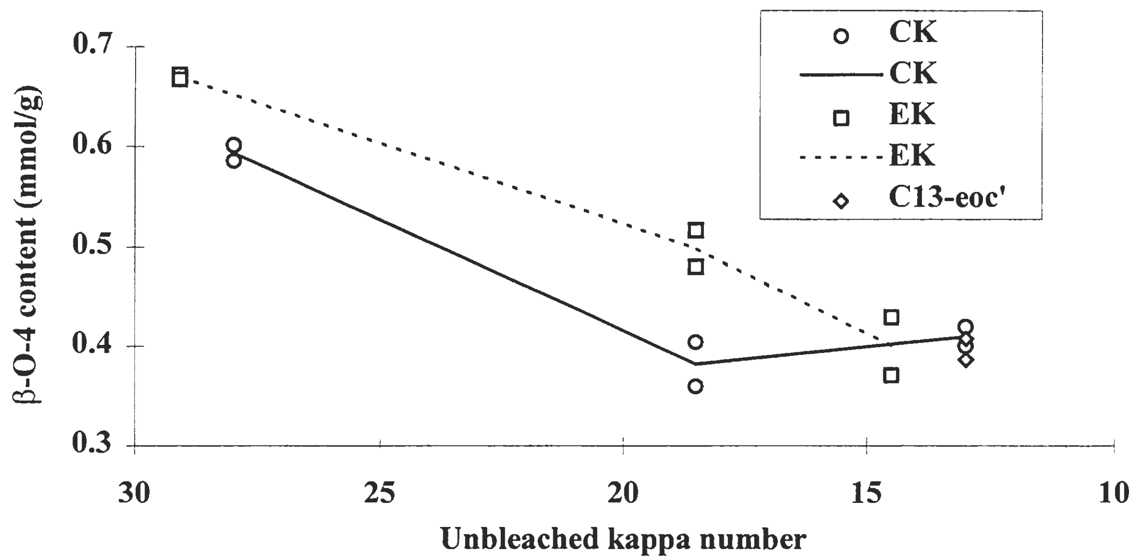


Figure 2.2. β-O-4 content of various CK and EK end of cook kraft lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of lignin acetates. Also included in the analysis is C13-eoc'.

The ^{1}H-NMR analysis in Figure 2.2 also found that the content of β-O-4 structures in EK kraft lignins was higher than CK kraft lignins at 28 and 18 kappa numbers. The different content of these structures in the EK and CK kraft lignins again suggests that the different process conditions used during EK pulping are influencing the structural features of the lignin.

^{13}C-NMR analysis

The quantitative ^{13}C-NMR analysis of the kraft lignins also allowed for the quantification of the β-O-4 structures by integrating regions 8 and 11 of the ^{13}C-NMR spectra. Figures 2.3 and 2.4 are plots of the contents of Cβ and Cγ in β-O-4 structures versus the unbleached kappa number. Tables 2.3 and 2.4 contain the results from the similar analysis of the ai and eo1 kraft lignins.

Table 2.3. Content of Cβ in β-O-4 structures in the ai and eo1 kraft lignins as determined by integrating region 8 in the quantitative ^{13}C-NMR.

Kraft lignin ID	Content of Cβ in β-O-4 (per aromatic unit)
C18-ai	0.349
E14-ai	0.415
E14-eo1	0.215

Table 2.4. Content of Cγ in β-O-4 structures in the ai and eo1 kraft lignins as determined by integrating region 11 in the quantitative ^{13}C-NMR.

Kraft lignin ID	Content of Cγ in β-O-4 (per aromatic unit)
C18-ai	0.280
E14-ai	0.323
E14-eo1	0.165

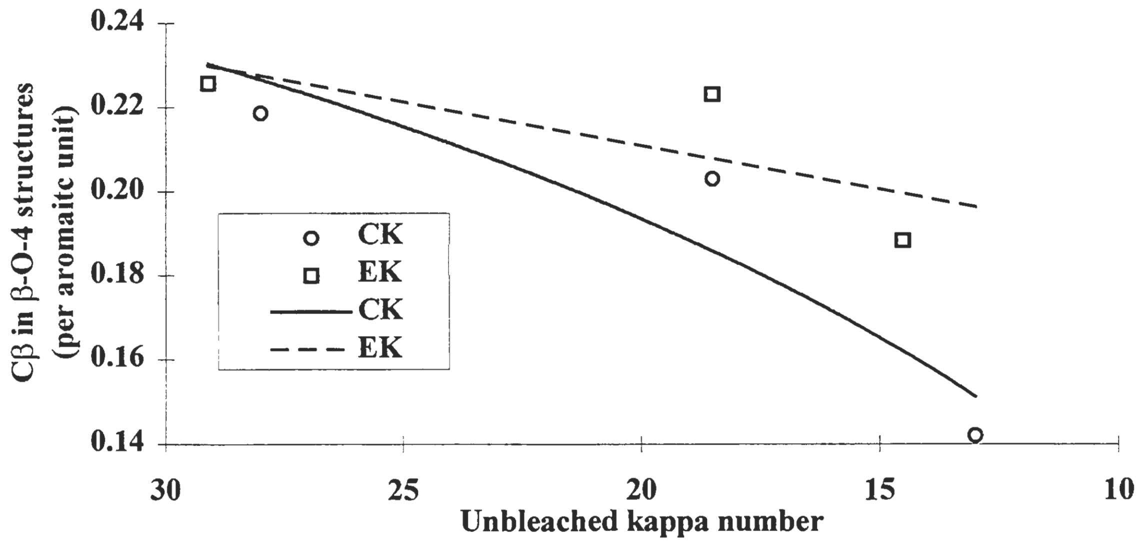


Figure 2.3. Content of Cβ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK eoc kraft lignins as determined by the integration of region 8 in the quantitative ^{13}C-NMR spectra.

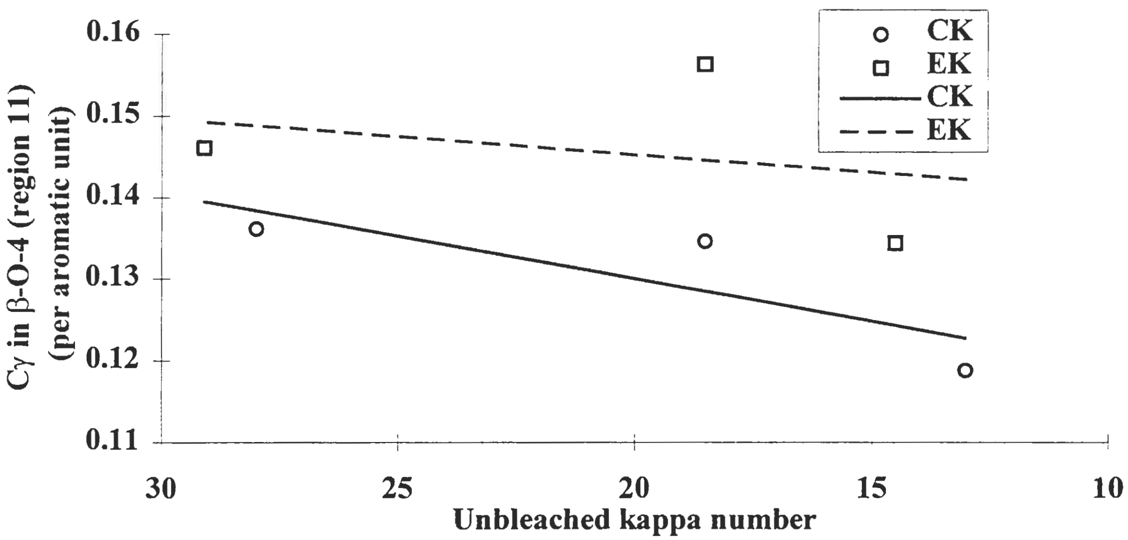


Figure 2.4. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK end of cook kraft lignins as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra.

The ^{13}C-NMR analysis substantiates the ^{1}H-NMR analysis, as it also found that the β-O-4 content of the kraft lignins decreased as delignification proceeded and the β-O-4 content of the EK kraft lignins was greater than the CK kraft lignins at comparable extents of delignification.

Condensed Structures

Condensed structures in the kraft lignins were analyzed indirectly by quantifying the content of aromatic protons by ^{1}H-NMR and substituted aromatic carbons by ^{13}C-NMR.

^{1}H-NMR analysis

Figure 2.5 is a plot of the aromatic proton content of the various eoc kraft lignins versus the unbleached kappa number. Table 2.5 contains the results from the similar analysis of the ai and eo1 kraft lignins.

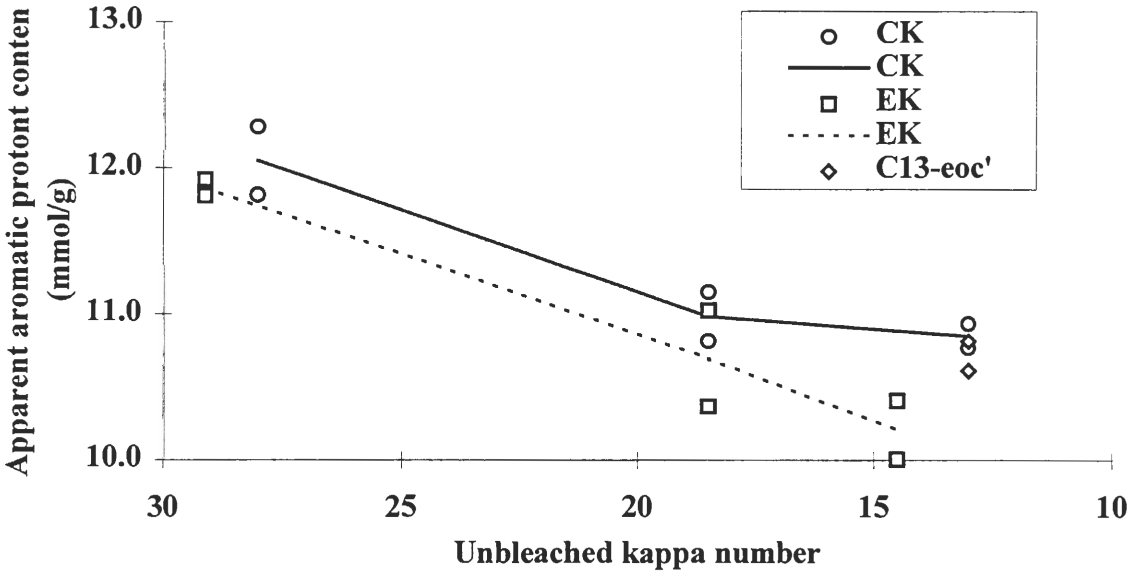


Figure 2.5. Apparent aromatic proton content of various CK and EK end of cook kraft lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of lignin acetates. Also included in the analysis is C13-eoc'.

Table 2.5. Aromatic proton content of the ai and eo1 kraft lignins as determined by ^{1}H-NMR of kraft lignin acetates.

Kraft lignin ID	Apparent aromatic proton content (mmol/g)†
C18-ai	10.98
E14-ai	10.44
E14-eo1	12.23

†Average of two samples

Figure 2.5 shows that there is a decrease in the apparent aromatic proton content in the eoc lignins as delignification is prolonged. The decrease indicates that the aromatic rings in the lignin are becoming more substituted (condensed). The apparent aromatic proton content of the ai lignins is quite low compared to the eo1 and eoc lignins. The low content is likely due to the absence of unsaturated structures, such as stilbenes and vinyl ethers, which can contribute to the apparent aromatic proton content. Such structures are known to be formed during kraft pulping, but apparently, the ai lignins have a low quantity of these structures. Their formation seems to require a prolonged time under the high temperature alkaline environment.

In general, it was found that EK kraft lignins had lower apparent aromatic proton contents compared to CK kraft lignins at similar degrees of delignification. Because the apparent aromatic proton content is influenced by both aromatic protons and olefinic protons, the lower content in EK lignins may be due to either a higher content of condensed structures and/or a lower content of unsaturated structures.

^{13}C-NMR analysis

Figure 2.6 is a plot of the substituted aromatic carbon content of the eoc kraft lignins versus the unbleached kappa number. Table 2.6 contains the results from the similar analysis of the ai and eo1 kraft lignins.

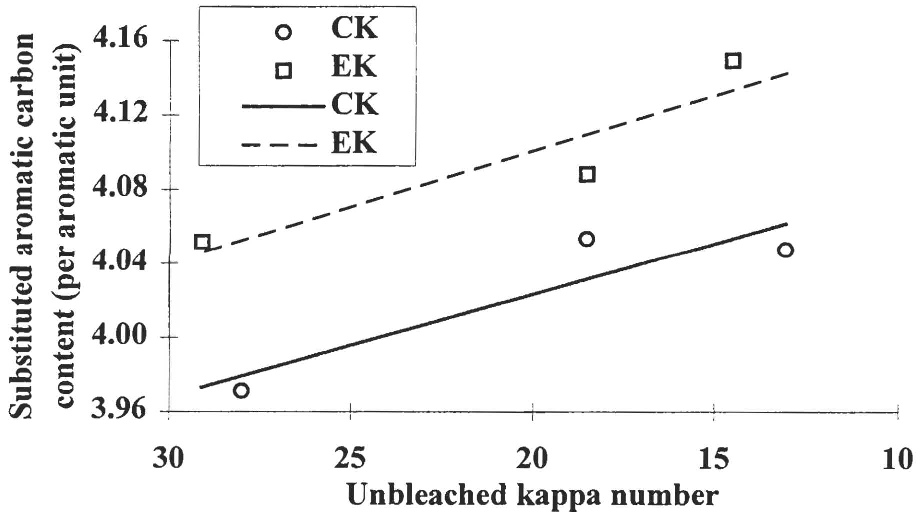


Figure 2.6. Content of substituted aromatic carbons (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for various CK and EK end of cook kraft lignins as determined by the integration of region 2-4 in the quantitative ^{13}C-NMR spectra.

Table 2.6. Content of substituted aromatic carbons in the ai and eo1 kraft lignins as determined by integrating regions 2-4 in the quantitative ^{13}C-NMR.

Kraft lignin ID	Content of substituted aromatic carbons (per aromatic unit)
C18-ai	3.81
E14-ai	3.74
E14-eo1	3.95

Figure 2.6 and Table 2.6 show that the content of substituted aromatic carbons increases in the kraft lignins as delignification proceeds, from a low content of 3.8 in the ai lignin to a high of 4.15 in the low kappa E14-eoc lignin. The increase implies that these lignins contain increasing contents of condensed structures. The data also show

that at a given kappa number the content of substituted aromatic carbons is greater in EK kraft lignins compared to CK kraft lignins.

In general, the analysis of condensed structures by ^{1}H-NMR and ^{13}C-NMR gave similar results. In addition to each analysis showing that as delignification proceeds the kraft lignins become increasingly condensed, the results also show that eoc EK kraft lignins have a slightly greater content of condensed structures compared to eoc CK kraft lignins at comparable degrees of delignification.

Kraft Treatment of E14-ai

An after impregnation kraft lignin (E14-ai) was treated for 2 hours under kraft pulping conditions and the modified structure analyzed by quantitative ^{13}C-NMR. The objective of this experiment was to understand the changes occurring in the dissolved lignin as the cook proceeds. The lignin was isolated from a black liquor that was extracted very early during the cook, with the expectation that the modification of this lignin from its native state was minor. Understanding how this lignin is altered during pulping is impossible from the analysis of the eoc kraft lignins because the later is a collective sample of lignin that is extracted from the wood during the length of the cook. The eoc lignin is therefore a collection of lignin that is dissolved early in the cook and has undergone significant structural modification during the cook and the lignin that was dissolved later in the cook that is more representative of the residual lignin remaining in the pulp.

Comparisons between the untreated and treated lignins by quantitative ^{13}C-NMR provide information about the structural modification lignin dissolved early during the cook undergoes during pulping. Figure 2.7 contains the ^{13}C-NMR spectra of the E14-ai kraft lignin before and after its 2 hour treatment under kraft pulping conditions. The spectra clearly show that significant changes have occurred to the lignin structure, including the cleavage of aryl ether linkages (decrease in signals 8, 9, 11, and C3 in etherified guaiacyl structures). A significant change in the aromatic region is also observed. The intensity of signal 4 was found to dramatically increase as a result of the kraft treatment. Model compound studies have found that both C5 substituted aromatic carbons and certain vinyl carbons can contribute to this signal. The formation of structures containing these types of carbon atoms has been suggested to occur during kraft pulping, and the results here support that such reactions are occurring. However, whether or not these signals are coming from substituted C5 carbons or vinyl carbons cannot be determined from this analysis alone. The results from the quantitative analysis are presented in Table 2.7.

Table 2.7. Results from quantitative ^{13}C-NMR of E14-ai before and after a 2 hour treatment under kraft pulping conditions. All numbers are expressed as number of carbon atoms per aromatic ring.

Lignin ID	Cβ in β-O-4 (region 8)	Cγ in β-O-4 (region 11)	Substituted aromatic carbons
E14-ai	0.42	0.32	3.84
E14-ai-120	0.16	0.11	4.18

The content of β-O-4 structures was dramatically reduced after the 2-hour kraft treatment. The fact that the content of β-O-4 structures decreased is not surprising

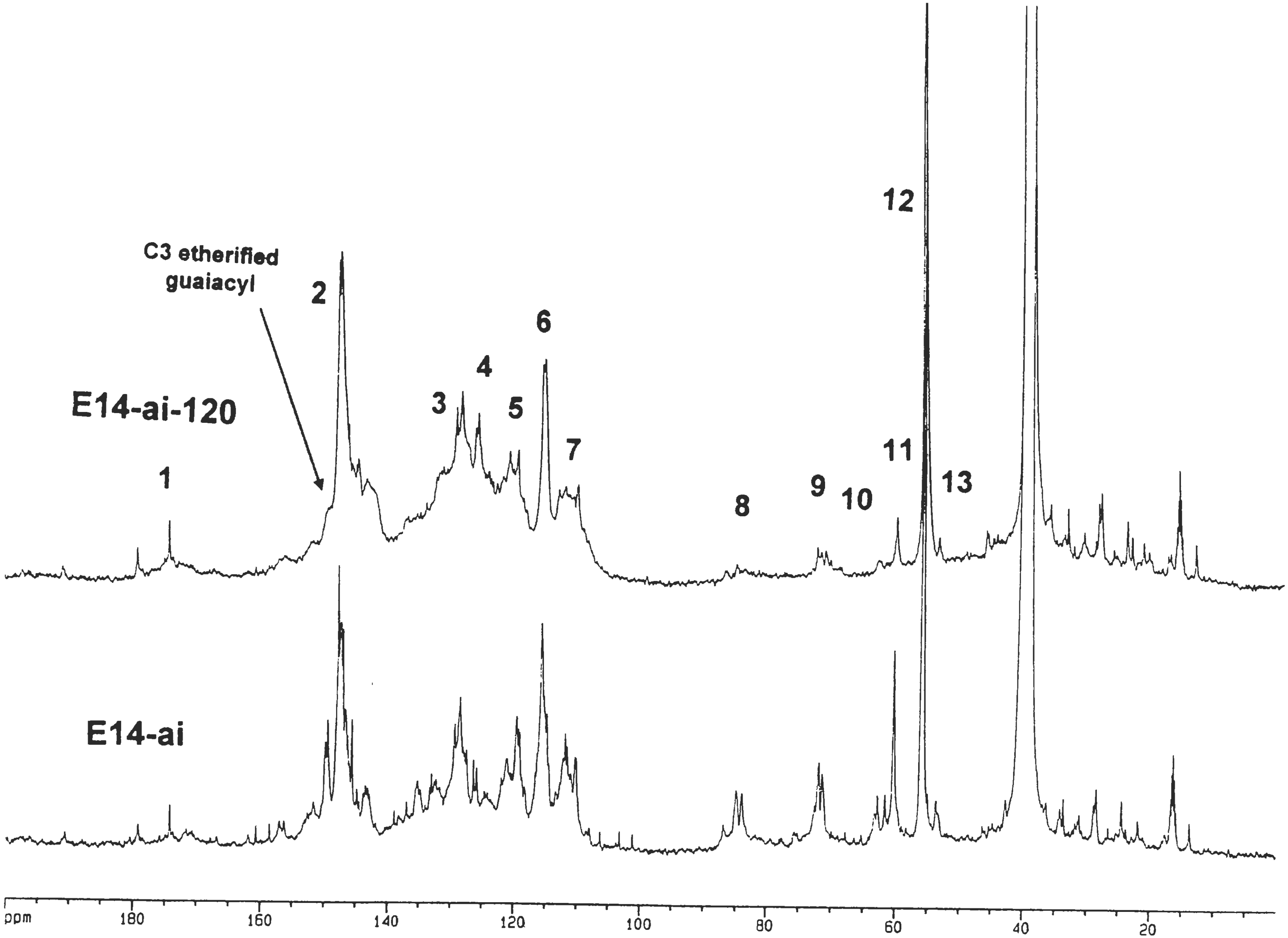


Figure 2.7. Quantitative ^{13}C-NMR spectra of E14-ai before and after a 2-hour treatment under kraft pulping conditions. Signal assignments are presented in Table 20 on page 91.

because the eoc kraft lignins have a substantially lower content of such structures compared to the ai kraft lignins. However, the fact that there remains a quantity of such structures that are resistant to pulping conditions was unanticipated. The result is also similar to the analysis of kraft-treated residual lignins in which there remains a quantity of β-O-4 structures that are resistant to pulping conditions. The resistant structures were found to be lower in the kraft lignins compared to the residual lignins (compare Figure 1.20 (page 122) to Table 2.7), indicating that the residual lignin may contain more unreactive β-O-4 structures. Even though the content of the structures appear to reach a floor level in the residual lignins treated under kraft pulping conditions, a longer treatment may result in additional fragmentation. A more definitive conclusion on the resistance of these structures can only be made after further study under prolonged conditions.

The residual content of β-O-4 structures in the eoc kraft lignins can most likely be thought of as a combination of resistant β-O-4 structures and reactive/sensitive β-O-4 structures. The latter probably dissolved toward the end of the cook and are still cleavable under the pulping conditions; yet, they were not exposed to the pulping chemicals long enough to be cleaved.

Table 2.7 shows that the content of substituted aromatic structures substantially increased in the kraft-treated ai kraft lignin. The increase is likely a result of the formation of condensed structures.

Comparison between CK and EK Kraft Lignins

The analysis on the structural features (phenolic groups, β-O-4 structures, and condensed structures) of the kraft lignins produced from CK and EK pulping indicated differences between the two types of lignins. The EK pulps used in this study were prepared by employing the following conditions that differ from conventional pulping:

- A more uniform alkali profile (splitting the white liquor addition)
- Lower concentration of dissolved lignin at the end of the cook (counter-current cooking stage in which black liquor is extracted during the simultaneous addition of weak white liquor)
- Lower maximum cooking temperature

At comparable extents of delignification, the CK kraft lignins were shown to have a higher phenolic hydroxyl content, a lower content of β-O-4 structures (at 29 and 18 kappa), and a slightly lower content of condensed structures.

The milder conditions employed during EK pulping and the counter-current cooking stage may be responsible for the observed structural differences. The milder EK conditions, together with the spilt white liquor addition, may result in a less modified lignin structure. A highly modified lignin would be expected to have a higher phenolic hydroxyl content, a lower β-O-4 content, and a higher content of condensed structures. All of these structural features are observed in the comparison between CK and EK kraft lignins except that the EK lignins were found to be more condensed.

The differences between CK and EK eoc kraft lignins may also be caused by the counter-current cooking conditions employed during EK pulping. The eoc CK kraft lignins are a collection of all the lignin dissolved during the cook. The EK eoc kraft lignins, however, are a collection of lignins that are enriched with lignin that is removed from the chips toward the end of the cook due to the counter-current stage (which occurs toward the end of the cook). During the counter-current stage, black liquor is extracted while weak white liquor is simultaneously added. The composition of the kraft lignin is therefore affected; the concentration of kraft lignin that is dissolved early in the cook is reduced, while the concentration of kraft lignin dissolved later in the cook is increased. Gellerstedt has shown in his flow-through studies of kraft pulping that the lignin being dissolved toward the end of the cook is more condensed than the lignin dissolved at the beginning (9). In Chapter 1 of the Results and Discussion section, it was also shown that as delignification is extended the content of condensed structures increases. These findings could explain the differences between EK and CK eoc kraft lignins. The EK eoc kraft lignins are composed of a greater content of lignin dissolved later on during the cook. Such a lignin would have a greater composition of condensed structures. The CK kraft lignins, on the other hand, are composed of lignin dissolved throughout the whole cook and would therefore contain more of the uncondensed lignin that is dissolved early on in the cook, although this lignin may undergo condensed reactions.

The counter-current cooking stage may also influence the content of β-O-4 and phenolic groups in the eoc lignins. The residual lignin has a higher content of β-O-4 structures and lower content of phenolic hydroxyl groups compared to kraft lignins, as will be shown in the next section. If EK kraft lignins are enriched with structures dissolved later during the cook, then these lignins would be expected to have a higher content of β-O-4 structures and a lower content of phenolic groups.

Comparison between Residual and Kraft Lignins

Because similar NMR analyses were performed on both the residual and kraft lignins, an interesting and informative comparison between the two types of lignin can easily be made. These additional comparisons, which elucidate structural differences between the two types of lignin, can also provide some insight into the chemistry of kraft delignification.

Figure 2.8 is a plot of the phenolic hydroxyl content of various CK and EK eoc kraft and residual lignins versus the unbleached kappa number. The phenolic content was determined by the ^{1}H-NMR analysis of the lignin acetates. The graph shows that the phenolic hydroxyl content of the kraft lignins is significantly higher than the residual lignins, as has already been demonstrated in the literature (8). This observation has been interpreted as the lignin requiring a certain amount of phenolic groups before the lignin can be dissolved.

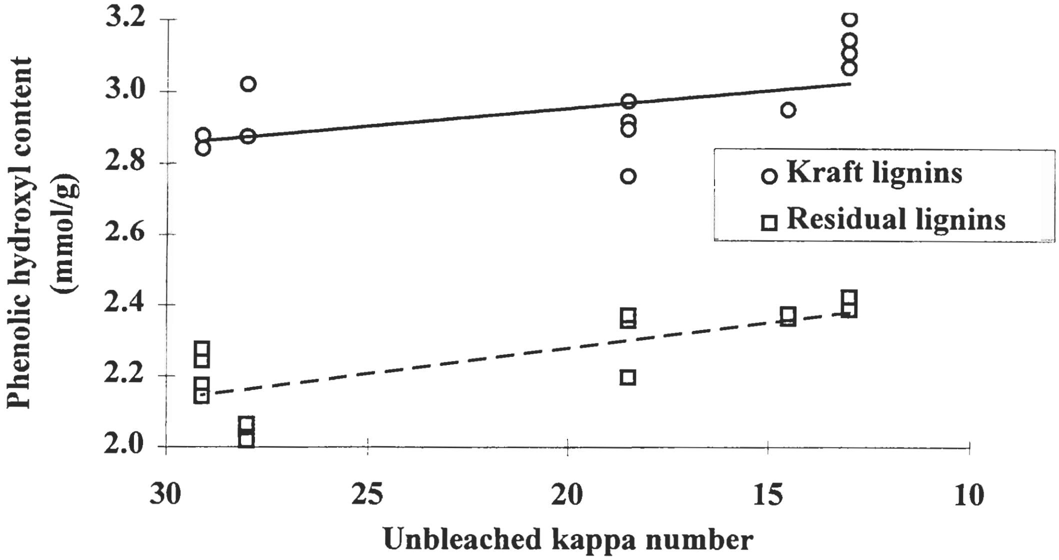


Figure 2.8. Phenolic hydroxyl content of various CK and EK kraft and residual lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of acetylated lignin.

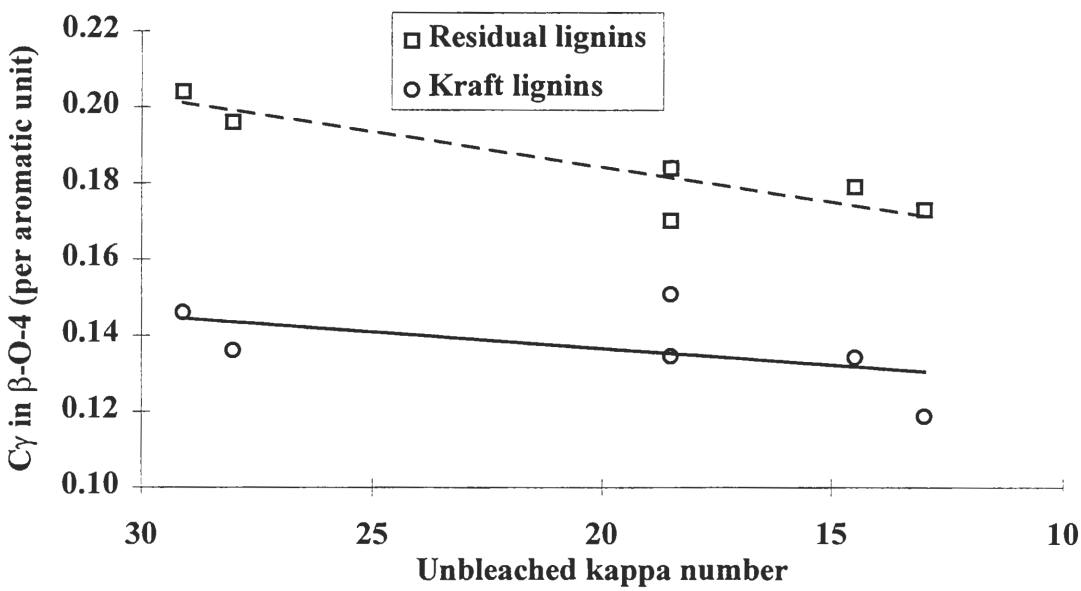


Figure 2.9. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) for various CK and EK kraft and residual lignin versus unbleached kappa number as determined by the integration of region 11 in the quantitative ^{13}C-NMR spectra.

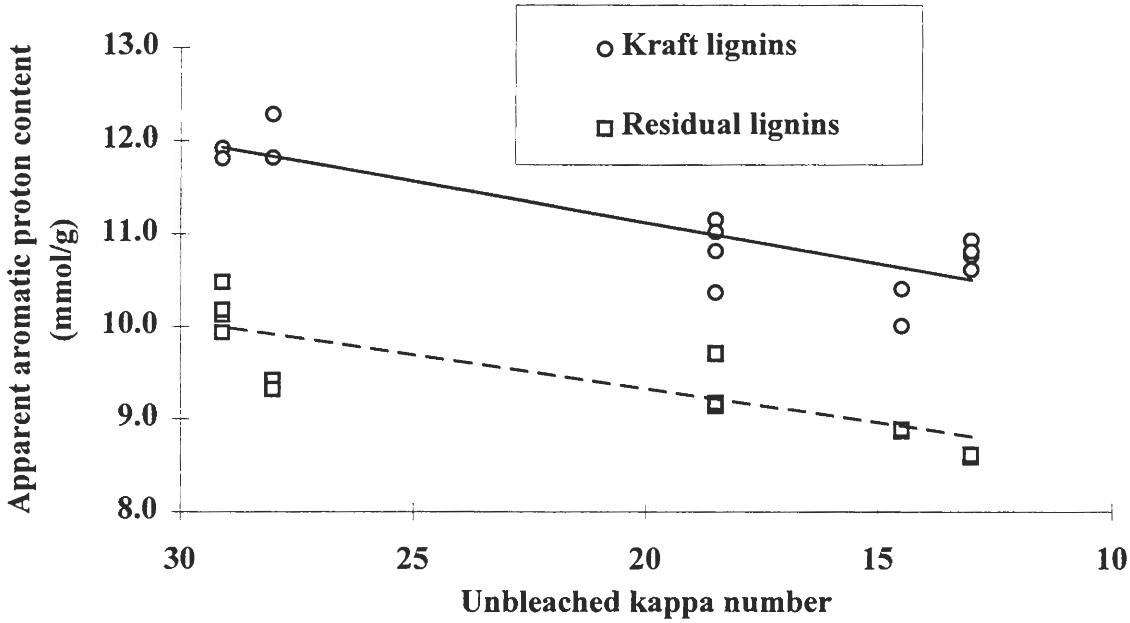


Figure 2.10. Apparent aromatic proton content of various CK and EK kraft and residual lignins versus unbleached kappa number of the resulting pulp as determined by ^{1}H-NMR of acetylated lignin.

Figure 2.9 is a plot of Cγ in β-O-4 structures as determined by quantitative ^{13}C-NMR versus the unbleached kappa number for various CK and EK kraft and residual lignins. The content of β-O-4 structures is higher in the residual lignins at comparable kappa numbers to the kraft lignins (6,23). The residual lignin appears to have been fragmented to a smaller degree than the kraft lignins, which is likely due to the homogenous reaction conditions of the kraft lignin, allowing for a more complete reaction.

Figure 2.10 is a plot of the apparent aromatic proton content for the various kraft and residual lignins as determined by ^{1}H-NMR of the lignin acetates. The apparent aromatic proton content is greater in the kraft lignins compared to the residual lignins, indicating that either the residual lignins are more condensed or contain less unsaturated structures, i.e., stilbenes. The fact that the residual lignins, when treated under kraft pulping conditions, showed an initial increase in the aromatic proton content suggested that unsaturated structures were formed. The lower aromatic proton content of the residual lignins may therefore be due to the fewer unsaturated structures. Verification of this conclusion can be found in the literature; it has been found that kraft lignin contains more stilbenes than residual lignin (6-7 per 100 C9 in kraft and ~3 per 100 C9 in residual lignin) (33).

It is interesting to note that the slope of the lines for the residual and dissolved lignins in Figures 2.8, 2.9, and 2.10 were similar. The similarity is difficult to interpret but may be indicative of the mechanism for delignification. Changes to the lignin structure are occurring in both the residual and dissolved lignins in a consistent manner suggesting that these changes are necessary for delignification to occur.

CONCLUSIONS

Many structural features of CK and EK kraft lignins isolated from black liquors extracted at various times during the cooks have been analyzed. Comparisons made between these lignins have been quite informative on the structural changes of lignin during pulping and on the differences between CK and EK kraft pulping to low kappa numbers. The differences observed can be interpreted in terms of kraft delignification chemistry and the different process variables used in conventional and modified kraft pulping.

The three types of kraft lignins analyzed in this chapter showed significantly different structural characteristics, which could be explained by the time at which they were isolated from the cook. The ai kraft lignin was isolated early during the cook and had a high content of β-O-4 structures and a low content of phenolic groups and condensed structures, suggesting that the lignin had not been significantly structurally modified. The eo1 kraft lignin, which was isolated during the middle of the cook, had significant structural differences compared to the ai lignin. The eo1 lignin had quite a low content of β-O-4 structures and a high content of phenolic groups and substituted aromatic carbons.

The eoc kraft lignins analyzed in this chapter have been isolated from both CK and EK cooks terminated at typical delignification conditions (i.e., kappa numbers ~28) and at extended delignification conditions (i.e., kappa numbers 18-13). These lignins have even greater structural differences compared to the ai and eo1 kraft lignins. Compared to the eo1 lignin, the eoc kraft lignins have a low content of β-O-4 structures and high content of phenolic groups and condensed structures. As delignification proceeds, further changes to the eoc lignins occur; the lower kappa kraft lignins have lower contents of β-O-4 structures, higher contents of phenolic groups (except for the EK kraft lignins, which have similar phenolic contents), and higher contents of condensed structures. These further changes to the lignins occur as a result of longer exposure time of the lignin under the pulping conditions, resulting in additional β-O-4 fragmentation and subsequent creation of phenolic groups. The increase in condensed structures may result from either their formation under the pulping conditions or by their enrichment due to the dissolution of condensed structures during the later stages of pulping. The latter explanation is supported by the analysis of the residual lignins, which were found to have increasing contents of condensed structures, while the former is supported by the kraft treatment of ai lignin.

A comparison of the eoc CK and EK kraft lignins found that significant differences exist between these lignins at similar degrees of delignification. The CK eoc kraft lignins had lower contents of β-O-4 structures compared to the EK kraft lignins at kappa numbers of 29 and 18, suggesting that the milder conditions employed during EK pulping do not result in as an extensive cleavage of this linkage. A similar result was found in the analysis of the residual lignins. The EK kraft lignins were also suggested to be slightly more condensed than CK kraft lignins. An explanation may be due to the counter-current cooking stage during EK pulping in which there is an enrichment of lignin dissolved later in the cook, which has been found to be more condensed.

A comparison between the kraft and residual lignins suggested that the residual lignins have a lower content of phenolic groups and a higher content of β-O-4 structures. The data also suggested that the kraft lignins had a higher content of unsaturated structures such as stilbenes, which is supported by the literature (33).

CHAPTER 3. RELATIONSHIP BETWEEN BLEACHABILITY AND RESIDUAL LIGNIN STRUCTURE

INTRODUCTION

Efficient delignification during ClO_2 delignification is believed to be influenced by the reactivity of chlorine dioxide toward residual lignin. The structure of residual lignin should play a key role in this reactivity, particularly the content of free phenolic groups, which are known to influence ClO_2 delignification (68). Studies by Germgard have shown that pulps with different phenolic contents (i.e., unbleached versus oxygen delignification and unbleached versus methylated) with similar lignin contents delignify much differently with ClO_2 (68). Pulps with the lower phenolic contents were shown to be harder to delignify.

The structure of residual lignin in unbleached kraft pulps has been shown, in Chapter 1 of the Results and Discussion section, to be influenced by the extent of delignification and pulping process variables. Higher kappa number pulps were found to have higher contents of β-O-4 structures and lower contents of phenolic groups and condensed structures. Additionally, EK pulps were shown to have a higher content of β-O-4 structures and a lower content of condensed structures compared to CK pulps at a given kappa number. Because literature results indicate that the delignification efficiency of ClO_2 is influenced by the structure of residual lignin, the various pulps with different structural features in their residual lignins would be expected to have different bleachabilities. This chapter explores the bleachability of the CK and EK pulps and the relationship between residual lignin structure and reactivity to bleachability.

The relationship between residual lignin structure and bleachability was explored by bleaching the CK and EK pulps in a D(EO) partial delignification sequence. The bleachability was measured by calculating the ClO_2 consumption per unit kappa number drop. Studying various kappa number CK and EK pulps allowed for the determination of how the extent of delignification (i.e., kappa number) and pulping process variables (i.e., CK versus EK pulping) affects bleachability. The residual lignin structures of these pulps have significant differences and should influence the reactivity with ClO_2. The bleachability will be an indirect measure of the residual lignin reactivity. An additional way, however, to explore the reactivity of residual lignin toward ClO_2 is to react isolated residual lignin with ClO_2 and monitor the functional group changes to the lignins. This was also performed and related to the observed bleachability results.

RESULTS AND DISCUSSION

Bleachability of Kraft Pulps

Five of the CK and EK pulps (C28, C18, E29, E18, and E14) were delignified in a D(EO) sequence. Duplicate samples of each pulp were independently bleached. The averaged data are summarized in Table 3.1 and discussed below.

Delignification in the D stage

The ClO_2 consumption per unit of kappa number reduction increased as the kappa number of the CK pulps was decreased. Expressed as total active chlorine (TAC) consumed per unit of kappa number reduction, it was 0.30 for the 28 kappa pulp, increasing to 0.37 at 18.5 kappa. In the case of the EK pulps, TAC consumption per unit of kappa number reduction in the D stage was increased from 0.30 to 0.33 when the kappa number was decreased from 29 to 14. When the unbleached kappa number was 18.5, significantly more lignin was removed from the EK pulp than from the CK pulp. This difference between CK and EK pulps at low kappa numbers is of interest inasmuch as it suggests that there are important structural differences between the two types of residual lignin, even though the kappa numbers are more similar after a subsequent oxidative extraction stage, as discussed below.

Table 3.1. Bleachability parameters for CK and EK pulps.

Parameter	CK		EK		
Unbleached Kappa No.	28.0	18.5	29.1	18.5	14.5
Kappa No. after D	11.0	9.2	11.0	7.5	6.0
TAC[1]/ΔKappa	0.30	0.37	0.30	0.31	0.33
Kappa No. after (EO)	3.8	3.5	3.3	3.0	2.3
TAC[1]/ΔKappa	0.21	0.23	0.21	0.22	0.23
Brightness after (EO)	47.4	49.9	49.8	50.2	53.5

[1]TAC-percent total active chlorine consumed

Delignification in the D(EO) partial sequence

For both pulp types, TAC consumption per unit of kappa number reduction increased slightly as unbleached kappa number decreased, as shown in Table 3.1 and

Figure 3.1. Decreasing the unbleached kappa number seems to slightly impair the bleachability of both CK and EK pulps. Brightness increased slightly, and in the case of the EK pulps, the kappa number after the extraction stage decreased significantly, from 3.3 at 29 kappa to 2.3 at 14.5 kappa.

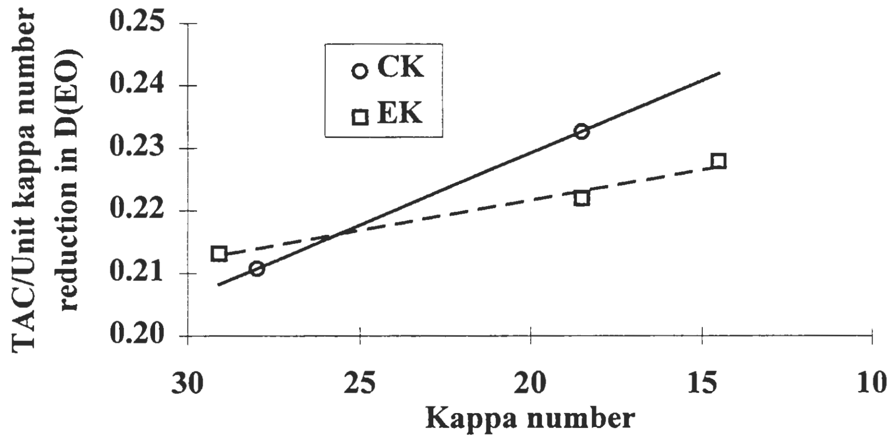


Figure 3.1. TAC per unit kappa number drop over the D(EO) partial delignification sequence for the various unbleached CK and EK kraft pulps.

Relationship between Residual Lignin Structure and Bleachability

The unbleached residual lignin structure of the various bleached pulps has been extensively characterized in Chapter 1 of the Results and Discussion section. Structural differences between high and low kappa and CK and EK pulps were found that may contribute to the observed bleachability differences. The higher kappa residual lignins had a lower phenolic hydroxyl content, a greater β-O-4 content, and a lower content of condensed structures compared to the lower kappa residual lignins. The CK residual lignins had similar phenolic hydroxyl contents, lower β-O-4 contents, and a greater content of condensed structures compared to EK residual lignins at similar kappa numbers.

The structural features of a residual lignin that would be expected to make the lignin more reactive toward ClO_2 and improve the pulp bleachability would include a high content of phenolic groups, a high content of β-O-4 structures, and possibly a low content of condensed structures. A residual lignin that is enriched with phenolic groups would be more reactive toward ClO_2 because ClO_2 is known to specifically react with phenolic groups, creating hydrophilic carboxylic acid groups (54,56). It has been suggested that β-O-4 structures in lignin are cleaved during ClO_2 bleaching, creating new reactive phenolic sites (66). A residual lignin that has a high content of such structures could conceivably have new phenolic sites created during ClO_2 bleaching, making the lignin more reactive toward the ClO_2. The presence of condensed structures in residual lignin could possibly make the lignin less reactive toward ClO_2, as such structures have been suggested to be less reactive compared to non-substituted guaiacyl rings (32,96).

The bleachability results in Table 3.1 and Figure 3.1 indicate that higher kappa pulps were easier to bleach than lower kappa pulps. These bleachability differences may be partially attributed to the structural differences in the residual lignins of these pulps. The phenolic hydroxyl content of the residual lignins does not correlate with the bleachability of these pulps because lower kappa number pulps were shown to be more difficult to bleach, yet they had a higher content of phenolic groups. The phenolic content of the residual lignins therefore seems not to be simply related to the bleachability with ClO_2; other structural features appear responsible.

There is a correlation between bleachability and the content of aryl ether linkages or condensed structures or both. The pulps with residual lignins containing higher contents of aryl ether linkages and lower contents of condensed structures had better bleachabilities. The higher content of aryl ether linkages would increase the reactivity of the ClO_2 toward the lignin because the cleavage of these linkages creates additional phenolic sites for the ClO_2. The lower content of condensed structures may also increase the reactivity of the ClO_2 toward the lignin because such structures are believed to make the lignin less reactive.

The overall conclusion of the relationship between unbleached residual lignin structure and pulp bleachability suggests that the higher kappa number pulps have structural features in the residual lignin that make the lignin more reactive toward ClO_2, causing a better pulp bleachability. The structural features responsible appear to be a combination of phenolic hydroxyl groups, β-O-4 structures, and condensed structures.

Reactivity of Residual Lignin with ClO_2

Isolated residual lignins from CK and EK pulps were reacted with ClO_2 in 9:1 dioxane:water and the reactivity measured by quantifying changes in the carboxylic acid and phenolic hydroxyl contents. Three charges of ClO_2 were used, equivalent to 0.05, 0.10, and 0.20 kappa factors (KF). After reacting with ClO_2, the oxidized residual lignins were isolated and reexamined by ^{31}P-NMR. Using this technique, Sun and Argyropoulos demonstrated that the reactivity of residual lignin toward ClO_2 can be inferred from the changes in phenolic and carboxylic acid groups upon the reaction with ClO_2 (72). Figure

3.2 contains the ^{31}P-NMR spectrum of an unbleached residual lignin and of lignin reacted with two charges of ClO_2. The spectra show the dramatic loss in signal intensity from phenolic hydroxyl groups and the increase in signal intensity of carboxylic acid groups.

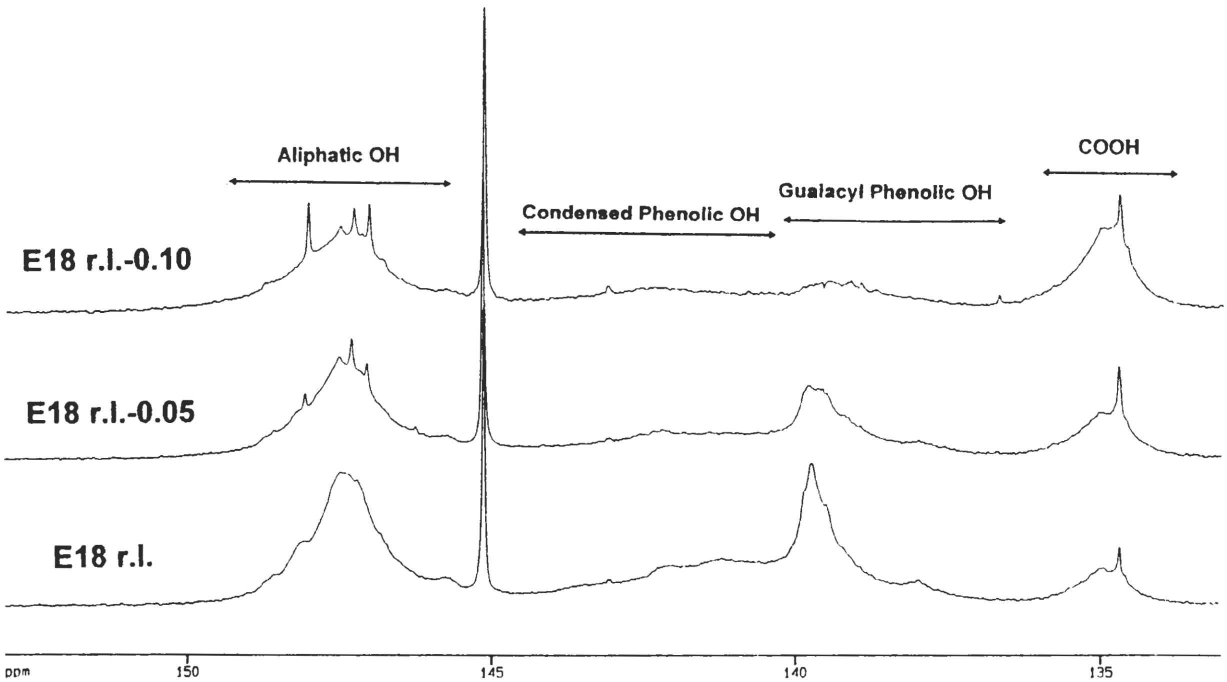


Figure 3.2. ^{31}P-NMR spectra of unbleached residual lignin and the same lignin reacted with two charges of ClO_2 corresponding to charges of 0.05 and 0.10 KF.

The oxidative formation of carboxylic acid groups is very important during bleaching because this group increases the lignin solubility, particularly in alkaline medium.

Gellerstedt has shown that a bleaching reagent that is more proficient at introducing carboxylic acid groups into the lignin is a more efficient delignifier (23). Chlorine dioxide reacts specifically with free phenolic groups, creating a variety of products, including muconic acid-type derivatives and ortho-quinones, as described in Figure 17 on page 37 (56). The formation of muconic acid derivatives is preferred because of their contributions to the lignin's solubility. The reactivity of lignin toward ClO_2 can be inferred by quantifying the introduction of carboxylic acid groups into the various CK and EK residual lignins. The residual lignin that resulted in the greatest introduction of carboxylic acid groups could be considered as being the most reactive lignin. The loss in phenolic groups can also be informative on the reactivity of the lignin because a greater loss would indicate that the lignin has undergone a more comprehensive oxidation. Although the phenolic content appeared not to be related to bleachability, such groups are indeed very important in the reaction of ClO_2 with residual lignin.

Introduction of carboxylic acid groups

The increase in carboxylic acid content versus the charge of ClO_2 for various residual lignins is summarized in Figures 3.3-3.5. The increase was calculated by subtracting the content of acid groups in the unbleached residual lignin from the content of acid groups in ClO_2-reacted residual lignin. A plot of the EK residual lignins shows the differences in reactivity of different kappa number residual lignins (Figure 3.3). Figures 3.4 and 3.5 are graphs of residual lignins with similar kappa numbers from different pulps showing the differences in reactivity between residual lignins in CK, EK, and ASAQ pulps.

Figures 3.3-3.5 show that the ClO_2 treatment of residual lignins results in a significant increase in the carboxylic acid content of the residual lignins. The increase is probably due to reactions of ClO_2 with phenolic structures that lead to ring-opening reactions, creating muconic acid-type structures, as shown in Figure 17 on page 37. The graphs show that higher charges of ClO_2 result in greater increases in carboxylic acid groups. There is a small but definite leveling off of the increase at 0.20 KF.

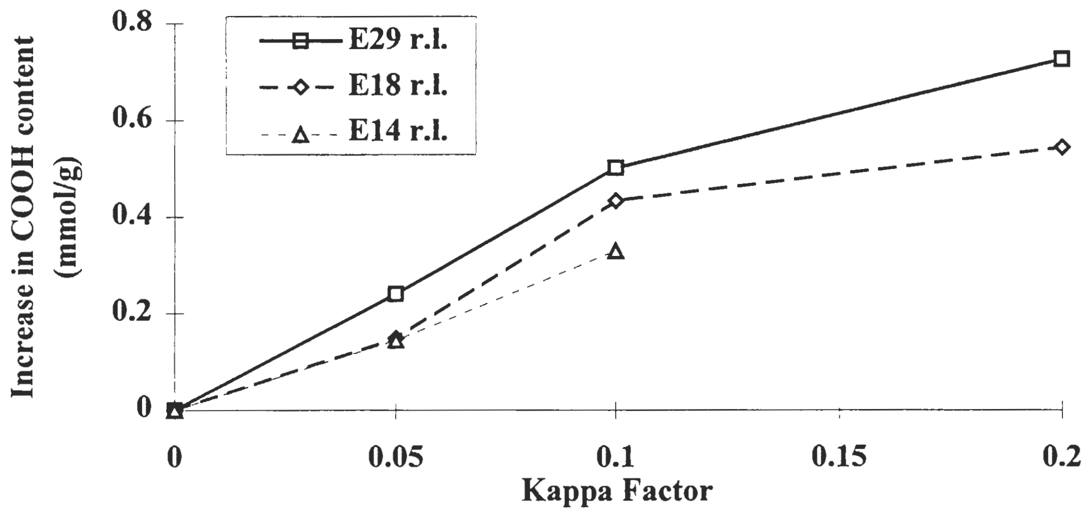


Figure 3.3. Increase in carboxylic acid groups of various residual lignins isolated from EK pulps after being treated with various charges of ClO_2 as determined by ^{31}P-NMR.

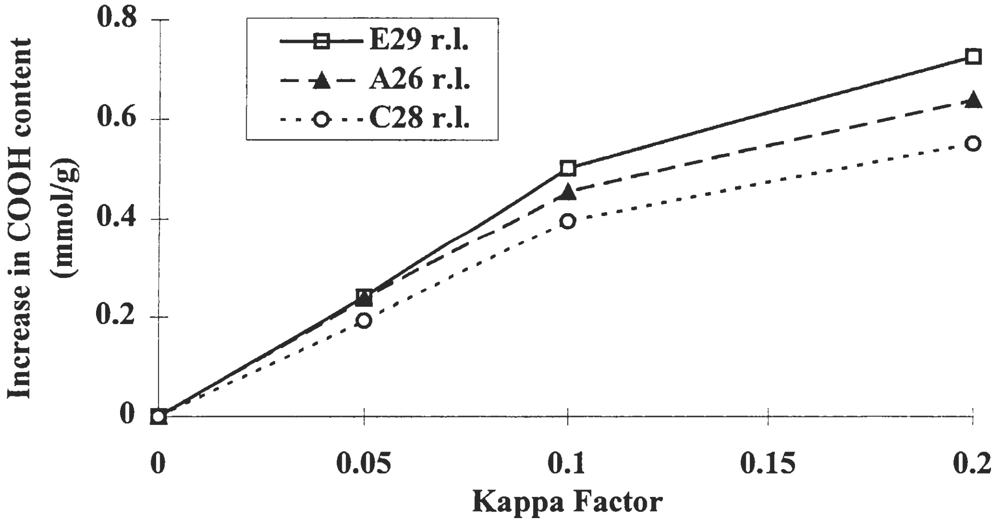


Figure 3.4. Increase in carboxylic acid groups of E29 r.l., A26 r.l., and C28 r.l. after being treated with various charges of ClO_2 as determined by ^{31}P-NMR.

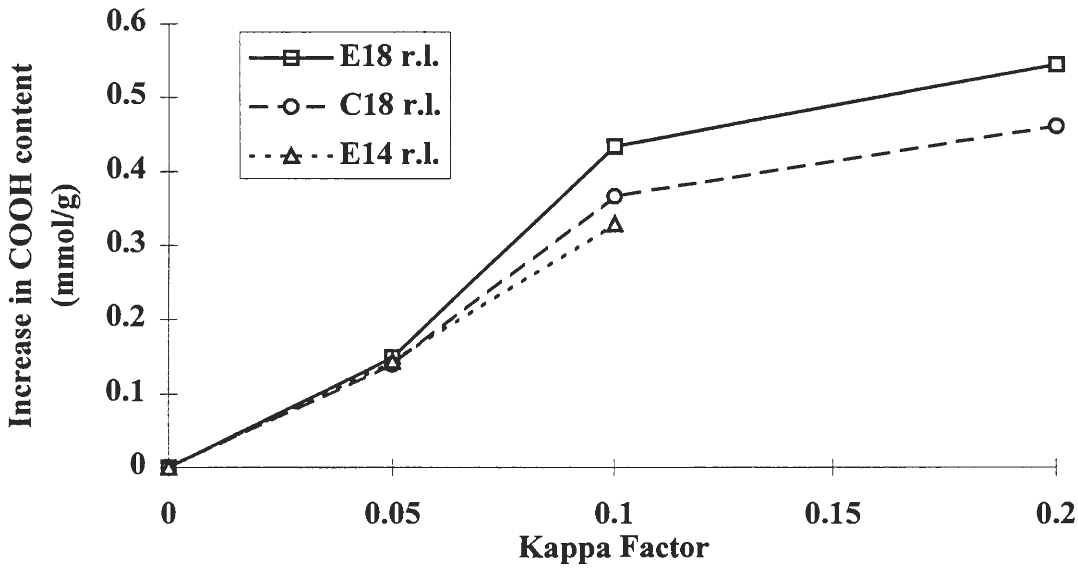


Figure 3.5. Increase in carboxylic acid groups of C18 r.l., E18 r.l., and E14 r.l. after being treated with various charges of ClO_2 as determined by ^{31}P-NMR.

Figure 3.3 shows that there is a significant difference in the reactivity of the residual lignins with different kappa numbers. The higher kappa number residual lignins showed a greater increase in carboxylic acid groups compared to the lower kappa residual lignins. This occurred for all charges of ClO_2 and for both CK and EK residual lignins. Clearly, if the introduction of carboxylic acid groups can be considered as a measure of the reactivity of residual lignins toward ClO_2, then the results suggest that the higher kappa residual lignins are more reactive toward ClO_2. This significant result suggests that the higher kappa number pulps have a lignin that is more reactive toward ClO_2. If a pulp has a residual lignin that is more reactive toward ClO_2, that is the ClO_2 treatment results in a greater increase in the carboxylic acid content, which improves the lignin's solubility in alkaline medium, then this pulp would be expected to have a good bleachability. The bleaching results suggested that the higher kappa number pulps have a better bleachability compared to the lower kappa number pulps. The reactivity experiments therefore provide a good explanation of the bleaching results because the higher kappa residual lignins are more reactive toward ClO_2.

The reason for the higher reactivity of the high kappa residual lignin can be explained from the structural analyses of the residual lignins. The higher kappa residual lignins have structural features that make the lignin more reactive toward ClO_2. The higher kappa residual lignins have a higher content of β-O-4 structures and a lower content of condensed structures. The cleavage of β-O-4 linkages in residual lignin during the reaction with ClO_2 creates additional phenolic hydroxyl groups that are reactive toward ClO_2. This reaction has been suggested to occur during ClO_2 bleaching (61,62). The reaction does not involve ClO_2, but rather hypochlorous acid and its equilibrium partner, elemental chlorine, which are formed when ClO_2 is reduced by lignin (Figure 17 on page 37) (56). The important role of hypochlorous acid during ClO_2 delignification has recently been demonstrated by Ni et al. who showed that delignification is retarded by adding a scavenger of hypochlorous acid (61). The lower contents of condensed structures in the higher kappa lignin may also be influencing the reactivity of the lignin with ClO_2, because such structures may be less reactive (32). The lower kappa residual lignins, with a higher content of such structures, would then be expected to be less reactive toward ClO_2.

Figures 3.4 and 3.5 are graphs of CK, EK, and ASAQ residual lignins with similar kappa numbers showing the differences in reactivity of these residual lignins toward ClO_2. Figure 3.4 shows that at any given charge, E29 r.l. introduces more carboxylic acid groups than A26 r.l. and C28 r.l.. Figure 3.5 is a similar graph for E18 r.l. and C18 r.l., which again shows the EK residual lignin to have a greater introduction of carboxylic acid groups than CK residual lignin at any given charge of ClO_2.

Figure 3.6 illustrates the relationship between the residual lignin kappa number and the increase in carboxylic acid groups during the treatment of the residual lignins with a charge of ClO_2 equivalent to 0.05 KF. The graph clearly shows that the EK residual lignins result in a greater increase in carboxylic acid groups compared to the CK lignins at similar kappa numbers.

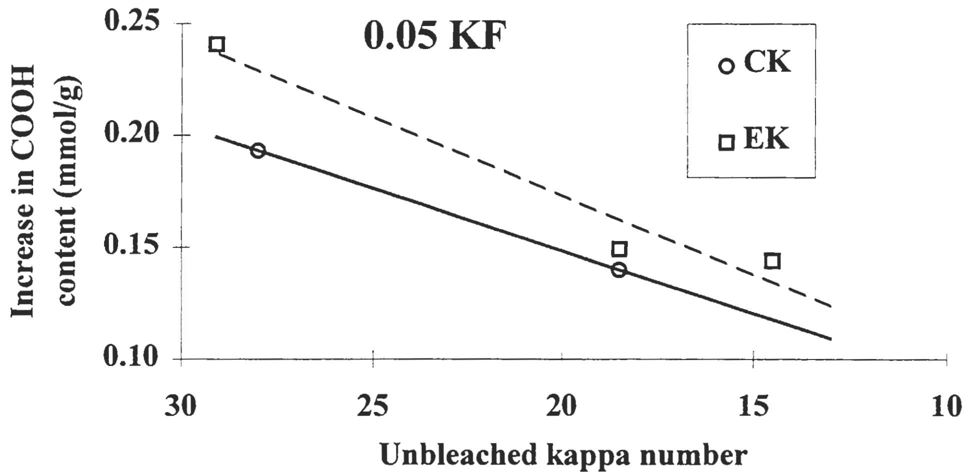


Figure 3.6. Increase in carboxylic acid groups of various residual lignins isolated from CK and EK pulps after a treatment with a charge of ClO_2 equivalent to 0.05 kappa factor versus the unbleached kappa number of the pulp from which the residual lignin was isolated from. The carboxylic acid content was determined by ^{31}P-NMR.

The results indicate that the EK residual lignins are more reactive (more bleachable) because more carboxylic acid groups are introduced. Because the reactivity difference could potentially influence bleachability, EK pulps should be easier to bleach than CK pulps. The results from the bleaching experiments suggested that the high kappa CK and EK pulps had similar bleachabilities. However, C18 pulp had a significantly poorer bleachability than E18 pulp, which may be partially attributed to the reactivity of the residual lignins because EK residual lignin was found to be more reactive than CK residual lignin.

The reason for the higher reactivity of the EK residual lignins compared to CK residual lignins at similar kappa numbers can again be explained by the structural analysis of the residual lignins. At similar kappa numbers, the EK lignins had a greater content of β-O-4 structures and a lower content of condensed structures.

The E29 and C28 pulps had similar bleachabilities, yet the structural analysis of their residual lignins and the reactivity of their residual lignins with ClO_2 suggested their bleachabilities would differ. One explanation for this may be that the content of carboxylic acid groups introduced when bleaching the C28 pulp is sufficient to cause a similar degree of delignification as the E29 pulp. As Figure 3.6 shows, the C28 residual lignin introduced a significant amount of carboxylic acid groups, second only to E29 r.l., suggesting that this lignin was indeed quite reactive. Only when the kappa number is reduced further does it seem that the bleachability differences between CK and EK become significant.

Loss of phenolic groups

Figure 3.7 is a graph showing the loss of phenolic hydroxyl groups for various EK residual lignins with increasing charge of ClO_2. Not surprisingly, the graph shows that there is a dramatic loss in phenolic groups when the lignins are treated with ClO_2. The loss in phenolic groups can be attributed to the reaction of ClO_2 with phenolic groups, creating either muconic acid-type structures, quinones, or some other products. The loss of phenolic groups is greater than the gain in carboxylic acid groups, suggesting that of the phenolic groups loss, many are not converted into muconic acid-type structures. Increasing the charge of ClO_2 increases the loss of phenolic groups. There appears to be a leveling off of this loss in phenolic groups, and even after the 0.20 KF treatment, there still remains a significant content of phenolic groups in ClO_2-treated lignins. Approximately 30-40% of the phenolic groups remain unreacted after the 0.20 KF treatment, depending on the residual lignin. These unreacted phenolic groups seem to be resistant toward the ClO_2, as will be discussed further later.

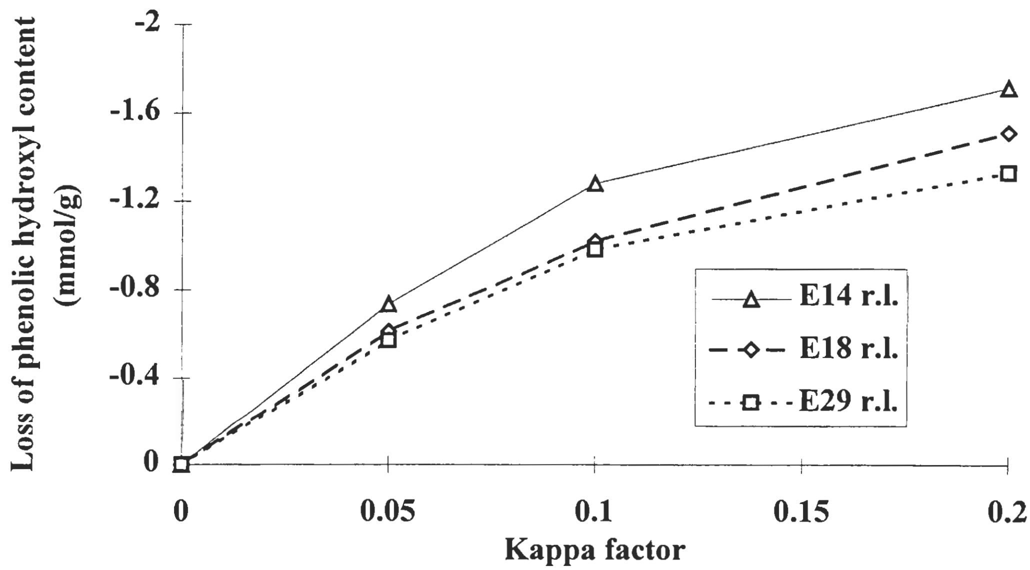


Figure 3.7. Loss of phenolic hydroxyl groups from various residual lignins isolated from EK pulps after being treated with various charges of ClO_2 as determined by ^{31}P-NMR.

Figure 3.7 contains the results from the three EK residual lignins treated with three charges of ClO_2. There were some significant differences in the reactivity of these residual lignins, considering the loss of phenolic groups. The lower kappa residual lignins consistently showed a greater loss of phenolic groups at each charge of ClO_2 compared to the higher kappa residual lignins. The result was interesting especially considering that the higher kappa residual lignins showed a greater increase in the carboxylic acid content. The lower kappa residual lignins may be even less efficient at introducing carboxylic acid groups because they had a greater loss of phenolic groups. Conceptually speaking, efficient delignification should require that a high percentage of the reacted phenolic groups be converted into carboxylic acid groups. These percentages have been calculated from the ^{31}P-NMR data and graphed in Figure 3.8, which is a plot of the percentage of reacted phenolic groups converted into carboxylic acids for the various EK lignins treated with different charges of ClO_2.

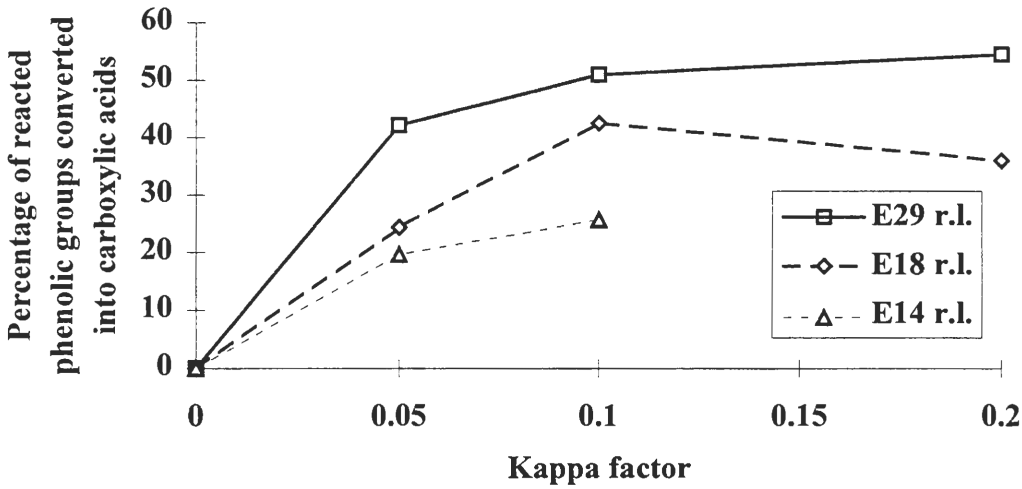


Figure 3.8. Percentage of reacted phenolic hydroxyl groups converted in carboxylic acid groups for the various EK residual lignins reacted with three charges of ClO_2. (Percent converted = (Increase in COOH / Loss in phenolic) * 100)

The data show two interesting results. The low kappa residual lignins were found to be much less efficient at introducing carboxylic acid groups into the reacted phenolic groups compared to the high kappa residual lignins. Only about 25% (the maximum at 0.10 kappa factor) of the reacted phenolic groups in the low kappa residual lignins are converted into carboxylic acid groups. The high kappa residual lignins introduced twice as much. The phenolic groups that are reacted in the low kappa residual lignins are converted into something other than carboxylic acid groups, perhaps ortho-quinones. Another interesting result from this data was that the percentage increased with increasing charge of ClO_2, suggesting that higher charges of ClO_2 caused a more efficient conversion of phenolic groups into carboxylic acid groups.

A major assumption was that all the carboxylic acid groups created are derived from the phenolic groups in the untreated residual lignins, when actually additional phenolic groups may be created during the ClO_2 treatment. This would significantly influence the data in Figure 3.8 because the creation of phenolic groups during the treatment and their subsequent conversion into carboxylic acid groups would erroneously increase the percentage of carboxylic acid groups derived from reacted phenolic groups.

The creation of phenolic groups during ClO_2 bleaching by fragmenting aryl ether linkages was suggested to cause the greater carboxylic acid increase in the higher kappa residual lignin because the higher kappa residual lignin had a greater content of β-O-4 structures (Figure 3.3). The same rationale can be used to explain the results for phenolic hydroxyl contents. Higher kappa residual lignins showed smaller losses in the content of phenolic groups compared to the lower kappa residual lignins. Again this may be due to the higher kappa residual lignins having the greater potential to create phenolic groups because of their higher content of β-O-4 structures. The creation of phenolic groups would counter-act their loss during the ClO_2 treatment, resulting in a lower observed loss in phenolic content for the higher kappa residual lignins.

The ^{31}P-NMR analysis cannot only quantify the total phenolic hydroxyl content but can also conveniently quantify both guaiacyl and condensed phenolic groups. Figure 3.9 is a graph of the loss in guaiacyl and condensed phenolic groups for E29 r.l. treated with the three charges of ClO_2. A clear difference in the reactivity of these phenolic groups is observed, particularly at higher charges as there is a greater loss of guaiacyl phenolic groups, suggesting that ClO_2 is more reactive toward guaiacyl phenolic groups than condensed phenolic groups. At low kappa factors, the difference is observed, but it is not as significant. The effect was observed for all the lignins, as shown in Figure 3.10, which again shows that the reactivity of the condensed phenolic groups is similar at a 0.05 kappa factor charge, but a significant break in the differences occurs at higher charges as the loss in condensed phenolic groups does not increase as dramatically as the loss in guaiacyl phenolic groups.

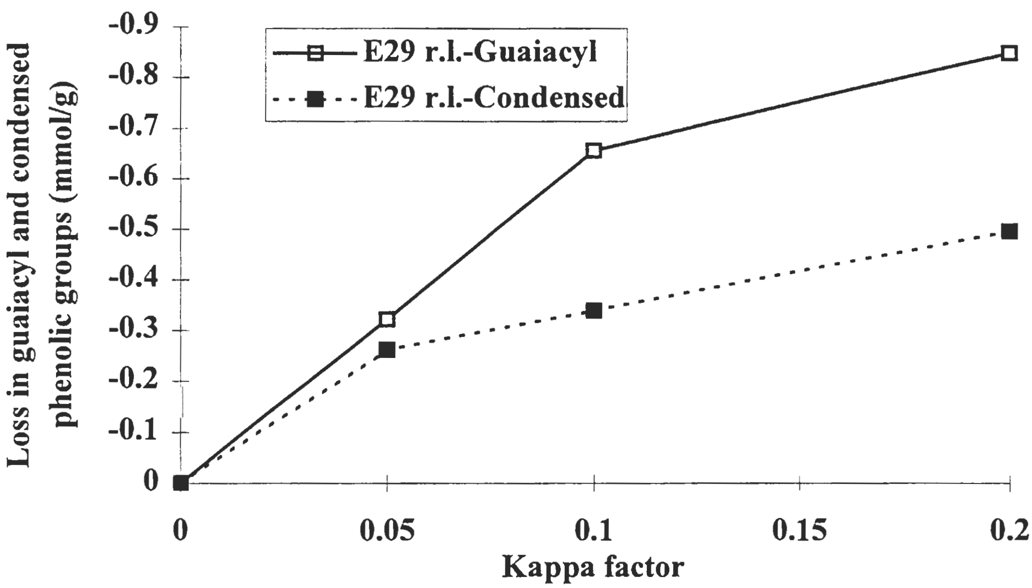


Figure 3.9. Loss of guaiacyl and condensed phenolic hydroxyl groups from E29 r.l. treated with three charges of ClO_2 as determined by ^{31}P-NMR.

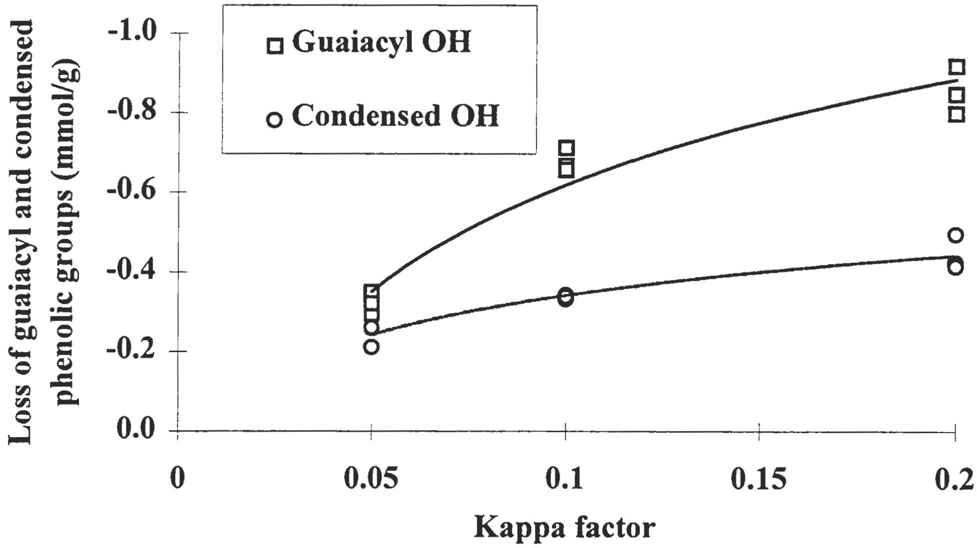


Figure 3.10. Loss of guaiacyl and condensed phenolic hydroxyl groups for various residual lignins treated with three charges of ClO_2 as determined by ^{31}P-NMR.

In unbleached residual lignin, 42-44% of the total phenolic groups are of the condensed type. After a treatment with 0.20 KF ClO_2, of the remaining phenolic groups, 54-63% are of the condensed phenolic type.

The reason for the enrichment of condensed phenolic structures after the reaction with ClO_2 may be interpreted in two different ways. Some condensed phenolic groups are just as reactive as guaiacyl phenolic groups and they disappear just as rapidly as the guaiacyl phenolic groups initially. After the more 'reactive' condensed phenolic groups are diminished, the additional loss of condensed phenolic groups is hindered due to their unreactive nature. Another explanation may be that if β-O-4 structures are being cleaved during this treatment, creating new phenolic groups, these new phenolic groups may be of the condensed type, which could result in a smaller loss in condensed phenolic groups.

Recall that in the residual lignin kraft treatment experiments a similar result was found, as the increase in phenolic groups was mainly attributed to condensed phenolic groups, which suggested that the β-O-4 structures that were cleaved were condensed. A similar effect may be occurring here, causing a smaller loss in condensed phenolic groups.

CONCLUSIONS

The bleachability of CK and EK pulps in a D(EO) sequence has been related to the residual lignin structure and its reactivity toward ClO_2. During ClO_2 delignification, the ClO_2 consumption per unit kappa number reduction increased slightly as the kappa numbers of both the CK and EK pulps decreased, suggesting that lower kappa number pulps have a poorer bleachability. This implies that higher kappa number pulps have a residual lignin that is more reactive toward ClO_2. Because ClO_2 is known to react specifically with phenolic hydroxyl groups, the content of such groups in the lignin should be expected to influence the bleachability. However, the content of free phenolic structures could not be simply related to the bleachability because the lower kappa number pulps had a higher content of phenolic groups. The structural analysis of the residual lignins in Chapter 1 of the Results and Discussion section revealed that the higher kappa number pulps had a higher content of β-O-4 structures and a lower content of condensed structures, suggesting these lignins are more reactive toward ClO_2. The higher content of aryl ether linkages and lower contents of condensed structures suggests that such a lignin may be more reactive toward ClO_2.

Experiments in which the isolated residual lignins were reacted with ClO_2 showed that higher kappa lignins, in spite of their lower phenolic content, had larger increases in carboxylic acid groups, suggesting a more reactive lignin. Higher kappa residual lignins also had smaller losses in phenolic content. The combined results suggest that β-O-4 structures are fragmented during a ClO_2 treatment, creating phenolic groups, which further react to form carboxylic acids. The higher content of β-O-4 structures in the higher kappa residual lignins would therefore result in a greater introduction of carboxylic acid groups and a smaller depletion of phenolic groups.

Condensed phenolic groups were also found to be less reactive than guaiacyl phenolic groups, which may partially explain the differences in reactivity between high and low kappa residual lignins. Lower kappa residual lignins have a higher content of condensed structures, making the lignin less reactive toward ClO_2.

The bleachability experiments also showed that the E18 pulp was more readily delignified in a D(EO) sequence than the C18 pulp. The residual lignin reactivity experiments suggested that the EK residual lignin was slightly more reactive than the CK residual lignin, as evidenced by the greater introduction of carboxylic acid groups. The reactivity experiments suggest that CK pulps would have a poorer bleachability than EK pulps, which is what was found for the 18 kappa pulps.

CHAPTER 4. ClO_2-BLEACHED RESIDUAL AND DISSOLVED LIGNINS

INTRODUCTION

The chemistry of chlorine dioxide bleaching has been primarily established through model compound studies in which lignin model compounds are reacted under idealized conditions with chlorine dioxide. Although these studies have proved valuable in the fundamental understanding of chlorine dioxide reactions with lignin structures, increasing our knowledge of residual lignin structure and how it is degraded by ClO_2 is of greater consequence. The difficulties in characterizing the substrate (i.e., unbleached pulp residual lignin) and its products after its reaction with chlorine dioxide have been the main impediments to accomplishing this task. Studies using advanced NMR techniques to characterize residual and dissolved lignins before and after their reactions with chlorine dioxide have begun to establish the reactions of chlorine dioxide with lignin in kraft pulp (23,63,70-72,97-99). These studies, although informative, have not been extensive and warrant further investigations involving residual lignin characterization to obtain a better understanding of chlorine dioxide bleaching chemistry. Important chemical reactions also occur during the alkaline extraction, yet this chemistry is also vaguely understood.

The NMR techniques used earlier in this dissertation have been employed to characterize residual and dissolved lignins that were reacted with ClO_2 and treated with alkali. Structural comparisons between residual lignin in unbleached pulps, which were characterized in Chapter 1, were made with residual lignins in ClO_2-bleached pulp and ClO_2-bleached/alkaline-extracted pulps. The important chemical modifications occurring during these treatments were elucidated, allowing for new insights into the chemistry of chlorine dioxide and alkaline extraction bleaching.

ClO_2 CHEMISTRY

In this first section, the chemistry of an initial ClO_2 delignification stage was studied by monitoring the structural changes occurring to the lignin during its reaction with ClO_2. This was accomplished by performing two different experiments. In one experiment, various kraft pulps were bleached with ClO_2, and the residual lignins from these pulps were isolated by acid hydrolysis. The residual lignins were then characterized by both ^{13}C-NMR and ^{1}H-NMR of underivatized lignins. The pulps used in these experiments were E29, C28, E18, and C18. The C28 pulp was bleached with kappa factors of 0.05 and 0.20, while the other pulps were bleached with a 0.20 KF. In another experiment, an isolated unbleached residual lignin sample (C33 r.l.) was reacted with two charges of ClO_2 (0.05 and 0.20 KF), and the oxidized lignins were analyzed by ^{13}C-NMR. Quantitative ^{1}H-NMR analysis of various isolated unbleached residual lignin treated with ClO_2 was also performed.

A variety of structural features of ClO_2-treated lignins were quantified and compared to the unbleached residual lignins, including the content of carboxylic acids, substituted aromatic carbons, aliphatic carbons linked to oxygen, methoxyl groups, phenolic hydroxyl groups, and aromatic protons.

The techniques involving derivatization of the lignins (^{31}P-NMR and ^{1}H-NMR analysis of lignin acetates) were not performed in this study because the oxidized lignins were not amenable toward derivatization. Most lignins that were oxidized with ClO_2 were incapable of being acetylated or phosphitlated, possibly due to their high content of carboxylic acids and low content of phenolic hydroxyl groups.

Qualitative Analysis of ^{13}C-NMR Spectra

Comparing the ^{13}C-NMR spectra of unbleached residual lignins with the spectra of residual lignins isolated from ClO_2-bleached pulps and the residual lignins treated with ClO_2 allows for qualitative differences between the lignins to be made. Figure 4.1 contains the ^{13}C-NMR spectra of C28 r.l., C28 D r.l. (0.05), and C28 D r.l. (0.20), while Figure 4.2 contains the ^{13}C-NMR spectra of C33 r.l., C33 r.l.-0.05, and C33 r.l.-0.20. Some regions of interest have been marked on the spectra and are discussed in detail below.

One of the most dramatic changes to the lignin structure is the introduction of carbonyl groups, suggested by the increasing intensity of the signals in the range from δ 180-165 ppm, which are assigned to carbonyl carbons in carboxylic acid and ester functional groups. Model compound studies have found that carboxyl carbonyl groups have chemical shifts in two distinct regions of the carbonyl region. Aliphatic carboxylic acids have chemical shifts from δ 180-170 ppm, while conjugated or aromatic acids, such as muconic and maleic acids, have chemical shifts just upfield of this region, from δ 170-165 ppm (63,71). Ester carbonyl groups have a chemical shift in the same region as the carbonyl group in conjugated carboxylic acids, δ 170-165 ppm. Ester functional groups in the ClO_2-treated lignins are in muconic acid methyl ester (MAME) structures and in

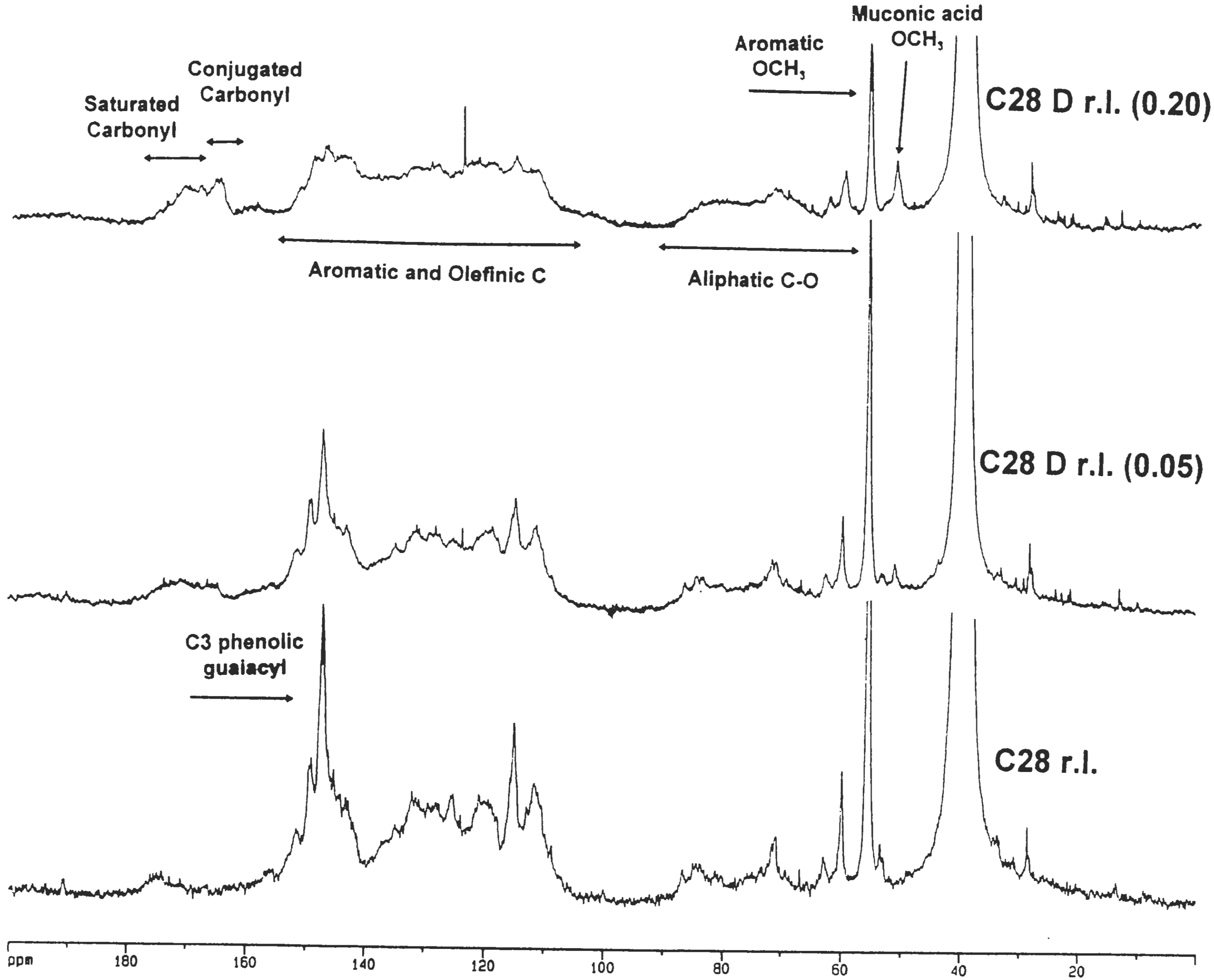


Figure 4.1. Quantitative [13]C-NMR spectra of residual lignins isolated from unbleached and ClO_2-bleached kraft pulps. The spectra have been labeled with areas of interest.

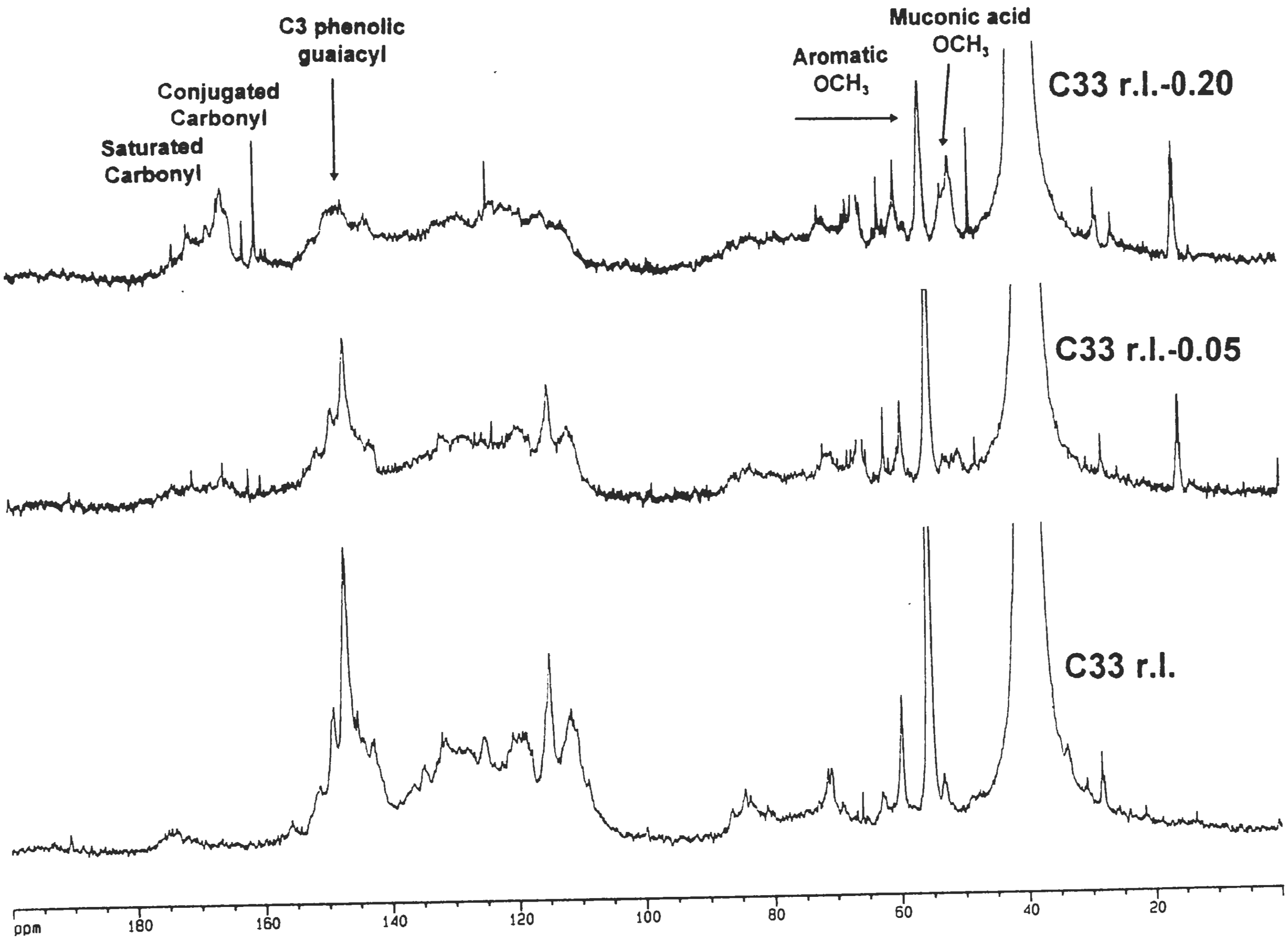


Figure 4.2. Quantitative ^{13}C-NMR spectra of residual lignin isolated from the unbleached C33 pulp and the spectra of this residual lignin treated with two charges of ClO_2 corresponding to 0.05 and 0.20 KF. The spectra have been labeled with areas of interest.

lactone structures (cyclized MAME), as discussed in the Literature Review section (Figure 17, page 37). This chemistry is depicted in Figure 4.3 along with the ^{13}C-NMR chemical shifts of the various carbonyl carbons.

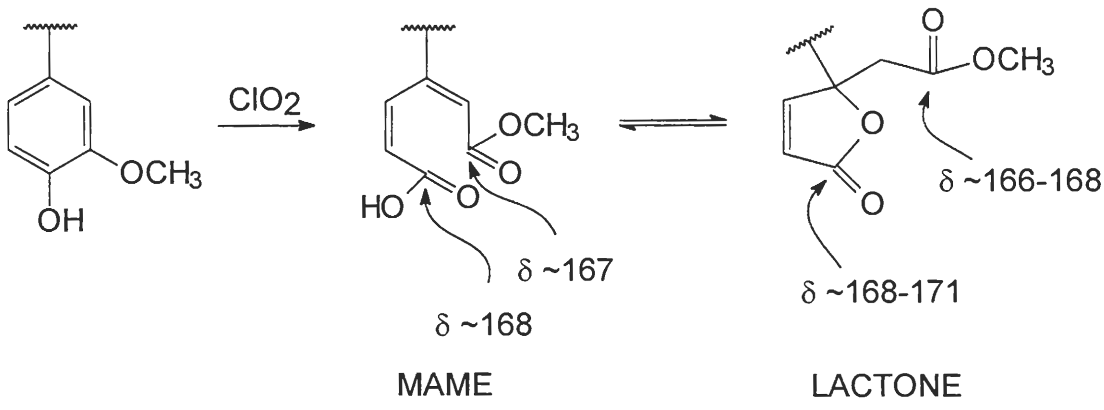


Figure 4.3. Ring-opening reaction between ClO_2 and a guaiacyl structure resulting in the formation of a muconic acid methyl ester (MAME) and its cyclized lactone. The approximate ^{13}C-NMR chemical shift of the carbonyl carbons is shown.

The signals in the region from δ 160-106 ppm are due chiefly to aromatic carbons. Some interesting differences in this region are observed between the various untreated and ClO_2-treated residual lignins. One major difference is the signal intensity from the C3 aromatic carbons in phenolic guaiacyl structures. The intensity of the signal in the unbleached residual lignin is significantly reduced after the ClO_2 treatment, indicating a loss in phenolic groups.

Another distinct and important difference in the ^{13}C-NMR spectra is the signal intensity of the aromatic methoxyl groups (δ ~ 56 ppm). The intensity decreases as the charge of ClO_2 increases, indicating that the lignin is being demethylated. However, ring-opened products creating MAME structures and their cyclized lactones change the chemical shift of the methoxyl group upfield from δ ~56 to ~52 ppm (Figure 4.4) (59,71). In the ^{13}C-NMR spectra of ClO_2-treated residual lignins, a clear signal is observed at δ 52 ppm, which is assigned to the methoxyl carbons in MAME structures and/or their corresponding lactone (Figures 4.1 and 4.2).

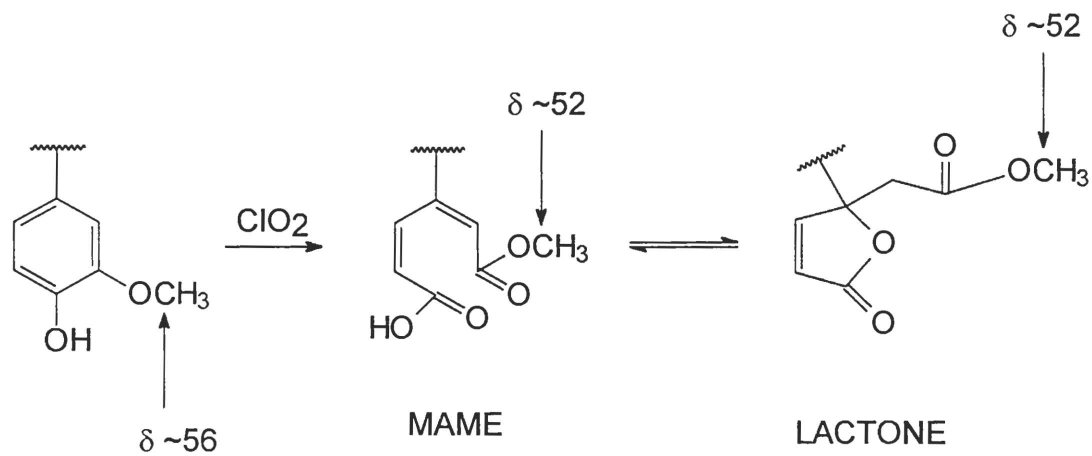


Figure 4.4. Ring-opening reaction between ClO_2 and a guaiacyl structure resulting in the formation of a muconic acid methyl ester (MAME) and its cyclized lactone. The approximate ^{13}C-NMR chemical shift of the methoxyl carbons is included (60,63).

Quantitative ^{13}C-NMR and ^{1}H-NMR Analysis

Various functional groups were analyzed quantitatively by ^{13}C-NMR and ^{1}H-NMR (Table 4.1). The quantitative ^{13}C-NMR spectra were analyzed in a similar manner as were the unbleached residual lignins, by reporting the number of carbon atoms per aromatic unit. Results from the quantitative analyses of carboxylic acid groups, phenolic groups, methoxyl groups, aromatic protons, substituted aromatic carbons, and aliphatic carbons linked to oxygen are discussed in the following sections.

Carboxylic acid content

^{13}C-NMR analysis allows for the quantification of carbonyl groups in carboxylic acids, lactones, and methyl esters in the ClO_2-treated lignins. Because a large portion of carbonyl groups in these lignins is due to carboxylic acid groups, the data in Table 4.1 are reported as carboxylic acid content, which is subdivided into the content of aliphatic and conjugated carboxylic acid groups. The formation of carboxylic acids was shown to be quite prevalent as the content of carbonyl groups, per aromatic ring, increased from ~0.2 in the unbleached lignins to ~0.5 in the 0.05 KF bleached residual lignin to ~0.9 in the 0.20 KF bleached residual lignins. The content of aliphatic carboxylic acid groups was consistently higher than the content of conjugated carboxylic acid groups. The high content of aliphatic carboxylic acid groups is interesting because model compound studies have shown that the products from the reaction of lignin structures with ClO_2 have conjugated but not aliphatic carboxylic acid groups. The high content of aliphatic carboxylic acid groups may be partially attributed to carbonyl groups in lactone structures, which may have chemical shifts in the 'aliphatic' carboxylic acid region (60).

The content of carboxylic acid groups in these lignins was also determined by ^{1}H-NMR. Because some conjugated carboxylic acids are believed to be in their lactone form, they would not be detected by this analysis; therefore, an underestimate of the carboxylic acid content would be expected from this analysis. The analysis showed that the carboxylic acid content increased after a treatment with ClO_2 and depended on the charge of ClO_2.

Table 4.1. Quantitative ^{13}C-NMR and ^{1}H-NMR analysis of various residual lignins isolated from unbleached and ClO_2-bleached kraft pulps.

NMR Analysis	Structural Feature	Lignin ID				
		C28 r.l.	C28 D r.l. (0.05)	C28 D r.l. (0.20)	E29 r.l.	E29 D r.l. (0.20)
^{13}C-NMR†	Total COOH	0.15	0.47	0.89	0.20	0.87
	Aliphatic	-	0.34	0.56	-	0.54
	Conjugated	-	0.13	0.33	-	0.33
	Substituted*	4.08	4.12	4.14	4.04	4.13
	Aliphatic C-O	1.16	1.54	1.75	-	-
	Aromatic OCH_3	0.86	0.75	0.49	0.85	0.53
	ME OCH_3	-	0.26	0.35	-	0.38
^{1}H-NMR‡	COOH	0.55	0.51	0.90	0.36	0.89
	Total Phenolic	2.67	1.71	1.35	2.53	1.37
	Aromatic H	12.52	9.39	6.72	12.73	7.04

NMR Analysis	Structural Feature	Lignin ID			
		E18 r.l.	E18 D r.l. (0.20)	C18 r.l.	C18 D r.l. (0.20)
^{13}C-NMR†	Total COOH	0.25	1.06	0.18	1.03
	Aliphatic	-	0.72	-	0.69
	Conjugated	-	0.34	-	0.34
	Substituted*	4.15	4.30	4.19	4.26
	Aliphatic C-O	1.15	1.88	-	2.11
	Aromatic OCH_3	0.86	0.54	0.86	0.57
	ME OCH_3	-	0.40	-	0.46
^{1}H-NMR‡	COOH	0.53	0.61	0.62	-
	Total Phenolic	2.63	1.26	2.86	1.32
	Aromatic H	11.91	6.60	12.00	6.80

NMR Analysis	Structural Feature	Lignin ID		
		C33 r.l.	C33 r.l.-0.05	C33 r.l.-0.20
^{13}C-NMR†	Total COOH	0.20	0.60	1.29
	Aliphatic	-	0.40	0.69
	Conjugated	-	0.20	0.60
	Substituted*	3.95	4.10	4.20
	Aliphatic C-O	1.35	-	-
	Aromatic OCH_3	0.83	0.72	0.61
	ME OCH_3	-	0.33	0.68

†^{13}C-NMR results reported as number of carbon atoms per aromatic unit; ‡^{1}H-NMR results reported as mmol/g lignin; *Substituted aromatic carbons; ME = methyl ester. See Materials and Methods section for a description of the lignin ID.

Phenolic hydroxyl content

The phenolic hydroxyl content of the residual lignins was analyzed by ^{1}H-NMR and was shown to decrease during the ClO_2 treatment. The amount of phenolic hydroxyl groups in the residual lignin of the 0.20 KF bleached pulps was approximately 50% of the amount in the unbleached residual lignins. The phenolic content of the ClO_2-bleached residual lignin is still relatively high, suggesting that some phenolic groups did not react with the ClO_2 even though an excess of ClO_2 was used. A similar result was found in the analysis of ClO_2-treated isolated residual lignins. Residual lignins treated with an excess of ClO_2 still had some phenolic groups that remained unreacted. Clearly there remains in the ClO_2-treated lignins a certain content of phenolic groups that has some stability toward the ClO_2. The stability of these phenolic groups is probably influenced by some structural feature of the phenolic group, such as a substituent at the C5 position, as shown from results in the previous chapter.

Methoxyl content

The methoxyl content of the residual lignins was quantified by integrating the methoxyl regions of the ^{13}C-NMR spectra. For unbleached lignins, the methoxyl content was determined by integrating the aromatic methoxyl signal at δ 56 ppm. For the ClO_2-treated lignin, in addition to the aromatic methoxyl signal being integrated, the methyl ester methoxyl signal was also integrated (δ ~52 ppm). The quantities of both methoxyl groups are given in Table 4.1.

The aromatic methoxyl content of the ClO_2-treated lignins was found to be quite smaller than the unbleached residual lignins apparently due to a combination of demethoxylation and the formation of structures containing methyl esters. The formation of structures containing methyl ester groups is important because it confirms that carboxylic acid groups of the muconic acid-type have been created and are indeed present in the ClO_2-bleached pulp. In the C28 pulp bleached with a 0.05 KF, an estimate of about 0.26 structures per aromatic unit was made, while in the 0.20 KF bleached pulp, an estimate of about 0.35 per aromatic unit was made. These estimates are probably high due to difficulties in phasing and correcting the baseline of the spectra. The estimates do, however, indicate that the quantity of these structures present in ClO_2-bleached residual lignin is quite significant.

The same analysis of the residual lignin treated with ClO_2 showed a more significant increase in the methyl ester methoxyl signal, suggesting that there was a greater introduction of such groups. Apparently the homogenous solution of lignin and ClO_2 and/or the aqueous dioxane solvent system resulted in a more efficient oxidation of the lignin. The reacted lignin can be considered as a combination of residual and dissolved lignin produced during bleaching, which may also explain its apparent greater degree of oxidation because dissolved lignin in a ClO_2 stage effluent is more oxidized.

Aromatic proton content

The aromatic proton region of the ^1H-NMR spectra of various residual lignins was integrated in an attempt to quantify the apparent aromatic proton content of the lignins.

The quantitative results from this NMR analysis are presented in Table 4.1. Some of the isolated residual lignins that were treated with ClO_2 (as discussed in Chapter 3) were also analyzed by quantitative ^{1}H-NMR. Four residual lignins (E29 r.l., E18 r.l., C28 r.l., and C18 r.l.) treated with three charges of ClO_2 were analyzed for their apparent aromatic proton content (Figure 4.5).

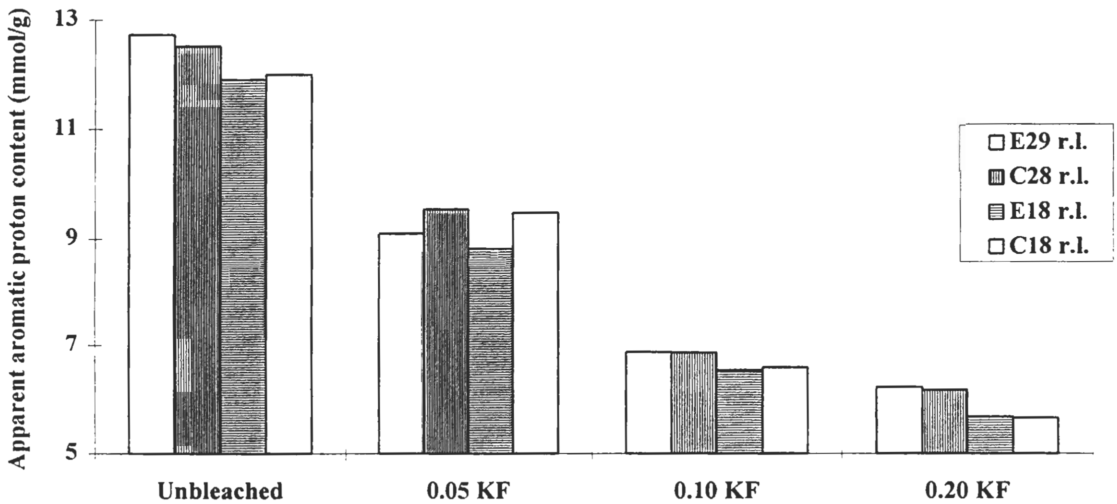


Figure 4.5. Aromatic proton content of various isolated unbleached residual lignins reacted with three charges of ClO_2. The aromatic proton content was determined by quantitative ^{1}H-NMR using underivatized lignins.

The analysis of the ClO_2-bleached residual lignins (Table 4.1) and the ClO_2-treated residual lignins after being reacted with ClO_2 (Figure 4.5) shows that the apparent aromatic proton content decreases during the reaction with ClO_2. Other studies have suggested that the content of aromatic protons in ClO_2-reacted lignins is low, but the quantification has never been performed, as has been done here (63,71). The quantitative analysis showed that lignin treated with a 0.05 KF charge of ClO_2 resulted in about a 25% loss in the apparent aromatic proton content, while a 0.20 KF charge caused a 50% loss.

The reduction was found to be greater in the isolated residual lignins treated with ClO_2, which again suggests that the homogeneous solution (or aqueous dioxane solvent system) resulted in a more complete oxidation of lignin. The loss in aromatic protons is a substantial modification to the lignin structure and can be interpreted by a few explanations. The loss can occur by ring-opening reactions, resulting in the loss of the aromatic structure of the lignin (with the subsequent formation of muconic acid and lactone structures); reactions involving the loss of olefinic protons in ring-conjugated structures (such as stilbenes); and chlorination reactions, resulting in ring substitution. Each explanation will be discussed in greater detail below.

The apparent aromatic proton content is determined by integrating the region of the spectrum that contains aromatic protons. Some olefinic protons, however, can have signals in this region. Ring-opening reactions result in the reduction of aromatic protons but create olefinic protons that may or may not contribute to the aromatic proton region. Model compound studies on the chemical shifts of muconic acid and lactone derivatives suggest that some olefinic protons have chemical shifts that are upfield of the aromatic proton region, suggesting that such protons would not contribute to the aromatic proton signal (59,60). Indeed, an analysis of the ^{1}H-NMR spectra of lignin treated with ClO_2 (Figure 4.6) provides some verification of this, as the spectra show there is an increase in signal intensity in the region upfield of the aromatic proton signals (δ 6.5-5.5 ppm), which may be indicative of olefinic protons.

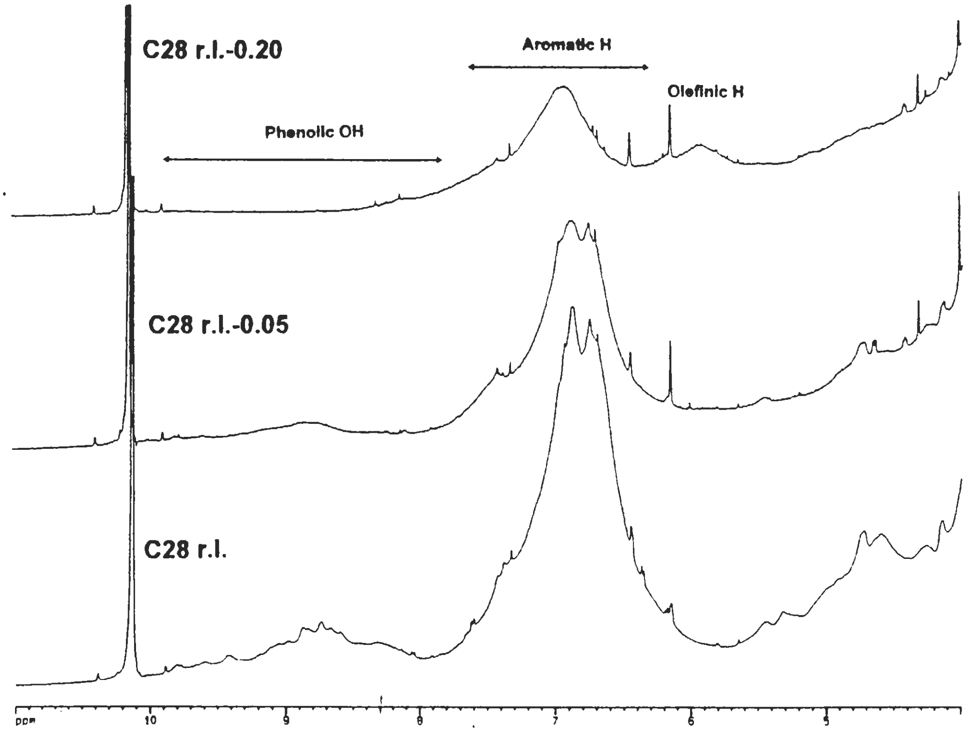


Figure 4.6. ^{1}H-NMR spectra of C28 r.l. and C28 r.l. treated with 0.05 KF ClO_2 and 0.20 KF ClO_2.

Stilbene and styrene structures are believed to be present in the residual lignin of unbleached pulp (33). The olefinic protons in these ring-conjugated structures also have chemical shifts in the aromatic region of the ^{1}H-NMR spectrum and would contribute to the apparent aromatic proton content in the unbleached residual lignin. Model compound studies have suggested that structures containing ring-conjugated unsaturated functional groups are quite reactive toward ClO_2 (67). ClO_2 preferentially reacts with the conjugated system, resulting in the loss of the olefinic protons. This effect would influence the observed loss in the apparent aromatic proton content of the lignins treated with ClO_2. However, because the content of these structures is believed to be relatively minor in the residual lignin of unbleached pulp, the observed dramatic loss in aromatic protons is probably influenced to a greater degree by other effects.

Chlorination of the aromatic ring via aromatic substitution reactions would also result in a net loss of aromatic protons during a ClO_2 treatment of lignin. Chlorination occurs due to the presence of hypochlorous acid and its equilibrium partner, elemental chlorine, which are formed during the reaction of ClO_2 with lignin. Such reactions have been shown to occur during ClO_2 delignification, as discussed in the Literature Review section. The contribution of this reaction to the overall loss of aromatic protons is difficult to determine from the data presented.

Substituted aromatic carbons

The relative content of substituted aromatic carbon atoms of the ClO_2-bleached residual lignins was found to be higher than the corresponding unbleached residual lignins, as determined by ^{13}C-NMR. This may be indicative of an increase in the amount of condensed aromatic structures in the ClO_2-bleached residual lignin, suggesting that the ClO_2 preferentially reacts with uncondensed lignin. A similar result was concluded in studies by Osterberg (63,71). This result is in agreement with the previous finding that 'condensed' lignin is less reactive toward ClO_2.

Aliphatic carbons linked to oxygen

The content of aliphatic carbons linked to oxygen was shown to increase in the ClO_2-treated lignins. This observation has been noted before for ClO_2-treated lignin and explained as being a result of either an increase in the aliphatic hydroxyl content or the creation of ether linkages (70,71). The increase in aliphatic hydroxyl content may partially contribute to this effect because Argyropoulos showed that residual lignins treated with ClO_2 resulted in an increase in aliphatic hydroxyl content; however, it was reported that the increase was not substantial (72). The content of ether linkages should not be increasing except for the formation of lactones. Carbon atoms adjacent to the ring oxygen in lactone structures have chemical shifts in this region (60).

ALKALINE EXTRACTION CHEMISTRY

After a pulp is bleached in an acidic ClO_2 stage, a large portion of the lignin can only be dissolved from the pulp by a subsequent treatment in an alkaline environment at elevated temperatures. The optimum conditions of an alkaline extraction stage, resulting in a pulp with the lowest residual lignin content, have been reviewed and shown to be affected by the exit pH, temperature, time, and the conditions used in the previous ClO_2 stage (100,101). The fact that a higher exit pH and a higher temperature affect the degree of delignification during an alkaline extraction stage suggests that some important chemical reactions may be influencing its dissolution. Lower kappa numbers after the extraction can be obtained by reinforcing the extraction stage with oxygen, which has become a common industrial practice today. The actual lignin content of the pulp has been found, however, not to be affected, suggesting oxygen-reinforced extracted pulp has a residual lignin that is more oxidized (102).

Analysis Overview

The important chemical modifications that occur to residual lignin during an alkaline extraction with and without oxygen reinforcement were studied by characterizing ClO_2-treated lignin before and after an alkaline treatment. The same pulps bleached with

ClO_2 in the previous section were alkaline extracted under various conditions (i.e., with and without oxygen reinforcement), and the residual lignins from these pulps were isolated and characterized by quantitative ^{13}C-NMR and ^{1}H-NMR. The lignins dissolved during the extraction stages were also isolated and characterized by quantitative ^{13}C-NMR and ^{1}H-NMR. Comparisons were then made between the ClO_2-bleached residual lignins and their corresponding alkaline-extracted residual and dissolved lignins. Structural differences between these lignins were then attributed to structural modifications occurring during the alkaline extraction.

The chemistry of the alkaline extraction stage was further explored by performing some reactions of ClO_2-treated lignin under alkaline extraction stage conditions. The lignins used in these experiments were residual lignin isolated from a ClO_2-bleached pulp and an isolated unbleached residual lignin that was treated with two charges of ClO_2.

Qualitative Analysis of ^{13}C-NMR Spectra

Some interesting observations can be made by comparing the spectra of ClO_2-bleached residual lignins with the spectra of alkaline-extracted residual and dissolved lignins. The quantitative ^{13}C-NMR spectra of lignin samples C28 D r.l. (0.20), C28 DE r.l. (0.20), and C28 DE d.l. (0.20) are presented in Figure 4.7. Comparing the carbonyl and methoxyl signals indicates that some important chemical modifications to the lignins have occurred. The ratio of signal intensities of the carbonyl signals in the aliphatic carboxylic acid region compared to the signals in the conjugated carboxylic acid region has changed. In the ClO_2-bleached residual lignins, the intensity of the δ 170-165 ppm

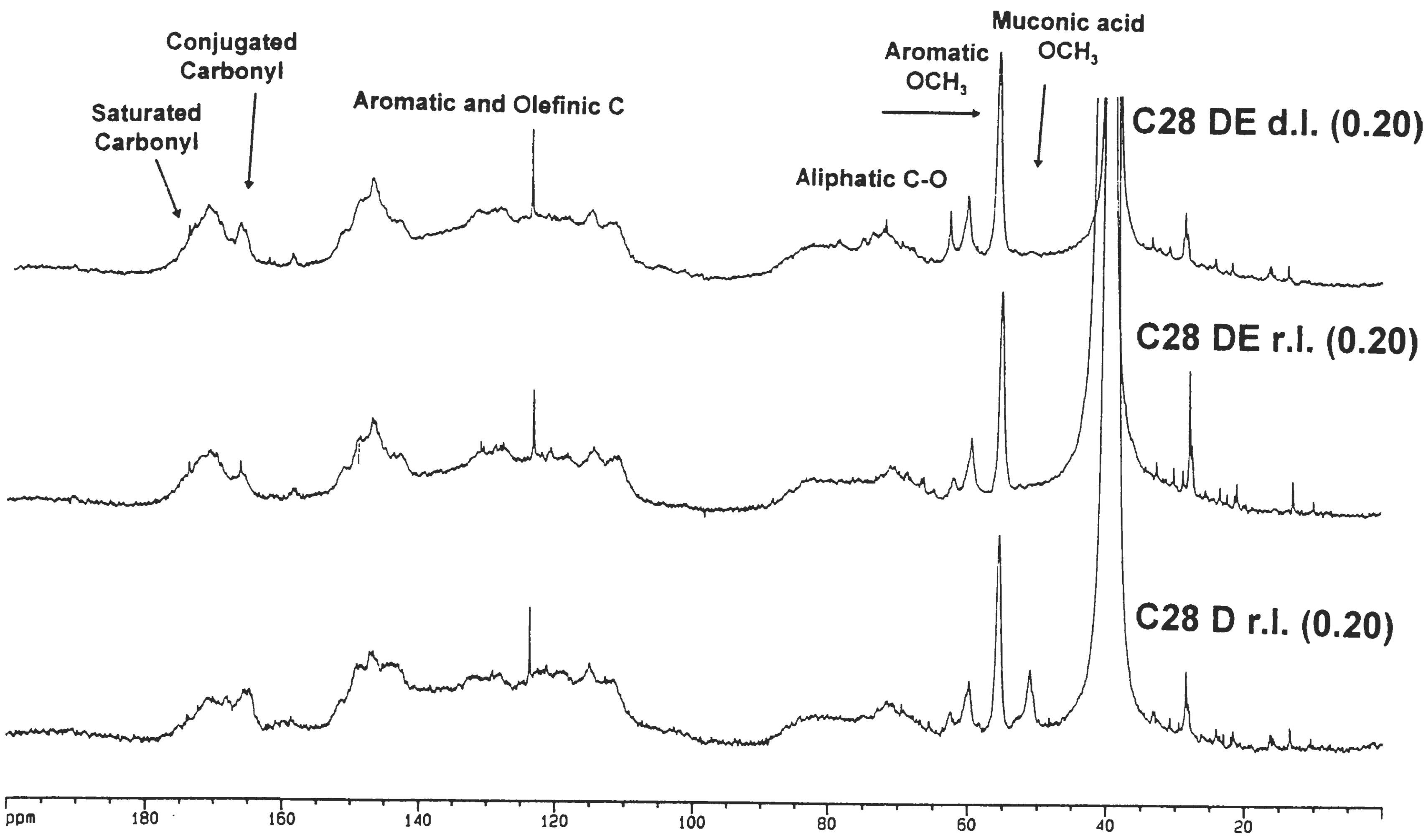


Figure 4.7. Quantitative ^{13}C-NMR spectra of residual lignin isolated from ClO_2-bleached C28 pulp (C28 D r.l. (0.20)), residual lignin isolated from this same pulp after an alkaline extraction (C28 DE r.l. (0.20)) and dissolved lignin isolated from its alkaline extraction stage effluent (C28 DE d.l. (0.20)).

region compared to the δ 180-170 ppm region is high, but after the alkaline extraction, the relative intensities are reversed as the δ 170-165 ppm region decreases as the δ 180-170 ppm region increases. The result can be partially explained by an analysis of the methyl ester methoxyl signal, which is completely gone in the alkaline-extracted lignins, indicating that this ester linkage did not survive the alkaline extraction. The ester linkage appears to have been saponified, creating a carboxylic acid group (Figure 4.8). The saponification would create an aliphatic carboxylic acid that would influence the chemical shift of the carbonyl group. This may partially explain the observed intensity differences in the carbonyl region.

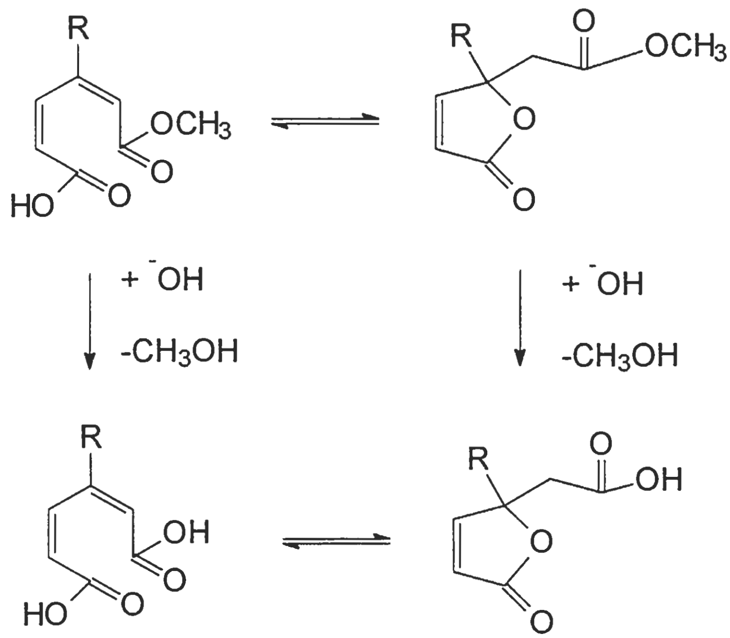


Figure 4.8. Saponification of the methyl ester group in muconic acid methyl ester and its cyclized lactone under alkaline extraction conditions.

Quantitative Analysis of Residual and Dissolved Lignins

Table 4.2 summarizes the results from the quantitative ^{13}C-NMR and ^{1}H-NMR analyses of residual and dissolved lignins produced from the alkaline extraction stage. Included in the table, for comparative purposes, is the quantitative analysis of ClO_2-bleached pulp residual lignin. The alkaline extractions were done with and without oxygen reinforcement, making comparisons between the isolated lignins informative on the chemical differences between the two processes. The following will be an analysis on some of the functional groups quantified.

Carboxylic acid content

The carboxylic acid content of the lignins was determined by ^{1}H-NMR and ^{13}C-NMR. The ^{1}H-NMR analysis clearly shows that the carboxylic acid content of the alkaline extracted residual and dissolved lignins was higher than the ClO_2-bleached residual lignin, indicating that carboxylic acid groups are formed during the alkaline extraction. The increase in carboxylic acids is likely due to saponification of methyl ester groups, which was indicated by the loss of the methyl ester methoxyl signal in the ^{13}C-NMR spectra. The increase may also be due to more ring-opened lactones in these lignins due to the alkaline treatment. McKague observed that some of the products from the reaction of lactones with NaOH were the ring opened, carboxylic acid form of the starting lactones (60).

Table 4.2. Quantitative ^{13}C-NMR and ^{1}H-NMR analysis of various residual (r.l.) and dissolved (d.l.) lignins isolated from ClO_2-bleached pulps, ClO_2-bleached and alkaline-extracted pulps, and alkaline extraction effluents. The extraction stages were performed both with and without oxygen reinforcement.

NMR Analysis	Structural Feature	Lignin ID		
		C28 D r.l. (0.05)	C28 DE r.l. (0.05)	C28 DE d.l. (0.05)
^{13}C-NMR†	Total COOH	0.47	0.56	0.70
	Aliphatic	0.34	0.44	0.58
	Conjugated	0.13	0.12	0.12
	Substituted*	4.12	4.12	4.19
	Aliphatic C-O	1.54	1.74	1.86
	Aromatic OCH_3	0.75	0.80	0.78
^{1}H-NMR	COOH	0.51	0.71	1.25
	Tot. Phenolic OH	1.71	1.52	1.20
	Aromatic H	9.39	10.08	8.67

NMR Analysis	Structural Feature	Lignin ID				
		C28 D r.l. (0.20)	C28 DE r.l. (0.20)	C28 DE d.l. (0.20)	C28 D(EO) r.l. (0.20)	C28 D(EO) d.l. (0.20)
^{13}C-NMR†	Total COOH	0.89	1.12	1.23	1.10	1.22
	Aliphatic	0.56	0.90	0.89	0.89	0.91
	Conjugated	0.33	0.22	0.34	0.21	0.31
	Substituted*	4.14	4.16	4.28	4.21	4.23
	Aliphatic C-O	1.75	2.32	2.06	2.23	2.22
	Aromatic OCH_3	0.49	0.66	0.67	0.64	0.66
^{1}H-NMR‡	COOH	0.90	1.54	-	1.44	2.06
	Tot. Phenolic OH	1.35	0.86	0.75	0.78	0.74
	Aromatic H	6.72	6.77	6.64	6.54	6.94

NMR Analysis	Structural Feature	Lignin ID				
		E29 D r.l. (0.10)	E29 DE r.l. (0.10)	E29 DE d.l. (0.10)	E29 D(EO) r.l. (0.10)	E29 D(EO) d.l. (0.10)
^{13}C-NMR†	Total COOH	-	0.80	1.00	0.84	1.03
	Aliphatic	-	0.68	0.80	0.69	0.82
	Conjugated	-	0.12	0.20	0.15	0.21
	Substituted*	-	4.24	4.17	4.18	4.17
	Aliphatic C-O	-	2.09	2.44	2.08	2.53
	Aromatic OCH_3	-	0.76	0.71	0.75	0.70
^{1}H-NMR‡	COOH	-	0.86	1.08	1.01	1.05
	Tot. Phenolic OH	-	1.09	0.82	1.11	0.75
	Aromatic H	-	7.52	7.89	8.00	7.64

NMR Analysis	Structural Feature	Lignin ID		
		E29 D r.l. (0.20)	E29 D(EO) r.l. (0.20)	E29 D(EO) d.l. (0.20)
^{13}C- NMR†	Total COOH	0.87	1.01	1.19
	Aliphatic	0.54	0.84	0.87
	Conjugated	0.33	0.17	0.32
	Substituted*	4.13	4.16	4.15
	Aliphatic C-O	-	2.28	2.26
	Aromatic OCH_3	0.53	0.69	0.66
^{1}H-NMR‡	COOH	0.89	1.38	1.65
	Tot. Phenolic OH	1.37	0.83	0.66
	Aromatic H	7.04	7.43	7.25

†^{13}C-NMR results reported as number of carbon atoms per aromatic unit; ‡^{1}H-NMR results reported as mmol/g lignin; *Substituted aromatic carbons; See Materials and Methods section for a description of the lignin ID.

The ^{13}C-NMR analysis shows that there is an increase in carbonyl groups of carboxylic acid and ester type (region from δ 180-165 ppm). This increase cannot be attributed to saponification and lactone ring-opening reactions because these reactions would not increase the content of carbonyl groups. The increase may be some other reactions in which carboxylic acid groups are formed.

The overall increase in the carboxylic acid content is quite an interesting aspect of alkaline extraction chemistry, particularly because the decarboxylation reactions have been suggested to occur during the alkaline extraction (75,102). Decarboxylation reactions are believed to result in the formation of sodium carbonate, which is found in the alkaline extraction effluent (75,102). The formation of carboxylic acids via saponification and other possible reactions must be more significant than the decarboxylation reactions, resulting in a net increase in the carboxylic acid content.

In addition to the alkaline-treated lignins having higher carboxylic acid contents than the ClO_2-treated lignins, the dissolved lignins in the alkaline extraction effluent were found to contain a greater content of carboxylic acids than the residual lignin isolated from the ClO_2-bleached and alkaline-extracted pulp. The greater content of carboxylic acids in the dissolved lignin suggests that there is a preferential dissolution of lignin with carboxylic acid groups. This is easy to interpret because carboxylic acid groups increase the water solubility of lignin. The content of carboxylic acid groups in residual lignin is still quite high, however, which indicates other factors are inhibiting the lignin from being dissolved. Residual linkages to carbohydrates may still be a significant impediment to the dissolution of residual lignin.

Phenolic hydroxyl content

The phenolic hydroxyl content of the lignins was determined by ^{1}H-NMR (Table 4.2). Some of these data for the C28 pulp bleached with different charges of ClO_2 and alkaline extracted have been graphed in Figure 4.9 for an easier visualization of the data. The results from the table and the figure clearly show that the content of phenolic hydroxyl groups is significantly lower in the alkaline-extracted lignins compared to the ClO_2-treated lignins, suggesting they have been depleted during the alkaline extraction. In addition, the phenolic content of dissolved lignins was found to be lower than the phenolic content in the alkaline-extracted residual lignins. Interestingly, this is the opposite of what is observed during kraft pulping, as the residual lignin has a lower phenolic content than the dissolved lignins. These are some significant differences that suggest some interesting chemistry is occurring during the alkaline extraction involving phenolic hydroxyl groups.

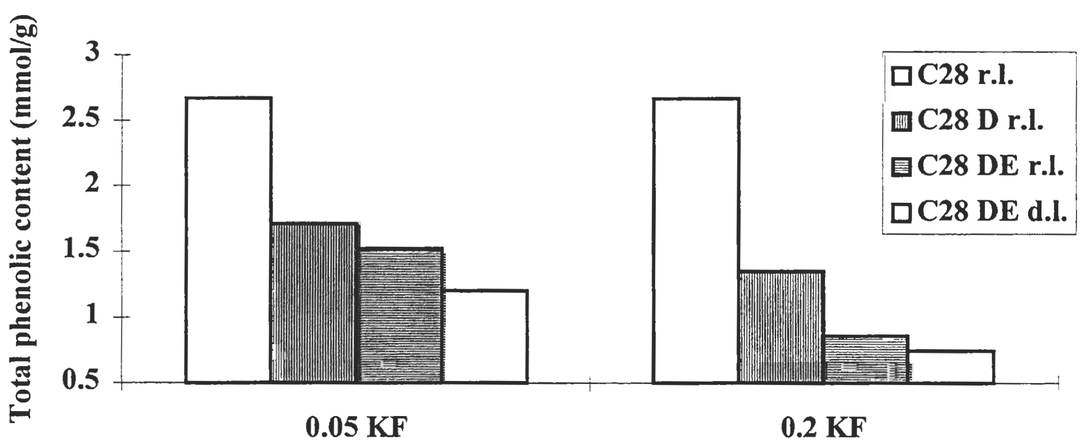


Figure 4.9. Phenolic content of various residual and dissolved lignins produced during the bleaching of C28 pulp with ClO_2 with kappa factors of 0.05 and 0.20. (data taken from Table 4.2 on page 196).

During an alkaline extraction of ClO_2-bleached pulps, lignin is believed to undergo nucleophilic addition reactions by hydroxide to quinonoid structures yielding hydroxylated or hydroxy substituted catechol structures (103). The formation of these hydrophilic groups is believed to increase the solubility of the lignin and aid in its dissolution during the alkaline extraction. However, if this reaction was occurring to any appreciable extent, an increase in the phenolic hydroxyl content would be observed. An increase is not observed and indicates that such reactions are not significant. The dissolution of lignin in alkaline medium following a ClO_2 stage seems to be more likely related to the increased solubility of the lignin by neutralization reactions and the introduction of carboxylic acid groups via saponification of methyl esters.

The depletion of phenolic groups during the alkaline extraction suggests that some of these groups have reacted with oxygen. Dissolved oxygen is present in an extraction stage, and under alkaline conditions, it can react with phenolic groups in lignin. Indeed, this is the premise behind oxygen delignification, which is also performed under alkaline conditions, but at higher temperatures and much higher pressures. The fact that dissolved lignins contained less phenolic groups compared to residual lignins may add some credibility to the explanation that phenolic groups are reacting with oxygen. Dissolved oxygen would be more prone to react with the dissolved lignin compared to residual lignin, causing a greater reduction in the phenolic content of the dissolved lignin.

The oxidation of lignin by oxygen can result in the formation of muconic acids, which may contribute to the increase in the carboxylic acid content observed for the alkaline-extracted lignins (103). However, the increase in carboxylic acids during an alkaline extraction stage will be suggested later not to have involved oxygen.

TREATMENT OF ClO_2-REACTED LIGNINS UNDER ALKALINE CONDITIONS

The structural comparison between ClO_2-treated lignins and ClO_2-treated and alkaline-extracted lignins suggested that the introduction of carboxylic acid groups and depletion of phenolic hydroxyl groups are major chemical modifications occurring during the alkaline extraction. These reactions were further explored in this section by treating different ClO_2-treated lignins under alkaline extraction stage conditions and monitoring the changes in the carboxylic acid and phenolic hydroxyl contents. Three lignins were used in these experiments, one was a residual lignin isolated from a ClO_2-bleached pulp (C28 D r.l. (0.20)) and the other two were from isolated unbleached residual lignins that had been reacted with two charges of ClO_2 (C33 r.l.-0.05 and C33 r.l.-0.20). The residual lignin isolated from the ClO_2-bleached pulp was treated under alkaline extraction conditions with and without oxygen reinforcement and in the complete absence of oxygen, while the isolated unbleached residual lignins that had been treated with two charges of ClO_2 were treated under identical alkaline extraction stage conditions. C33 r.l.-0.20 was also treated under alkaline extraction conditions with a low pH. Each of these experiments will be discussed separately.

ClO_2-Bleached Residual Lignin

The residual lignin isolated from the C28 pulp bleached with a 0.20 KF was treated under two different alkaline extraction conditions and the content of carboxylic acid and phenolic hydroxyl groups measured before and after the treatment. The conditions of the alkaline extraction treatment were 160% charge of NaOH on lignin (a typical charge on lignin during an alkaline extraction), 70°C for 60 minutes without (E) and with (EO) pressurized oxygen. A blank was also performed in which all experimental parameters were identical to E conditions except no NaOH was added. The results from the carboxylic acid analysis, as determined by quantitative ^{1}H-NMR, are reported in Figure 4.10.

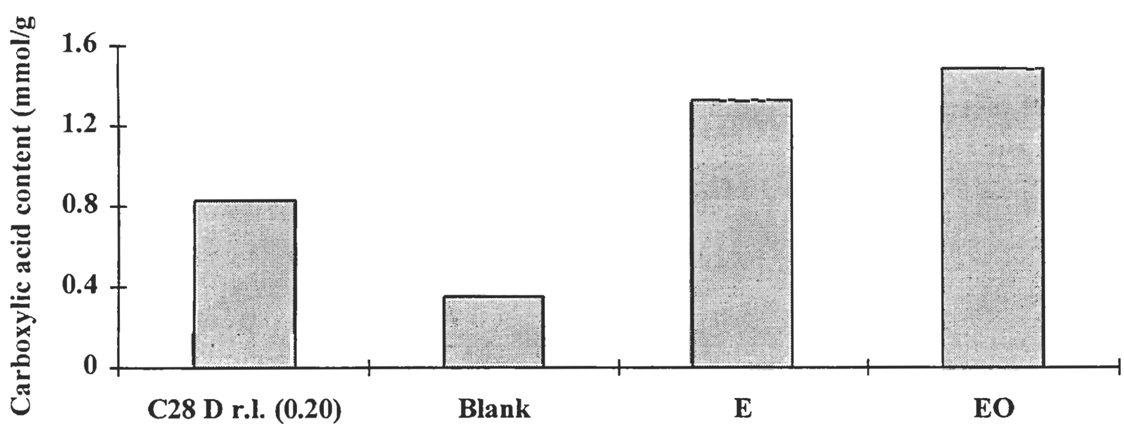


Figure 4.10. Carboxylic acid content of residual lignin isolated from a ClO_2-bleached pulp (C28 D r.l. (0.20)) and after a blank alkaline extraction treatment (Blank), an alkaline extraction treatment without oxygen reinforcement (E), and an alkaline extraction treatment with oxygen reinforcement (EO). For conditions, see Table 18 on page 88. The carboxylic acid content was determined by quantitative ^{1}H-NMR and the averages of two samples reported.

Figure 4.10 shows that the content of carboxylic acid groups decreased in the lignin treated under the blank extraction conditions. An explanation for this is presumably due to the experimental methods employed in the work-up and purification after the reaction and before the NMR analysis. After the reaction, the lignin solution is acidified to a pH of ~2 and the precipitate collected after repeated washing with water at pH ~2 and centrifuging. The purified lignin is then freeze dried from a suspension of water. The repeated washing steps may result in the loss of some highly water-soluble lignin containing a large fraction of carboxylic acid functional groups. This may result in the observed low content of carboxylic acid groups in the blank.

The lignins treated under the alkaline conditions showed a significant increase in the content of carboxylic acid groups. In comparison to the blank, which is a more relative comparison, there was about a threefold increase in carboxylic acid content for both the E and EO lignins. The increase in the EO lignin was found to be slightly greater than the increase in the E lignin, which could be interpreted as the pressuized O_2 causing the formation of additional muconic acid-type structures. The lignins were also analyzed by ^{31}P-NMR, but solubility problems made the quantitative analysis suspect. The spectra are shown in Figure 4.11 and also suggest that the EO lignin has the highest content of carboxylic acid groups followed by E and C28 D r.l. (0.20).

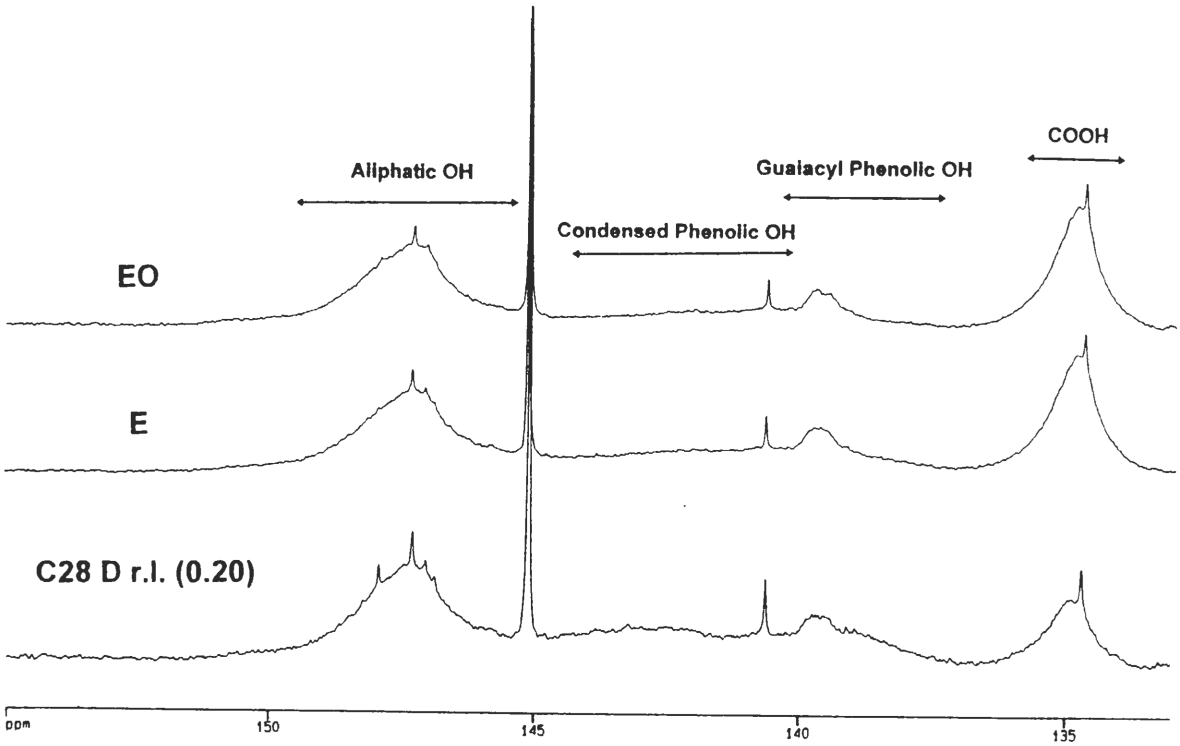


Figure 4.11. Quantitative ^{31}P-NMR spectra of residual lignin from ClO_2 bleached pulp and of this lignin after its treatment under various alkaline extraction conditions.

The results from these analyses substantiate the results from the residual and dissolved lignin analysis of ClO_2-bleached and alkaline-extracted pulps. The alkaline extraction conditions caused an increase in the content of carboxylic acid groups, which seems to be an important chemical reaction occurring during the alkaline extraction stage. The analysis supports the model compound studies, which showed that model compounds treated with ClO_2, followed by a treatment with NaOH, results in the formation of carboxylic acids. These acid groups are probably formed by the saponification of methyl esters (Figure 4.8).

Reinforcing the extraction stage with oxygen causes a slightly greater increase in the carboxylic acid content of lignin treated under alkaline conditions. The effect was also observed in the comparative analysis of residual and dissolved lignins isolated from DE and D(EO) bleached pulps and E and EO effluents. An explanation to this observance may be that oxygen is able to react with phenolic groups in lignin to create carboxylic acid groups. Both model compound studies and analyses of residual and dissolved lignins from oxygen-delignified pulps and effluents have found that oxygen delignification results in an increase in the content of carboxylic acid groups (96,103,104).

The phenolic hydroxyl content of these lignins was also analyzed and shown to decrease during the alkaline treatment (Figure 4.12), substantiating the effect observed in the residual and dissolved lignins analysis. Oxygen is known to be reactive toward phenolic groups, and because oxygen is present in both the E and EO treatments, the loss may due to the oxidative attack of phenolic groups by oxygen (103). The loss in phenolic content was slightly greater in the lignin that was reinforced with oxygen, suggesting that pressurized oxygen can be used to force the reaction of oxygen with phenolic groups, but for the most part, a large proportion of the phenolic groups seems to reactive toward oxygen under atmospheric pressures.

To determine if indeed the presence of oxygen affects the phenolic and carboxylic acid contents during the alkaline extraction, an experiment was performed in which the alkaline treatment was done in the complete absence of oxygen. Careful precautions were made to remove all the dissolved oxygen in the lignin solution, and the reaction was under an argon environment. The lignin was analyzed by ^{1}H-NMR and compared with the starting material and the E lignin (Figure 4.13).

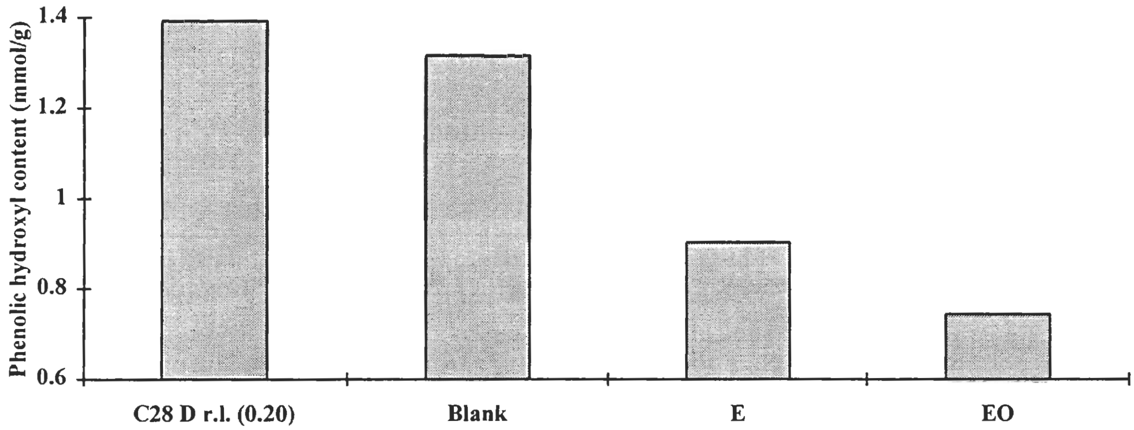


Figure 4.12. Phenolic content of same lignins analyzed in Figure 4.7. The phenolic contents were determined by quantitative ^{1}H-NMR.

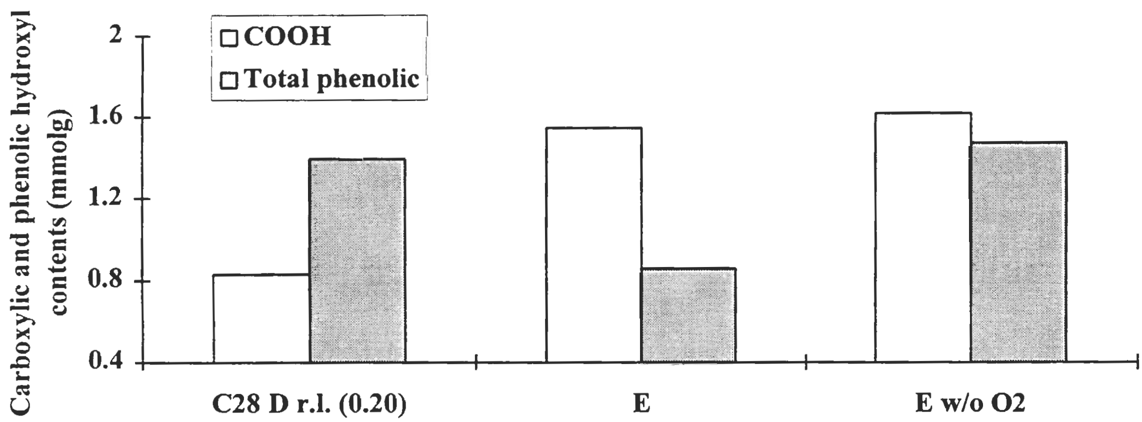


Figure 4.13. Content of carboxylic acid and phenolic groups in ClO_2-bleached residual lignin treated under alkaline extraction conditions in the presence and complete absence of oxygen.

The analysis showed some very interesting observations concerning the chemistry of an alkaline extraction. The introduction of carboxylic acid groups into the ClO_2-

bleached residual lignin was the same regardless of whether or not oxygen was present in the system; both alkaline extractions resulted in roughly the same introduction of carboxylic acids. Phenolic groups were not depleted during the alkaline extraction in the absence of oxygen, as the content of such groups remained the same after the alkaline extraction without oxygen. This implies that the introduction of carboxylic acid groups is probably due entirely to the reaction of lignin with hydroxide ions, which causes the saponification of methyl esters, and possibly other reactions, creating carboxylic acid groups. The oxidation of phenolic groups, which obviously occurs during the alkaline extraction in the presence of oxygen, seems not to contribute to the creation of carboxylic acids because the dramatic loss of phenolic groups in the E lignin did not result in a higher content of carboxylic acids compared to the E without O_2 lignin. The products from the oxidation of phenolic groups with oxygen must be something other than carboxylic acids, perhaps quinones (104).

ClO_2-Treated Isolated Unbleached Residual Lignin

An alkaline extraction stage would seem to be at its optimal efficiency when the conditions employed cause the greatest introduction of carboxylic acid groups because the introduction of carboxylic acid groups would aid in the dissolution of the lignin. The optimum alkaline extraction stage conditions have been found to be influenced by both the conditions used in the ClO_2 stage and by the pH, time, and temperature in the extraction stage (100). Saponification reactions creating carboxylic acid groups would be favored by more severe alkaline extraction conditions, i.e., higher charge of alkali, higher temperatures, and longer reaction times; the same factors that influence the optimal efficiency of the extraction stage. Additionally, because some of the introduction of carboxylic acids is coming from the saponification of methyl esters in MAME and lactone structures, then a greater concentration of such structures in the lignin would cause a greater introduction of acids during the alkaline extraction. Earlier it was shown that a higher charge of ClO_2 in the D stage creates more MAME and lactone structures, which would imply that their increased concentration would result in a greater increase of carboxylic acid groups during a subsequent alkaline extraction and enhance the lignin's dissolution.

To explore what influence the charge of ClO_2 in a D stage has on the introduction of carboxylic acid groups, an experiment was performed in which a lignin that had been treated with two different charges of ClO_2 was treated under identical alkaline extraction conditions, and the introduction of carboxylic acid groups was monitored. Additionally, to determine how the charge of NaOH influences the introduction of carboxylic acids, a ClO_2-treated lignin was treated under alkaline extraction stage conditions with different charges of NaOH (as measured by pH), and the change in carboxylic acid content was measured.

The isolated unbleached residual lignin C33 r.l. was treated with two charges of ClO_2 (0.05 and 0.20) and then treated under identical alkaline extraction conditions (pH 11, 70°C, 60 min). The C33 r.l.-0.20 lignin was also treated under a different pH condition to determine the effect of pH on the introduction of carboxylic acids (pH 9, 70°C, 60 min). The pH remained constant throughout the reaction for the lignins that were treated at pH 11. However, the lignin treated at an initial pH of 9 dropped to 7 by the end of the reaction period. The carboxylic acid content of these lignins was measured and is reported in Figure 4.14.

The quantitative analysis presented in Figure 4.14 reveals some very important results that can be used to answer some fundamental questions regarding the efficiency of the alkaline extraction stage. A comparison of the introduction of carboxylic acid groups in the lignins treated with different charges of ClO_2 and treated under the same alkaline extraction conditions shows that there is a substantially greater amount of carboxylic acid groups introduced into the lignin treated with a higher charge of ClO_2. This was explained as the lignin treated with a higher charge of ClO_2 having a greater content of methyl ester functional groups that result in a significantly greater introduction of carboxylic acid groups.

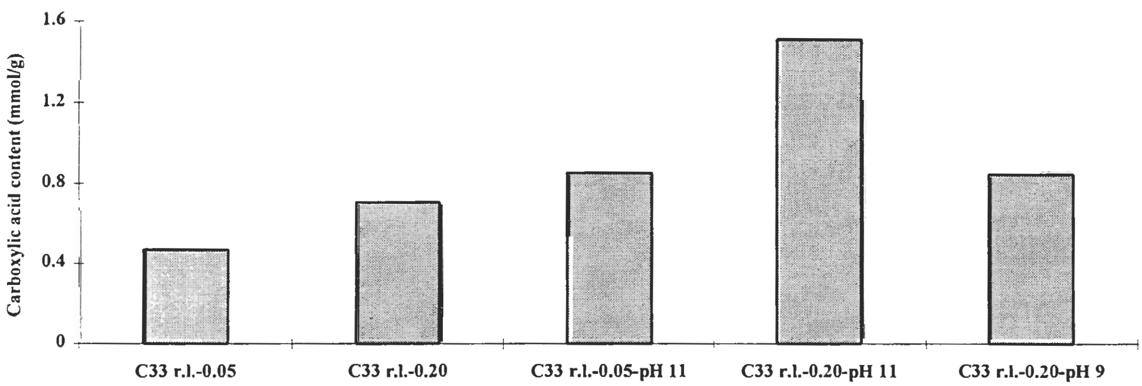


Figure 4.14. Carboxylic acid content of isolated unbleached residual lignins treated with ClO_2 and their contents after being treated under alkaline extraction stage conditions as determined by quantitative ^{1}H-NMR.

The lignins treated with the same charge of ClO_2 but different alkali charges showed that the introduction of carboxylic acid groups was significantly greater in the lignin treated with a higher charge of NaOH. The methyl esters in this case are consuming NaOH, resulting in the formation of carboxylic acids. Because a relatively small charge of NaOH was supplied to the lignin that introduced the smaller quantity of carboxylic acids, not all the methyl esters were capable of being saponified, and hence, a lower introduction of carboxylic acids was observed.

The results from these experiments can be used to explain an important phenomenon that is observed during the alkaline extraction of ClO_2-bleached pulp. Pulp bleached with higher charges of ClO_2 requires or consumes more alkali during the alkaline extraction (100,101). The results here suggest that a higher alkali charge is necessary not only to neutralize the greater content of carboxylic acid groups but also to saponify the greater content of methyl ester groups.

Comments on the Alkaline Extraction Stage

Muconic acid structures are present in the ClO_2-treated and alkaline-extracted lignins. These structures are in equilibrium with their cyclized product, lactones; the equilibrium constant being a function of the pH. Because the carboxylic acid functionality assists in the solubility of the lignin, and under alkaline conditions, the carboxylic acid form is prevalent, this structure may influence the dissolution of lignin during the alkaline extraction. During the alkaline extraction of a ClO_2-bleached pulp, the lactone form of muconic acid structure, which is apparently the favored form, when the lignin is under the acidic conditions of the ClO_2 stage, is ring opened to the carboxylic acid form causing the lignin to be more hydrophilic and assisting in the lignin's dissolution. Higher pH's would drive this equilibrium toward the carboxylic acid form, making the lignin more soluble. This may help to explain why the exit pH of an alkaline extraction influences the efficiency of delignification.

CONCLUSIONS

The chemistry of delignification during a partial delignification sequence involving ClO_2 and an alkaline extraction has been investigated by structurally characterizing numerous lignins that had been reacted with ClO_2 and subsequently treated under alkaline conditions. The result from this extensive analysis has provided new insights into the chemistry of these processes that can be interpreted from model compound studies and be used to explain some of the common observations noticed during ClO_2/alkaline extraction delignification sequences.

The analysis of residual lignin isolated from pulps that were bleached with different charges of ClO_2 suggested that some important chemical modifications occur to the lignin structure. A structural comparison between residual lignins in unbleached and ClO_2-bleached pulps revealed that the ClO_2 treatment caused a decrease in phenolic hydroxyl content, an increase in carboxylic acid content, and a decrease in the aromatic proton content. In addition, methyl ester groups of muconic acid structures were detected and quantified. These structures were found to be quite prominent in ClO_2-bleached lignin and may influence the lignin's dissolution in a subsequent alkaline extraction.

An analysis of the residual and dissolved lignins after an alkaline extraction stage suggested that some interesting chemistry is occurring during the alkaline treatment of

ClO_2-reacted lignins. The methyl ester functional groups that were found to be prevalent in the ClO_2-reacted lignins were not found in the alkaline-extracted lignins, indicating that these functional groups had been saponified during the alkaline treatment. Indeed, an analysis of the carboxylic acid content showed that the content of carboxylic acid groups was higher in the alkaline extracted-lignins. The phenolic content of the alkaline-extracted lignins was found to be lower than the corresponding ClO_2-reacted lignins, indicating that phenolic groups were oxidized during the alkaline extraction. The oxidation was determined to be due to the presence of oxygen and did not result in any noticeable formation of carboxylic acid groups.

The studies on the reaction of ClO_2-reacted lignins treated under alkaline extraction stage conditions have substantiated the residual and dissolved lignin analysis of alkaline extracted lignins. The creation of carboxylic acid groups during the alkaline extraction does not involve oxygen, indicating that saponification reactions are causing the increase in the carboxylic acid contents of these lignins.

The introduction of carboxylic acids may not be the only factor that influences the efficiency of an alkaline extraction stage. Lactone structures are present in these lignins that are in equilibrium with their ring open muconic acid form that would increase the solubility of the lignin during an alkaline extraction. The equilibrium of the acid/lactone may be an important chemical phenomenon that governs the dissolution of the lignin and hence the efficiency of an alkaline extraction stage.

CONCLUSIONS

A variety of lignins have been isolated from kraft pulps, black liquors, ClO_2-bleached pulps, ClO_2-bleached and alkaline-extracted pulps, and alkaline extraction effluents. These lignins have been characterized by employing advanced NMR analyses in an attempt to further understand the chemical mechanisms leading to delignification, the process by which lignin is removed from wood and lignin-containing pulps.

An analysis of residual lignin in CK and EK kraft pulps, with similar kappa numbers ranging from 29 to 13, revealed that structural differences between high and low kappa residual lignins were quite significant. Differences included the content of β-O-4 linkages and condensed structures. These structural differences could influence the reactivity of residual lignin toward further fragmentation and dissolution. Structural differences in CK and EK pulps with similar kappa numbers were also observed that suggested that EK residual lignins would be more reactive at a given kappa number. Improving the selectivity seems to be possible by modifying the pulping conditions such that a reactive lignin structure is maintained in the fiber, which can allow the cook to be extended to greater levels of delignification.

A structural analysis of the kraft lignins found that kraft lignins underwent similar structural changes as residual lignins. The lignins became enriched in condensed structures while simultaneously becoming less prevalent in β-O-4 structures. Differences between CK and EK kraft lignins were observed and explained as being due to the different pulping process variables used during CK and EK pulping.

The efficiency of delignification during ClO_2 bleaching was studied by bleaching the various kappa number pulps and pulp types in a D(EO) partial delignification sequence. As the kappa number of these pulps was lowered, the pulps became more difficult to delignify. Also, the E18 pulp was easier to delignify than the C18 pulp. The differences in bleachability were interpreted as being due to the differences in the structural features of the residual lignins. Experiments in which the isolated residual lignins were reacted with ClO_2 found that higher kappa residual lignins were more reactive than lower kappa residual lignins as indicated by their greater introduction of carboxylic acid groups, suggesting that higher kappa number pulps would be easier to delignify. EK residual lignins were also shown to be more reactive toward ClO_2 than CK residual lignins, at a given kappa number, suggesting that EK pulps would be easier to delignify. The reactivity experiments confirmed the bleaching results and suggested that a meaningful and important relationship exists between residual lignin structure and pulp bleachability. Perhaps an even more important result from this analysis is that pulping conditions can theoretically be optimized to enhance pulp bleachability.

Delignification during ClO_2 bleaching was also studied by structurally characterizing the residual and dissolved lignins produced during the ClO_2 treatment and the subsequent alkaline extraction. As expected, the unbleached residual lignins (both in the presence and absence of pulp) treated with ClO_2 were found to undergo some dramatic structural modifications. Changes to the lignin structure included the introduction of carboxylic acids (including the formation of methyl ester muconic acid structures), a dramatic but not complete loss of phenolic groups, and a large decrease in the apparent aromatic proton content.

During an alkaline treatment of the ClO_2-treated lignins, additional chemical modifications occur to the lignin, which assist in the lignin's dissolution. Although decarboxylation reactions occur during the alkaline extraction, an overall increase in the carboxylic acid content was observed. The increase in acid groups was suggested to be mainly due to the saponification of methyl esters. The increase in acid content was found not to be affected by the presence of oxygen, indicating that the introduction of these acids is not a result of the oxidation of phenolic groups by oxygen but rather from the nucleophilic reaction of hydroxide ions with lignin, indicative of saponification. The phenolic hydroxyl contents of the lignins treated under alkaline extraction conditions were found to decrease, and strong evidence was found to suggest that this was due to the oxidation of phenolic groups by air (oxygen).

Delignification during kraft pulping and ClO_2 bleaching is quite complex. Using advanced NMR analyses for the characterization of residual and dissolved lignins produced from these processes have provided new insights into the chemistry of delignification. With the continuing need to comprehend and advance these technologies further, the results from this research can be used to propel these technologies into the next generation.

RECOMMENDATIONS FOR FUTURE WORK

The results from this extensive structural analysis of lignins have been informative on the chemical mechanisms leading to delignification during kraft pulping and ClO_2 bleaching. Clearly in such a complicated field as delignification of lignocellulosics materials, which has been studied for many years by many wood chemists, biochemists, and chemical engineers, no one dissertation can lead to a complete enlightenment, particularly a dissertation on just the chemistry because other physical factors certainly influence the process. Throughout this dissertation, many conclusions were drawn from an even greater number of observations made, such is the scientific method. The conclusions drawn were informative on the chemistry of delignification during kraft pulping and ClO_2 bleaching, but certainly there exists the need, and indeed the requirement, to explore this chemistry further. The following is a list of recommendations for future areas of study drawn from the conclusions made in this dissertation.

Kraft Pulping

- The conclusions from the study of residual lignins in kraft pulps suggested that as delignification proceeds the residual lignin becomes less and less reactive toward the pulping conditions and pulping under 'modified' conditions seems to slightly retard this effect, leaving the lignin in a more reactive form at a given degree of delignification. Why this occurs seems to be related to the pulping conditions used, but whether it actually aids in the poor selectivity of kraft pulping has not been firmly established and certainly should be if kraft pulping technology is to be advanced beyond its current limited state.

- Condensation reactions occurring in the dissolved lignins under kraft pulping conditions were observed, but whether or not they occur in the residual lignin, which is still in a solid phase during pulping, could not be conclusively determined, although residual lignin in solution was observed to be condensed under kraft pulping conditions. Determining if condensation reactions occur in the residual lignin resulting in an enrichment of condensed structures in the residual lignin is important because they could be the cause of the poor delignification selectivity during kraft pulping.

ClO_2 Bleaching

- Bleachability differences were observed between conventional and 'modified' kraft pulps that could be related to the residual lignin structure and its reactivity toward ClO_2. The results imply that pulping conditions, which influence residual lignin structure, which, in turn, influences bleachability, can be modified and optimized to yield a more bleachable pulp that uses bleaching chemicals at their optimal performance.

- ClO_2-treated residual lignins were found to contain appreciable amounts of methyl ester groups, which are saponified during the alkaline extraction, creating additional carboxylic acid groups in the lignin. The importance of this reaction on the efficiency of an alkaline extraction stage is an interesting area of study.

- An important conclusion that was drawn from the observations was that aryl ether linkages in the residual lignin are cleaved during ClO_2 bleaching, creating phenolic groups that can further react with ClO_2. This was used to interpret the greater reactivity of the higher kappa residual lignin toward ClO_2. A highly informative experiment could be performed to show whether or not such a reaction contributes to the greater reactivity of higher kappa residual lignin. Isolated residual lignin can be methylated to remove all phenolic hydroxyl groups and reacted with ClO_2 with and without the presence of sulfamic acid, a scavenger of hypochlorous acid. Measuring the changes in the content of carboxylic acid and phenolic hydroxyl groups can be informative on whether or not hypochlorous acid results in the cleavage of aryl ether linkages and the creation of carboxylic acid groups.

ACKNOWLEDGMENTS

I would like to sincerely thank the members of my thesis committee for their time, guidance, and constructive and critical evaluations of this dissertation. Faculty members like these make IPST the great place that it is. My advisor, Dr. A. J. Ragauskas, has kindly donated endless hours of conversation, from which many of the ideas in this dissertation were developed, often well into the night, making his family (Cate, Emma, Alyse, and Luke) deserving of an equal appreciation. My committee members, Drs. D. Dimmel and T. McDonough, whose experience and expertise in the areas of wood chemistry, pulping, and bleaching are surpassed by few, were invaluable in the completion of this thesis, and I only hope that someday a young man or woman will have the same respect for me that I have for them. Thanks also to the Member Companies of IPST for financial support.

I would also like to thank my parents, John and Eileen, and my grandmother, Constance, for teaching me the values of hard work and perseverance; my siblings, Becky, Andy, John Paul, Tom, Bill, and Sarah and their spouses for their support; and all the students, staff, and faculty at IPST for making IPST the great institution that it is and the time here enjoyable and worthwhile. A special thanks also to Dr. Cook for all his valuable assistance.

Finally, I would like to thank Mei, for her support and love while she waited patiently for well over a year for me to finish and join her, forever. I could not have done it without you!

LITERATURE CITED

1. Rydholm, S.A. Pulping Processes. New York, Interscience Publishers, 1965 p. 576.

2. Pulp and Paper Manufacture. Vol. 5 Alkaline Pulping. Atlanta, TAPPI Press, 1987 pp. 45-73.

3. Jiang, J.; Greenwood, B.; Phillips, J.; Becker, E. Extended Delignification with a Prolonged Mild Counter-Current Cooking Stage. Appita 45(1):19-22 (1992).

4. Jiang, J. Extended Delignification of Southern Pine with Polysulfide and Anthraquinone. TAPPI Pulping Conference Proceedings, Atlanta, GA, Nov. 1-3, Vol. 1:313-321 (1993).

5. Gellerstedt, G.; Lindfors, E. Structural Changes in Lignin During Kraft Pulping. Holzforschung 38(3):151-158 (1984).

6. Gellerstedt, G.; Lindfors, E. Structural Changes in Lignin During Kraft Cooking. Part 2. Characterization by Acidolysis. Svensk Papperstidning 9:R61-R67 (1984).

7. Robert, D.; Bardet, M.; Gellerstedt, G.; Lindfors, E. Structural Changes in Lignin During Kraft Cooking. Part 3. On the Structure of Dissolved Lignins. Journal on Wood Chemistry and Technology 4(3):239-263 (1984).

8. Gellerstedt, G.; Lindfors, E. Structural Changes in Lignin During Kraft Cooking. Part 4. Phenolic Hydroxyl Groups in Wood and Kraft Pulps. Svensk Papperstidning 15:R115-118 (1984).

9. Gellerstedt, G.; Gustafsson, K. Structural Changes in Lignin during Kraft Cooking Part 5. Analysis of Dissolved Lignin by Oxidative Degradation. Journal of Wood Chemistry and Technology 7(1):65-80 (1987).

10. Gellerstedt, G.; Lindfors, E. On the Formation of Enol Ether Structures in Lignin During Kraft Cooking. Nordic Pulp and Paper Research Journal 2:71-75 (1987).

11. Gellerstedt, G.; Robert, D. Quantitative ^{13}C-NMR Analysis of Kraft Lignin. Acta Chemica Scancinavica B41:541-546 (1987).

12. Gellerstedt, G.; Gustafsson, Kraft.; Northey, R.A. Structural Changes in Lignin During Kraft Pulping. Part 8. Birch Lignins. Nordic Pulp and Paper Journal 2:87-94 (1988).

13. Sarkanen, K.V.; Ludwig, C.H. Lignin, Occurrence, Formation, Structure and Reactions. New York, Wiley (Interscience) (1971).

14. Sjostrom, E. Wood Chemistry: Fundamentals and Applications. Orlando, Academic Press 1981.

15. Bjorkman, A. Studies on Finely Divided Wood Part 3. Extraction of Lignin-Carbohydrate Complexes with Neutral Solvents. Svensk Papperstidning 60(7):243-251 (1957).

16. Eriksson, O. and Lindgren, B.O. About the Linkage Between Lignin and Hemicelluloses in Wood. Svensk Papperstidning 80:59-63 (1977).

17. Minor, J.L. Chemical Linkage of Pine Polysaccharides to Lignin. Journal of Wood Chemistry and Technology 2(1):1-16 (1982).

18. Iverson, T. Lignin-Carbohydrate Bonds in a Lignin-Carbohydrate Complex Isolated from Spruce. Wood Science and Technology 19:243-251 (1985).

19. Obst, J.R. Frequency and Alkali Resistance of Lignin-Carbohydrate Bonds in Wood. Tappi J. 65(4):109-112 (1982).

20. Adler, E. Lignin Chemistry-Past, Present, and Future. Wood Science and Technology 11:169-218 (1977).

21. Gierer, J. Chemical Aspects of Kraft Pulping. Wood Science and Technology 14:241-266 (1980).

22. Axegard, P.; Wiken, J. Delignification Studies - Factors Effecting the Amount of "Residual Lignin." Svensk Papperstidning 86:R178-184 (1983).

23. Gellerstedt, G.; Lindfors, E. On the Structure and Reactivity of Residual Lignin in Kraft Pulp Fibers. International Pulp Bleaching Conference Proceedings, Stockholm, Sweden, SPCI, Vol. 1:73-88 (1991).

24. Iversen, T.; Wannstrom, S. Lignin-Carbohydrate Bonds in a Residual Lignin Isolated from Pine Kraft Pulp. Holzforschung 40(1):19-22 (1986).

25. Gierer, J.; Wannstrom, S. Formation of Ether Bonds between Lignins and Carbohydrates during Alkaline Pulping Processes. Holzforschung 40(6):347-352 (1984).

26. Sjoblom, K.; Mjoberg, J.; Hartler, N. Extended Delignification in Kraft Cooking through Improved Selectivity. Part 1. The Effects of the Inorganic Composition of the Cooking Liquor. Paperi ja Puu 65(4):227-239 (1983).

27. Sjoblom, K.; Mjoberg, J.; Soderqvist, M.; Hartler, N. Extended Delignification in Kraft Cooking through Improved Selectivity. Part II. The Effects of Dissolved Lignin. Paperi ja Puu 70(5):452-461 (1988).

28. MacLeod, J.M. Extended Delignification: A Status Report. Appita 46(6):445-451 (1994).

29. Jiang, J.E. Extended Modified Cooking with Polysulfide for Simultaneous Pulp Yield and Strength Improvement. TAPPI Pulping Conference Proceedings, Boston, MA, Nov. 1-5, Vol. 2:683-690 (1992).

30. Dimmel, D.; Bovee, L. Pulping Reactions of Vinyl Ethers. Journal of Wood Chemistry and Technology 13(4):583-592 (1993).

31. Gierer, J. Chemistry of Delignification. Part 1. General Concept and Reactions during Pulping. Wood Science and Technology. 19:289-312 (1985).

32. Gellerstedt, G. Chemical Structure of Pulp Components. In: Bleaching Pulp Principles and Practice. Eds. C.W. Dence and D.W. Reeve Atlanta, Tappi Press 1996 pp. 91-111.

33. Yamasaki, T.; Hosoya, S.; Chen, C-L.; Gratzl, J.S.; Chang, H-M. Characterization of Residual Lignin in Kraft Pulp. International Symposium on Wood and Pulping Chemistry Proceedings, "Ekman Days 1981" Stockholm, Sweden, June 9-12, Vol.2:34-42 (1981).

34. Francis, R.; Lai, Y.Z.; Dence, C.W.; Alexander, T. Estimating the Concentration of Phenolic Hydroxyl Groups in Wood Pulps. Tappi J. 74(9):219-222 (1991).

35. Lai, Y.Z., Mun, S.P.; Luo, S.; Chen, H.T.; Ghazy, M.; Xu, G.; Jiang, J. Variation of Phenolic Hydroxyl Content in Unbleached Kraft Pulps. Holzforschung 49(4):319-322 (1996).

36. Jiang, Z.H. and Argyropoulous, D. The Stereoselective Degradation of Arylglycerol-beta-aryl Ethers During Kraft Pulping. Journal of Pulp and Paper Science 20(7):J183-188 (1994).

37. Granata, A.; Argyropoulous, D.S. 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. Journal of Agriculture and Food Chemistry 43:1538-1544 (1995).

38. Evstigneyev, E.; Maiyorova, H.; Platonov, A. Lignin Functionalization and the Alkaline Delignification Rate. Tappi J. 75(5):177-182 (1992).

39. Hortling, B.; Tamminen, T.; Tenkanen, M.; Teleman, A.; Pekkala, O. Investigations of Residual Lignin and Its Interaction with Polysaccharides in Chemical Pulps. International Symposium of Wood and Pulping Chemistry Proceedings, Helsinki, Finland, June 6-9, Vol. 1:231-238 (1995).

40. Gellerstedt, G. The Chemistry of Delignification in Prebleaching of Kraft Pulps. EUCEPA/ATICELCA 22nd Conference Development and Trends in Science and Technology of Pulp and Papermaking, Florence, Oct. 6-10. Vol. 2, Paper #27 (1986).

41. Kringstad, K.; Morck, R. ^{13}C-NMR Spectra of Kraft Lignin. Holzforschung 37(5):237-244 (1983).

42. Gellerstedt, G. Chemical Degradation Methods: Permanganate Oxidation In: Lin, S.Y. and Dence, C.W. (eds.) Methods in Lignin Chemistry, Springer Verlag Berlin Heidelberg 322-333 (1992).

43. Gierer, J.; Imsgard, F.; Pettersson, I. Possible Condensation and Polymerization of Lignin Fragments During Alkaline Pulping Processes. Applied Polymer Symposium 28:1195-1211 (1976).

44. Fullerton, T.J. The Condensation Reactions of Lignin Model Compounds in Alkaline Pulping Liquors. Journal of Wood Chemistry and Technology 7(4):441-462 (1987).

45. Kondo, R.; McCarthy, J. Condensation of Lignin with Coniferyl Alcohol in Alkaline Aqueous Solutions. Journal of Wood Chemistry and Technology 5(1):37-52 (1987).

46. Gellerstedt, G.; Robert, D. The Structural Modification of Lignin in Bleaching. International Symposium on Wood and Pulping Chemistry Proceedings, Raleigh, NC, May 22-25, Vol.1:211-215 (1989).

47. Hortling, B.; Ranua, M.; Sundquist, J. Investigation of the Residual Lignin in Chemical Pulps. Part 2. Purification and Characterization of Residual Lignin after Enzymatic Hydrolysis of Pulps. Nordic Pulp and Paper Research Journal 3(7):144-151 (1992).

48. Robert, D.; Gellerstedt, G.; Bardet, M. Carbon-13 NMR Analysis of Lignins Obtained after Sulfonation of Steam Exploded Aspen Wood. Nordic Pulp and Paper Research Journal 3:18-25 (1986).

49. Drumond, M.; Aoyama, M.; Chen, C.-L.; Robert, D. Substituent Effects on C-13 Chemical Shifts of Aromatic Carbons in Biphenyl Type Lignin Model Compounds. Journal of Wood Chemistry and Technology 9(4):421-441 (1989).

50. Pan, X; Lachenal, D.; Neirinck, V.; Robert, D. Structure and Reactivity of Spruce Mechanical Pulp Lignins IV: ^{13}C-NMR Spectral Studies of Isolated Lignins. Journal of Wood Chemistry and Technology 14(4):483-506 (1994).

51. Hortling, B.; Ranua, M.; Sundquist, J. Investigation of the Residual Lignin in Chemical Pulps. Part 1. Enzymatic Hydrolysis of the Pulps and Fractionation of the Products. Nordic Pulp and Paper Research Journal 5(1):33-37 (1990).

52. McDonough, T.J.; Berry, R.M.; Betts, J.L.; Du Manoir, J.R.; Reeve, D.W.; Turnbull, J.K. Chlorine Dioxide in the Chlorination Stage-A Summary of Existing Published Information. International Pulp Bleaching Conference Proceedings, Quebec City, Canada, June 18-21, Vol. 1:143-153 (1985).

53. Reeve, D.W. Chlorine Dioxide in Delignification In: Bleaching Pulp Principles and Practice Eds. C.W. Dence and D.W. Reeve Atlanta, TAPPI Press 1996 pp. 261-290.

54. Lindgren, B.O. Chlorine Dioxide and Chlorite Oxidation of Phenols Related to Lignin. Svensk Papperstidning 74(3):57-63 (1971).

55. Nonni, A.J.; Dence, C.W. The Reactions of Creosol and Propioguaiacone with Chlorine, Chlorine Dioxide and Their Combinations. Svensk Papperstidning 84:R17-R24 (1981).

56. Brage, C.; Eriksson, T.; Gierer, G. Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part I. Holzforschung 45(1):23-30 (1991).

57. Brage, C.; Eriksson, T.; Gierer, G. Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part II. Holzforschung 45(2):147-152 (1991).

58. McKague, A.B.; Kang, G.J.; Reeve, D.W. Reaction of a Lignin Model Dimer with Chlorine and Chlorine Dioxide. Holzforschung 47:497-500 (1993).

59. McKague, A.B.; Kang, G.J.; Reeve, D.W. Reactions of Lignin Model Dimers with Chlorine Dioxide. Nordic Pulp and Paper Research Journal. 2:84-87 (1994).

60. McKague, A.B.; Reeve, D.W.; Xi, F. Reaction of Lignin Model Compounds Sequentially with Chlorine Dioxide and Sodium Hydroxide. Nordic Pulp and Paper Research Journal 2:114-118 (1995).

61. Ni, Y., Shen, X.; van Heiningen, A.R.P. Studies on the Reactions of Phenolic and Non-Phenolic Lignin Model Compounds with Chlorine Dioxide. Journal of Wood Chemistry and Technology 14(2):243-262 (1994).

62. Dence, C.W. Chemistry of Chemical Pulp Bleaching In: Bleaching Pulp Principles and Practice Eds. C.W. Dence and D.W. Reeve Atlanta, TAPPI Press 1996 pp. 125-159.

63. Osterberg, F.; Lindstrom, K. Characterization of High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL) Part II. Acidic SBL. Holzforschung 39(3):149-158 (1985).

64. Linden, N.G.; Nicholls, G.A. Chlorine Dioxide Modification of *Picea glauca* Lignin. Tappi J. 59(11):110-113 (1976).

65. Kolar, J.J.; Lindgren, B.O.; Pettersson, B. Chemical Reactions in Chlorine Dioxide Stages of Pulp Bleaching. Intermediately Formed Hypochlorous Acid. Wood Science and Technology 17:117-128 (1983).

66. Ni, Y.; Kubes, G.J.; van Heiningen, A.R.P. Development of Phenolic Lignin During ClO_2 Bleaching of Kraft Pulp. Journal of Wood Chemistry and Technology 15(1):153-161 (1995).

67. Brage, C.; Eriksson, T.; Gierer, G. Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part III. Reactions with Model Compounds Representing Olefinic Structures in Native and Residual Lignins. Holzforschung 49:127-138 (1995).

68. Germgard, U. Technical Consequences of New Knowledge on Prebleaching with a High Fraction of Chlorine Dioxide. Tappi J. 12:81 (1982).

69. Francis, R.C.; Reeve, D.W. Hydrogen Peroxide Delignification-The Effects of Methylation and Demethylation. International Pulp Bleaching Conference Proceedings, Quebec City, Canada, June 18-21, Vol.1:61 (1985).

70. Gellerstedt, G.; Lindfors, E.L., Pettersson, M.; Sjoholm, E.; Robert, D. Chemical Aspects on Chlorine Dioxide as a Bleaching Agent for Chemical Pulps. International Symposium on Wood and Pulping Chemistry Proceedings, Appita, Parkville, Victoria, Australia, Vol.1:331 (1991).

71. Lindstrom, K.; Osterberg, F. Characterization of High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL) Part 1. Alkaline SBL. Holzforschung 38(4):201-212 (1984).

72. Sun, Y.; Argyropoulos, D. A Comparison of the Reactivity and Efficiency of Ozone, Chlorine Dioxide, Dimethyldioxirane and Hydrogen Peroxide with Residual Kraft Lignin. Holzforschung 50(2):175-182 (1996).

73. Joncourt, M.J.; Froment, P.; Lachenal, D.; Chirat, C. Reduction of the Formation of AOX During Chlorine Dioxide Bleaching. TAPPI Pulping Conference Proceedings, Chicago, IL, Oct. 1-5, Vol.1:149-152 (1995).

74. Rapson, H. and Anderson, C.B. Bleaching in Five Stages to the Asymptotic Limit Using Only One Oxidant and Sodium Hydroxide. International Pulp Bleaching Conference Proceedings, Quebec City, Canada, June 18-21, Vol.1:227-230 (1985).

75. Ni, Y.; van Heiningen, A. What Are the Differences between Caustic Extractions of Cl_2 and of ClO_2 Bleached Pulps. Nordic Pulp and Paper Research Journal 1:57-61 (1995).

76. H. Ludemann and H. Nimz, Biochemical and Biophysical Research Communications 52(4):1162-1169 (1973).

77. H. Nimz and H. Ludemann, Holzforschung 30(2):33-40 (1976).

78. Robert, D. Carbon-13 Nuclear Magnetic Resonance Spectrometry. In: Lin, S.Y. and Dence, C.W. (eds.) Methods in Lignin Chemistry, Springer Verlag Berlin Heidelberg 251-273 (1992).

79. Ludwig, C.; Nist, B.; McCarthy, J.L. The High Resolution Nuclear Magnetic Resonance Spectroscopy of Protons in Compounds Related to Lignin. The Journal of the American Chemical Society 86:1186-1196 (1964).

80. Ludwig, C.; Nist, B.; McCarthy, J.L. The High Resolution Nuclear Magnetic Resonance Spectroscopy of Protons in Acetylated Lignins. The Journal of the American Chemical Society 86:1196-1202 (1964).

81. Lundquist, K.; Olsson, T. NMR Studies of Lignins. 1. Signal Due to Protons in Formyl Groups. Acta Chemica Scandinavica B31(9):788-792 (1977).

82. Lundquist, K. NMR Studies of Lignins. 2. Interpretation of the ^{1}H-NMR Spectrum of Acetylated Birch Lignin. Acta Chemica Scandinavica B33(1):27-30 (1979).

83. Lundquist, K. NMR Studies of Lignins. 3. ^{1}H Spectroscopic Data for Lignin Model Compounds. Acta Chemica Scandinavica. B33(6):418-420 (1979).

84. Lundquist, K. NMR Studies of Lignins. 4. Investigation of Spruce Lignin by ^{1}H-NMR Spectroscopy. Acta Chemica Scandinavica. B34(1):21-26 (1980).

85. Lundquist, K. ^{1}H-NMR Spectral Studies of Lignins. Quantitative Estimates of Some Types of Structural Elements. Nordic Pulp and Paper Research Journal 3:140-146 (1991).

86. Lundquist, K.; Stern, K. Analysis of Lignins by ^{1}H-NMR Spectroscopy. Nordic Pulp and Paper Research Journal 3:210-213 (1989).

87. Lundquist, K. Proton (^{1}H) NMR Spectroscopy. In: Lin, S.Y. and Dence, C.W. (eds.) Methods in Lignin Chemistry, Springer Verlag Berlin Heidelberg 242-249 (1992).

88. Li, S.; Lundquist, K. A New Method for the Analysis of Phenolic Groups in Lignins by ^{1}H-NMR Spectrometry. Nordic Pulp and Paper Research Journal 3:191-195 (1994).

89. Lebo, S.E.; Lonsky, W.F.W.; McDonough, T; Medvecz, P.J.; Dimmel, D.R. The Occurrence and Light-Induced Formation of ortho-Quinonoid Lignin Structures in White Spruce Refiner Mechanical Pulp. Journal of Pulp and Paper Science. 16(5):J139-J143 (1990).

90. Argyropoulos, D.S.; Bolker, H.I.; Heitner, C.; Archipov, Y. ^{31}P-NMR Spectroscopy in Wood Chemistry. Part V. Qualitative Analysis of Lignin Functional Groups. Journal of Wood Chemistry and Technology. 13(2):187-212 (1993).

91. Argyropoulos, D.S. ^{31}P-NMR Spectroscopy in Wood Chemistry. A Review of Recent Progress. International Symposium on Wood and Pulping Chemistry Proceedings, Beijing, May 25-28, Vol. 2:776-786 (1993).

92. Pepper, J.M.; Baylis, P.E.T.; Adler, E. The Isolation and Properties of Lignins Obtained by the Acidolysis of Spruce and Aspen Woods in Dioxane-Water Medium. Canadian Journal of Chemistry 37:1241 (1959).

93. Gellerstedt, G.; Pranda, J.; Lindfors, E.-L. Structural and Molecular Properties of Residual Birch Kraft Lignins. Journal of Wood Chemistry and Technology 14(4):467-482 (1994).

94. Zwierzak, A. Cyclic Organophosphorous Compounds. I. Synthesis and Infrared Spectral Studies of Cyclic Hydrogen Phosphites and Thiophosphites. Canadian Journal of Chemistry 45:2501 (1967).

95. Marton, J.; Adler, E. Reactions of Lignin with Methanolic Hydrochloric Acid. A Discussion of Some Structural Questions. Tappi J. 46(2):92-98 (1963).

96. Gellerstedt, G. and Lindfors, E.-L. Hydrophilic Groups in Lignin After Oxygen Bleaching Tappi J. 70(6):119-122 (1987).

97. Gellerstedt, G. Bleaching and Environment. Two Compatible Concepts. International Symposium on Wood and Pulping Chemistry Proceedings, Beijing, May 25-28, Vol. 1:9-15 (1993).

98. Backman, L.; Gellerestedt, G. Reactions of Kraft Pulp Lignin with Alkaline Hydrogen Peroxide. International Symposium on Wood and Pulping Chemistry Proceedings, Beijing, May 25-28, Vol.1:223-229 (1993).

99. Lachenal, D. Behavior of Residual Lignin in Kraft Pulp During Bleaching. Journal of Pulp and Paper Science 21(5):J173-177 (1994).

100. van Lierop, B.; Liebergott, N.; Teodorescu, G. Caustic Extraction, Part I: Process Variables. 1989 Bleach Plant Operations:45-51 (1989).

101. Berry, R. (Oxidative) Alkaline Extraction In: Bleaching Pulp Principles and Practice. Eds. C.W. Dence and D.W. Reeve Atlanta, TAPPI Press 1996 pp. 291-320.

102. Berry, R.M.; Fleming, B.I. The Consumption of Alkali in Extraction Stages. International Pulp Bleaching Conference Proceedings, Quebec City, Canada, June 18-21, Vol.1:93-98 (1985).

103. Gierer, J. Chemistry of Delignification Part 2: Reactions of Lignins During Bleaching. Wood Science and Technology 20:1-33 (1986).

104. McDonough, T.J. Oxygen Delignification In: Bleaching Pulp Principles and Practice Eds. C.W. Dence and D.W. Reeve Atlanta, TAPPI Press 1996 pp. 213-239.

105. TAPPI Test Method T 236 cm-85. Kappa Number of Pulp.

106. Tasman, J.E. and Berzins, V. The Permanganate Consumption of Pulp Materials. Tappi J. 40(9):691 (1957).

APPENDICES

APPENDIX I

BLEACHING EXPERIMENTS

Data from the ClO_2 bleaching experiments described in the Materials and Methods section and discussed in Chapters 3 and 4 are presented in this appendix. Relevant data for both the bleachability study (Chapter 3) and the analysis of residual and dissolved lignins from ClO_2-bleached and alkaline-extracted pulps (Chapter 4) are presented.

Bleachability

Five pulps were used in this study, namely E29, E18, E14, C28, and C18. Replicate bleaches were performed on each pulp. Relevant data from the ClO_2 stage are presented in Table A1.1 and from the alkaline extraction in Table A1.2.

Table AI.1. Relevant data from the ClO_2 stage from the pulps bleached for the bleachability study.

Unbleached Pulp	Unbleached Kappa #	Charge of ClO_2 as TAC	Exit pH (repl.)	Kappa # (repl.)	TAC/ Δ kappa #
C28	28.0	5.10	2.20 (2.15)	11.01 (10.87)	0.299
C18	18.5	3.42	2.24 (2.30)	9.39 (9.04)	0.368
E29	29.1	5.50	1.60 (1.60)	11.30 (10.81)	0.305
E18	18.5	3.45	1.88 (1.98)	7.75 (7.17)	0.313
E14	14.5	2.79	2.04 (2.30)	6.02 (5.91)	0.327

All pulps were bleached with about a 0.19 KF for 30 minutes at 45°C; TAC-Total Active Chlorine; repl.-replicates.

Table AI.2. Relevant data from the EO stage of the pulps bleached in the bleachability study.

Unbleached Pulp	Unbleached Kappa #	Charge of NaOH	Exit pH (repl.)	Kappa # (repl.)	TAC/ Δ kappa #
C28	28.0	2.55	12.0 (12.2)	3.82 (3.75)	0.216
C18	18.5	1.71	11.6 (11.7)	3.45 (3.64)	0.229
E29	29.1	2.75	12.0 (11.9)	3.20 (3.35)	0.213
E18	18.5	1.72	11.5 (12.1)	3.02 (2.90)	0.222
E14	14.5	1.40	11.8 (12.1)	2.33 (2.35)	0.229

The extraction stage was performed at 70°C for 60 minutes. Oxygen was added at an initial pressure of 60 psig and decreased 12 psi every 5 minutes.

Residual and Dissolved Lignins

Tables A1.3-A1.4 contain some relevant data for the ClO_2 and E/EO stages used in the analysis of residual and dissolved lignins produced during ClO_2 bleaching.

Table AI.3. Relevant data for the ClO_2 stage used for the analysis of residual lignins in ClO_2-bleached pulp.

Pulp ID	Charge of $_{ClO2}$ TAC (KF)	Exit pH	Residual lignin ID
C28	1.35(0.05) 5.12 (0.20)	2.0 1.6	C28 D r.l. (0.05) C28 D r.l. (0.20)
C18	3.42 (0.20)	1.8	C18 D r.l. (0.20)
E29	2.84(0.10) 5.68(0.20)	2.2 2.0	E29 D r.l. (0.10) E29 D r.l. (0.20)
E18	3.60 (0.20)	1.8	E18 D r.l. (0.20)

Table AI.4. Relevant data for the alkaline extraction stage used for the analysis of residual and dissolved lignins in ClO_2-bleached and alkaline-extracted pulps.

Pulp ID	NaOH (% on pulp)	Oxygen	Exit pH	Residual lignin ID	Dissolved lignin ID
C28 D (0.05)	1.50	no	11.7	C28 DE r.l. (0.05)	C28 DE d.l. (0.05)
C28 D (0.20)	2.56	no	12.0	C28 DE r.l. (0.20)	C28 DE d.l. (0.20)
C28 D (0.20)	2.57	yes	12.0	C28 D(EO) r.l. (0.20)	C28 D(EO) d.l. (0.20)
C18 D (0.20)	1.71	yes	11.6	C18 D(EO) r.l. (0.20)	C18 D(EO) d.l. (0.20)
E29 D (0.10)	1.42	no	10.7	E29 DE r.l. (0.10)	E29 DE d.l. (0.10)
E29 D (0.10)	1.42	yes	10.1	E29 D(EO) r.l. (0.10)	E29 D(EO) d.l. (0.10)
E29 D (0.20)	2.84	yes	12.3	E29 D(EO) r.l. (0.20)	E29 D(EO) d.l. (0.20)
E18 D (0.20)	1.80	yes	11.6	E18 D(EO) r.l (0.20)	E18 D(EO) d.l (0.20)

APPENDIX II

RESIDUAL LIGNIN ISOLATION

Residual lignins were isolated from the unbleached pulps by employing an acid hydrolysis procedure in which pulp is refluxed for 1 hour in a 0.05 N HCl 9:1 dioxane:water solution. The conditions used during this isolation (time, acid concentration, and dioxane:water ratio) were optimized after an extensive study was performed to determine the best conditions to employ. Some details from this study are discussed in this appendix. The yields from the various CK and EK pulps have also been reported in this appendix.

Optimizing the Acid Hydrolysis Conditions

The acid hydrolysis technique is an easy method to isolate a carbohydrate-free residual lignin sample from kraft pulps. The fact that the residual lignin is carbohydrate-free makes it much easier to characterize by NMR techniques. The mechanism believed to be responsible for the liberation of lignin is the hydrolysis of covalent linkages between lignin and carbohydrates. This mechanism is justified by an extraction of pulp with dioxane/water alone, which does not remove any residual lignin from the pulp even though dioxane:water is a good lignin solvent (93). The technique, however, suffers from two drawbacks; one being that the conditions used are quite severe and may cause some unwanted chemical modifications to the lignin's structure, and the other being that the yield is dependent on the severity of the isolation conditions. Increasing the yield requires that more severe conditions be used (i.e., higher acid concentration and longer times). Optimizing the isolation conditions is necessary.

Experiments were designed to determine how time, acid concentration, and solvent ratio influence the yield of residual lignin. The pulp used in these experiments was a softwood, 18.3 kappa lab-produced EK pulp. The time, acid concentration, and solvent ratio were varied and the yield of lignin determined. The yields were determined by calculating the percentage of isolated product from the theoretical amount of lignin present in the pulp, which was determined by the kappa number/lignin content relationship. In the first set of experiments, two times (2 and 8 hours), two acid concentrations (0.1 N and 0.2 N), and two solvent ratios (4:1 and 9:1 (dioxane:water)) were studied. Replicates were performed for each experiment, and the results are given in Table AII.1.

Table AII.1. Yield of residual lignin from acid hydrolysis experiments employing different concentrations of acid, times, and dioxane:water ratios.

	Acid Conc.	2 hours 4:1 ratio	2 hours 9:1 ratio	8 hours 4:1 ratio	8 hours 9:1 ratio
1st experiment	**0.1 N**	44.3	50.6	60.9	63.2
	0.2 N	52.4	57.6	59.3	70.1
Replicate	**0.1 N**	48.1	50.7	53.7	-
	0.2 N	49.8	53.3	-	70.6

The data from these experiments show that each condition influences the yield of residual lignin with the time having the greatest influence. Increasing the time from 2 to 8 hours caused a more significant increase in yield compared to the other effects, suggesting that increasing the time is an effective way to enhance the residual lignin yield. The experiments found that the highest yield could be attained with a 0.2 N HCl concentration, a 9:1 dioxane:water ratio, and a refluxing time of 8 hours.

Because increasing the acid concentration from 0.1 N to 0.2 N had a relatively minor effect yield, it was decided to determine the effects of using lower acid concentrations. A few more experiments were therefore performed in which the acid concentrations were 0.05 N and 0.01 N. The results from these experiments, along with some data from the 0.1 N and 0.2 N experiments, are reported in Table AII.2.

Table AII.2. Yield of residual lignin under various acid concentrations and times during an acid hydrolysis of kraft pulp.

Acid Conc.	Time = 2 hrs	Time = 8 hrs	Time = 16 hrs	Time = 24 hrs
0.2 N	55.5 % (2)	70.4 % (2)	-	-
0.1 N	50.7 % (2)	63.2 % (1)	-	-
0.05 N	45.2 % (4)	60.2 % (2)	-	72.3 % (1)
0.01 N	23.6 % (1)	-	40.3 % (1)	-

Dioxane:water ratio = 9:1. All percentages are reported as the percent of original lignin, as determined by multiplying the kappa number by 0.147. The number in parentheses is the number of times the experiment was performed; the percentages are therefore averages if more than one experiment was done.

Lowering the acid concentration from 0.2 N to 0.1 N and from 0.1 N to 0.05 N decreased the yield of residual lignin by approximately 5% for each case (at a refluxing time of 2 hours). When the acid concentration was further reduced from 0.05 to 0.01 N, the yield, compared to the 0.05 N conditions, was approximately 21% lower. Even after 16 hours of refluxing at 0.01 N, a yield comparable to the 0.05 N, 2 hours, could not be reached.

Increasing the refluxing time from 2 to 8 hours increased the yield by about 15% for the experiments using 0.2 N, 0.1 N, and 0.05 N HCl concentrations. This is a significant improvement in yield compared to the 5% increase attained by doubling the acid concentration. Additionally, it was found that by refluxing for 24 hours in 0.05 N HCl, the yield can be increased by an additional ~12%.

Attempts were made to improve the residual lignin yield during the acid hydrolysis by beating the pulp prior to the acid hydrolysis and by doing a two-stage acid hydrolysis. Beating the pulp prior to isolating the lignin would be expected to open the porous structure of the fiber, making the lignin more accessible for dissolution during the acid hydrolysis. The pulp was beaten 10,000 revolutions in a PFI mill (125 ml CSF) prior to the acid hydrolysis. The acid hydrolysis conditions used for this experiment were 0.05 N HCl, 9:1 dioxane:water ratio, and 2 hours of refluxing. The percent yield was 32.2% compared to 45.2% without beating. The reason for this poorer yield can partially be explained by the dissolution of some lignin during the processing of the pulp prior to and during beating. During the disintegration of the pulp prior to beating and during the actual beating process, some lignin is removed from the fiber, as evidenced by the brown-colored effluent. The dissolution of lignin during disintegration and beating suggests that some of the 'residual' lignin is soluble in water yet incapable of being washed from the fiber after pulping.

Another attempt was made to improve the yield by stopping the acidolysis after 2 hours, filtering the pulp, adding a fresh dioxane/water/HCl solution, and refluxing for an additional 6 hours. The addition of this fresh solvent solution may help to improve the yield of the final 6 hours of extraction. This experiment was also done to possibly protect the lignin that is dissolved during the first 2 hours from an additional 6 hours under refluxing conditions. The conditions used for these experiments were a 0.05 N HCl concentration and a 9:1 dioxane:water ratio. Two different experiments were performed in which the acid hydrolysis was stopped after 2 hours and the dissolved lignin collected and yields determined. The pulps after these experiments were then treated for an additional 6-hour extraction. The difference between these experiments was that in one experiment the pulp was air dried and in the other experiment the pulp remained saturated with the solvent after being thoroughly washed. The dissolved lignins after the additional 6-hour treatment were collected and the yields determined. The results from these experiments are presented in Table AII.3 along with data form the continuous 8 hour acid hydrolysis.

Table AII.3. A comparison in yields between a continuous 8-hour acid hydrolysis in 0.05N HCl and an interrupted extraction between which fresh dioxane:water:HCl is added.

Experiment	2 hour yield	Additional 6 hour yield	Total yield
8 Hour Acid hydrolysis	-	-	60.2% (2)
Interrupted Acid hydrolysis (air dried after 2 hours)	45.1% (2)	8.6% (2)	53.7% (2)
Interrupted Acid hydrolysis (pulp not allowed to dry)	41.4% (1)	16.2% (1)	57.6% (1)

Number in parentheses is the number of times the experiment was performed. The percentages are therefore averages of the replicates.

The results show that the total yield for both interrupted acid hydrolysis experiments was lower than the continuous 8-hour experiment, indicating that interrupting the experiment does not improve the yield. The pulp that was air dried before a subsequent addition acid hydrolysis was shown to result in a lower total yield compared to the pulp that was not allowed to dry. Apparently the pore structure of the fibers was modified after drying, restricting the dissolution of the lignin in the subsequent acid hydrolysis. The results from this experiment also clearly show that of the ~60% of the lignin extracted over the 8-hour period, more than 75% is extracted in the first 2 hours. It was also found that after 1 hour, ~34% of the lignin is removed, which is 56% of the lignin removed after 8 hours.

Acid Hydrolysis Conditions

The conditions used to isolate residual lignin from the unbleached CK and EK pulps were determined from the results of this study. The requirements for the optimum conditions must balance the concerns of yield and unwanted chemical modifications to the lignin's structure. The conditions used that resulted in the highest yield of residual lignin were 0.2 N HCl, 9:1 dioxane:water ratio, and 8 hours of refluxing. Although these conditions optimize yield, they would not be optimal for the isolation because the high acid concentration and long times are more likely to cause unwanted structural modifications to the lignin. A lower concentration of acid and shorter refluxing time would be expected to yield a lignin that is more representative of the true residual lignin.

Because a large percentage of the total lignin capable of being extracted from the pulp is extracted during the first hour of the acid hydrolysis and that the acid concentration does not significantly inhibit the yield until an acid concentration lower than 0.05 N HCl is employed, it was decided to employ a refluxing time of 1 hour, an acid concentration of 0.05 N, and a 9:1 dioxane:water ratio.

Lignin Isolation Yield from Various CK and EK Pulps

The yields of lignin for the various CK and EK pulps have been determined by weighing the freeze-dried isolated product and calculating its weight percent of the theoretical amount of residual lignin in the pulp, as determined by the relationship between the lignin content and kappa number (% lignin in pulp = kappa number * 0.15). The yields of the various residual lignins are plotted in Figure AII.1 versus the kappa number of the pulp from which the lignin was isolated.

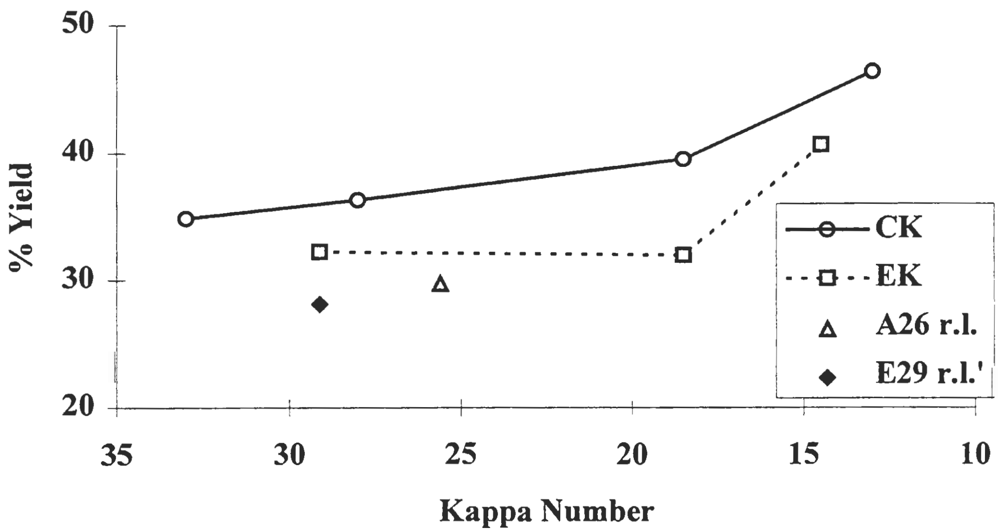


Figure AII.1. Yield of residual lignin from the acid hydrolysis of various CK and EK pulps plotted against the kappa number of the pulp. The yield was calculated as weight percent of the theoretical amount of lignin in the pulp as determined by the kappa number / lignin content relationship.

The yield of residual lignin was shown to be dependent on both the type of pulp and the kappa number of the pulp. At a given kappa number CK pulps gave consistently higher yields compared to EK pulps and lower kappa number pulps gave higher yields than higher kappa number pulps. The reason or reasons for this are unknown, but considering the mechanism by which lignin is believed to be removed from the pulp, the CK pulps and lower kappa number pulps may contain more linkages to the carbohydrates that are labile under the acid hydrolysis conditions. The linkage between lignin and carbohydrate that is believed to cleaved during the acid hydrolysis is at the benzyl position of the phenylpropane unit in lignin. These linkages may exist in the residual lignin either as a result of their formation during pulping or by their survival, provided such linkages are present in the native lignin. The more of these linkages present in pulp, the more lignin should be capable of being solubilized during the isolation. CK pulps may therefore contain more benzyl ether linkages to the carbohydrates than EK pulps causing the greater yield of lignin during the acid hydrolysis. The same argument can be made for the lower kappa number pulps, which may contain a greater amount of such linkages. The longer the cook proceeds a greater percentage of lignin remaining in the pulp becomes attached to the carbohydrates causing a greater yield of lignin during the acid hydrolysis.

APPENDIX III

QUANTITATIVE ^{13}C-NMR ANALYSIS

Data from all the quantitative ^{13}C-NMR spectra have been tabulated and recorded in Tables AIII.1-AIII.5. These tables contain data from unbleached residual lignins and their products from the kraft treatments, kraft lignins, ClO_2-bleached residual lignins, ClO_2-bleached and alkaline-extracted residual lignins, and dissolved lignins from the alkaline extraction stage.

Table AIII.1. Quantitative ^{13}C-NMR analysis of various unbleached residual lignins and kraft-treated residual lignins (numbers expressed as number of carbon atoms per aromatic ring (as described in Materials and Methods section on page 69)).

Region	Functional Group	Integral Region	E29 r.l.	E29 r.l.'	E18 r.l.	E14 r.l.	C28 r.l.	C18 r.l.	C13 r.l.	A26 r.l.	C28 r.l.-15	C28 r.l.-120	E14 r.l.-15	E14 r.l.-120	C33 r.l.
1	-COOH	180.1-165.1	0.20	0.21	0.25	0.20	0.15	0.18	0.18	0.15	0.22	0.30	0.28	0.27	0.20
2	C3/C3' C5-C5	160.13-154.14	0.10	0.18	0.16	0.12	0.14	0.15	0.17	0.13	0.13	0.18	0.15	0.15	0.12
2	C3, C4 (-CAr-O)	154.14-139.79	1.90	2.04	2.02	1.93	2.02	2.03	2.04	2.00	1.94	1.95	1.93	1.92	1.91
3	C1, (-CAr-C)	139.79-126.75	1.41	1.41	1.43	1.47	1.41	1.45	1.50	1.49	1.46	1.49	1.50	1.53	1.40
4	C5, (-CAr-C)	126.75-122.54	0.53	0.51	0.54	0.59	0.52	0.55	0.57	0.51	0.59	0.61	0.63	0.65	0.52
5	C6, (-CAr-H)	122.54-116.57	0.77	0.74	0.74	0.73	0.75	0.73	0.70	0.72	0.74	0.71	0.72	0.71	0.78
6	C5, (-CAr-H)	116.57-113.58	0.48	0.46	0.45	0.45	0.48	0.46	0.45	0.44	0.47	0.43	0.42	0.40	0.49
7	C2, (-CAr-H)	113.58-106.36	0.81	0.67	0.67	0.70	0.69	0.63	0.58	0.71	0.68	0.64	0.66	0.65	0.77
2-4	Substituted aromatic C	160.1-122.54	3.94	4.14	4.15	4.12	4.08	4.19	4.27	4.14	4.12	4.23	4.21	4.24	3.95
5-7	Unsubstituted aromatic C	122.54-106.36	2.06	1.87	1.85	1.89	1.92	1.81	1.73	1.87	1.89	1.78	1.79	1.76	2.05
8	Aliphatic C-O (Cβ in βO4)	89.53-78.44	0.39	0.36	0.31	0.27	0.33	0.27	0.25	0.34	0.26	0.25	0.21	0.18	0.40
9	Aliphatic C-O (Cα in βO4)	78.44-67.37	0.48	0.47	0.46	0.48	0.45	0.48	0.54	0.41	0.36	0.35	0.34	0.31	0.52
10	Aliphatic C-O	67.37-61.33	0.19	0.27	0.20	0.22	0.18	0.26	0.23	0.19	0.15	0.17	0.15	0.15	0.21
11	Cγ (βO4)	61.33-57.39	0.20	0.20	0.18	0.18	0.20	0.17	0.17	0.23	0.12	0.12	0.11	0.11	0.21
12	OCH_3	57.39-53.88	0.82	0.83	0.86	0.85	0.86	0.86	0.84	0.88	0.81	0.77	0.74	0.73	0.83
13	Cβ in β-β; Cβ in β-5	53.88-51.23	0.15	0.17	0.15	0.17	0.13	0.14	0.15	0.13	0.11	0.11	0.10	0.10	0.23

Table AIII.2. Results from quantitative ^{13}C-NMR analysis of various kraft lignins (numbers expressed as number of carbon atoms per aromatic ring (as described in Materials and Methods section on page 69)).

Region	Functional Group	Integral Region	E14-ai	C18-ai	E14-eo1	E29-eoc	E18-eoc	E14-eoc	C28-eoc	C18-eoc	C13-eoc	E14-ai-120
1	-COOH	180.1-165.1	0.23	0.17	0.14	0.20	0.16	0.22	0.16	0.19	0.21	0.23
2	C3/C3' C5-C5	160.13-154.14	0.14	0.12	0.08	0.10	0.10	0.12	0.07	0.09	0.06	0.14
2	C3, C4 (-CAr-O)	154.14-139.79	1.77	1.77	1.90	1.90	1.92	1.89	1.85	1.88	1.86	1.77
3	C1, (-CAr-C)	139.79-126.75	1.49	1.47	1.42	1.48	1.48	1.53	1.46	1.49	1.50	1.62
4	C5, (-CAr-C)	126.75-122.54	0.43	0.44	0.56	0.58	0.59	0.61	0.59	0.60	0.63	0.65
5	C6, (-CAr-H)	122.54-116.57	0.84	0.87	0.81	0.78	0.77	0.75	0.80	0.77	0.77	0.73
6	C5, (-CAr-H)	116.57-113.58	0.66	0.67	0.55	0.51	0.49	0.47	0.52	0.51	0.51	0.49
7	C2, (-CAr-H)	113.58-106.36	1.00	0.66	0.69	0.66	0.65	0.63	0.71	0.67	0.68	0.60
2-4	Substituted aromatic C	160.1-122.54	3.84	3.81	3.95	4.05	4.09	4.15	3.97	4.05	4.05	4.18
5-7	Unsubstituted aromatic C	122.54-106.36	2.50	2.20	2.05	1.95	1.91	1.85	2.03	1.95	1.95	1.82
8	Aliphatic C-O (Cβ in βO4)	89.53-78.44	0.40	0.35	0.22	0.23	0.22	0.19	0.22	0.20	0.14	0.16
9	Aliphatic C-O (Cα in βO4)	78.44-67.37	0.50	0.45	0.30	0.32	0.42	0.38	0.31	0.41	0.31	0.24
10	Aliphatic C-O	67.37-61.33	0.24	0.24	0.15	0.21	0.24	0.18	0.23	0.26	0.18	0.13
11	Cγ (βO4)	61.33-57.39	0.30	0.28	0.17	0.15	0.16	0.13	0.14	0.13	0.12	0.11
12	OCH_3	57.39-53.88	0.81	0.81	0.82	0.82	0.81	0.76	0.80	0.79	0.77	0.73
13	Cβ in β-β; Cβ in β-5	53.88-51.23	0.14	0.11	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.11

Table AIII.3. Results from quantitative ^{13}C-NMR analysis of various ClO_2-bleached pulp residual lignins and C33 r.l. treated with ClO_2 (numbers expressed as number of carbon atoms per aromatic ring (as described in Materials and Methods section on page 69)).

Region	Functional Group	Integral Region	C28 D r.l. (0.05)	C28 D r.l. (0.20)	C18 D r.l. (0.20)	E29 D r.l. (0.20)	E18 D r.l. (0.20)	C33 r.l.	C33 r.l.-0.05	C33 r.l.-0.20
1	-COOH (alipahtic)	180.1-169	0.34	0.56	0.69	0.56	0.72	0.20	0.40	0.69
1	-COOH (conjugated)	169-165	0.13	0.33	0.34	0.34	0.34	-	0.20	0.60
1	Total COOH	180-165	0.47	0.89	1.03	0.90	1.06	0.20	0.60	1.29
2	C3/C3' C5-C5	160.13-154.14	0.18	0.20	0.21	0.21	0.23	0.12	0.22	0.27
2	C3, C4 (-CAr-O)	154.14-139.79	1.95	1.78	1.83	1.79	1.89	1.91	1.92	1.75
3	C1, (-CAr-C)	139.79-126.75	1.48	1.60	1.66	1.59	1.62	1.40	1.42	1.54
4	C5, (-CAr-C)	126.75-122.54	0.51	0.56	0.58	0.54	0.56	0.52	0.54	0.64
5	C6, (-CAr-H)	122.54-116.57	0.79	0.85	0.81	0.84	0.80	0.78	0.81	0.90
6	C5, (-CAr-H)	116.57-113.58	0.46	0.42	0.39	0.43	0.39	0.49	0.48	0.41
7	C2, (-CAr-H)	113.58-106.36	0.65	0.61	0.55	0.62	0.51	0.77	0.62	0.50
2-4	Substituted aromatic C	160.1-122.54	4.12	4.14	4.26	4.13	4.30	3.95	4.10	4.20
5-7	Unsubstituted aromatic C	122.54-106.36	1.89	1.88	1.75	1.89	1.70	4.61	4.69	4.83
8-11	Aliphatic C-O	90-60	1.54	1.75	2.11	1.78	1.88	1.35	-	-
12	OCH_3	57.39-53.88	0.75	0.49	0.57	0.49	0.54	0.83	0.72	0.61
	Methyl ester, OCH_3	53.8-49.3	0.26	0.35	0.46	0.38	0.40	-	0.33	0.68

Table AIII.4. Results from quantitative ^{13}C-NMR analysis of various residual lignins isolated from ClO_2-bleached and alkaline extracted pulps (numbers expressed as number of carbon atoms per aromatic ring (as described in Materials and Methods section on page 69)).

Region	Functional Group	Integral Region	C28 DE r.l. (0.05)	E29 D(EO) r.l. (0.10)	E29 DE r.l. (0.10)	E29 D(EO) r.l. (0.20)	E18 D(EO) r.l. (0.20)	C28 DE r.l. (0.20)	C28 D(EO) r.l. (0.20)	C18 D(EO) r.l. (0.20)
1	-COOH (aliphatic)	180.1-169	0.44	0.69	0.67	0.84	1.04	0.90	0.89	1.03
1	-COOH (conjugated)	169-165	0.12	0.15	0.12	0.17	0.17	0.22	0.21	0.22
1	Total COOH	180-165	0.56	0.84	0.80	1.01	1.22	1.13	1.10	1.25
2	C3/C3' C5-C5	160.13-154.14	0.20	0.21	0.23	0.19	0.18	0.18	0.19	0.21
2	C3, C4 (-CAr-O)	154.14-139.79	1.97	1.95	1.99	1.89	1.91	1.81	1.83	1.81
3	C1, (-CAr-C)	139.79-126.75	1.46	1.52	1.52	1.53	1.68	1.58	1.61	1.70
4	C5, (-CAr-C)	126.75-122.54	0.50	0.49	0.50	0.55	0.60	0.59	0.58	0.61
5	C6, (-CAr-H)	122.54-116.57	0.78	0.79	0.77	0.80	0.76	0.81	0.79	0.76
6	C5, (-CAr-H)	116.57-113.58	0.46	0.44	0.43	0.44	0.39	0.42	0.41	0.39
7	C2, (-CAr-H)	113.58-106.36	0.64	0.60	0.55	0.60	0.48	0.62	0.59	0.53
2-4	Substituted aromatic C	160.1-122.54	4.12	4.18	4.24	4.16	4.37	4.16	4.21	4.33
5-7	Unsubstituted aromatic C	122.54-106.36	1.88	1.83	1.76	1.84	1.64	1.84	1.80	1.68
8-11	Aliphatic C-O	90-60	1.74	2.08	2.09	2.28	2.89	2.32	2.23	2.50
12	OCH_3	57.39-53.88	0.80	0.75	0.76	0.69	0.80	0.66	0.64	0.69

Table AIII.5. Results from quantitative ^{13}C-NMR analysis of various dissolved lignins isolated from the alkaline extraction effluents (numbers expressed as number of carbon atoms per aromatic ring (as described in Materials and Methods section on page 69)).

Region	Functional Group	Integral Region	C28 DE d.l. (0.05)	E29 D(EO) d.l. (0.10)	E29 DE d.l. (0.10)	E29 D(EO) d.l. (0.20)	E18 D(EO) d.l. (0.20)	E14 D(EO) d.l. (0.20)	C28 DE d.l. (0.20)	C28 D(EO) d.l. (0.20)	C18 D(EO) d.l. (0.20)
1	-COOH (aliphatic)	180.1-169	0.58	0.82	0.80	0.86	0.84	0.92	0.89	0.91	1.07
1	-COOH (conjugated)	169-165	0.12	0.21	0.21	0.32	0.35	0.34	0.34	0.31	0.20
1	Total COOH	180-165	0.70	1.03	1.00	1.19	1.18	1.26	1.23	1.23	1.27
2	C3/C3' C5-C5	160.13-154.14	0.18	0.21	0.19	0.16	0.19	0.20	0.18	0.20	0.21
2	C3, C4 (-CAr-O)	154.14-139.79	1.91	1.82	1.82	1.75	1.74	1.71	1.80	1.79	1.80
3	C1, (-CAr-C)	139.79-126.75	1.57	1.62	1.63	1.64	1.68	1.81	1.67	1.66	1.79
4	C5, (-CAr-C)	126.75-122.54	0.54	0.52	0.53	0.59	0.59	0.60	0.62	0.58	0.60
5	C6, (-CAr-H)	122.54-116.57	0.78	0.80	0.80	0.82	0.81	0.77	0.80	0.80	0.73
6	C5, (-CAr-H)	116.57-113.58	0.44	0.43	0.44	0.45	0.42	0.38	0.41	0.42	0.39
7	C2, (-CAr-H)	113.58-106.36	0.59	0.60	0.59	0.59	0.58	0.51	0.52	0.55	0.47
2-4	Substituted aromatic C	160.1-122.54	4.19	4.17	4.17	4.15	4.20	4.33	4.28	4.23	4.40
5-7	Unsubstituted aromatic C	122.54-106.36	1.82	1.83	1.83	1.86	1.81	1.66	1.73	1.77	1.59
8-11	Aliphatic C-O	90-60	1.86	2.53	2.44	2.26	1.88	1.76	2.38	2.22	2.16
12	OCH_3	57.39-53.88	0.78	0.70	0.71	0.66	0.61	0.59	0.67	0.66	0.65

APPENDIX IV

QUANTITATIVE ^{1}H-NMR ANALYSIS

Data from the quantitative ^{1}H-NMR spectra of various acetylated and underivatized lignins have been tabulated and reported in this appendix in Tables AIV.1-AIV.8. Tables AIV.1 and AIV.2 contain data for the acetylated lignins, while Tables AIV.3-AIV.9 contain data for the underivatized lignins. The procedures for performing these experiments and calculations can be found in the Materials and Methods section.

Table AIV.1. Quantitative ^{1}H-NMR data for various acetylated residual lignins.

Lignin ID	C28 r.l.	C28 r.l.	C18 r.l	C18 r.l	C13 r.l.	C13 r.l.	E29 r.l.	E29 r.l.	E18 r.l.	E18 r.l.	E14 r.l.	E14 r.l.	E29 r.l.'	E29 r.l.'	A26 r.l.
		(replicate)		(replicate)		(replicate)		(replicate)		(replicate)		(replicate)		(replicate)	
Internal standard solution															
Internal standard: pentafluorobenzaldehyde (PFB)															
amount of PFB (g)	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625	0.1648625
ml of CDCl3	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Formula weight PFB (g/mol)	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07	196.07
conc. of IS soln (mol/ml)	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05
Lignin sample															
Weight of dry lignin (mg)	22.03	21.91	22.27	22.11	22.04	22.04	22.15	21.98	21.94	22.35	21.84	21.82	22.01	22.25	21.95
ml of IS soln	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
mol of PFB	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05
Integration Regions															
Internal standard	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Aromatic H	12.34	12.207	12.85	12.766	11.26	11.292	13.086	13.232	11.92	12.196	11.515	11.532	13.322	13.863	12.729
Ha b-O-4	0.603	0.616	0.604	0.585	0.343	0.344	0.656	0.749	0.493	0.492	0.401	0.447	0.773	0.835	0.64
OCH3	16.6685	16.614	17.33	17.14	15.342	15.297	18.581	18.187	17.1	17.373	15.826	15.932	18.664	19.001	18.647
Aromatic OH	8.112	7.9295	9.357	9.354	9.532	9.388	8.59	8.401	8.591	8.757	9.204	9.245	8.806	9.03	8.541
Aliphatic OH	13.6635	13.756	14.549	14.369	13.659	13.76	15.309	14.907	14.317	14.551	13.499	13.51	15.217	15.376	14.767
Results (mol H/g lignin)															
Correction Factor (mol/unit area)	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05
Aromatic H	9.42	9.37	9.70	9.71	8.59	8.62	9.94	10.12	9.14	9.18	8.87	8.89	10.18	10.48	9.75
Ha b-O-4	0.46	0.47	0.46	0.44	0.26	0.26	0.50	0.57	0.38	0.37	0.31	0.34	0.59	0.63	0.49
OCH3	4.24	4.25	4.36	4.35	3.90	3.89	4.70	4.64	4.37	4.36	4.06	4.09	4.75	4.79	4.76
Aromatic OH	2.06	2.03	2.36	2.37	2.42	2.39	2.17	2.14	2.19	2.20	2.36	2.38	2.24	2.27	2.18
Aliphatic OH	3.48	3.52	3.66	3.64	3.47	3.50	3.87	3.80	3.66	3.65	3.46	3.47	3.88	3.87	3.77

Table AIV.2. Quantitative ^{1}H-NMR data for various acetylated kraft lignins.

Lignin ID	**C28-eoc**	**C28-eoc**	**C18-eoc**	**C18-eoc**	**C13-eoc**	**C13-eoc**	**E29-eoc**	**E29-eoc**	**E18-eoc**	**E18-eoc**
		(replicate)		(replicate)		(replicate)		(replicate)		(replicate)
conc. of IS soln (mol/ml)	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05
Weight of dry lignin (mg)	22.28	22.17	22.25	22	22.04	22.39	22.33	22.24	22.27	22.19
ml of IS soln	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
mol of PFB	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05
Integration Regions										
Internal standard	1	1	1	1	1	1	1	1	1	1
Aromatic H	16.276	15.579	14.757	14.15	14.409	14.338	15.828	15.62	14.601	13.68
Ha b-O-4	0.797	0.772	0.535	0.471	0.553	0.533	0.892	0.882	0.684	0.633
OCH3	19.806	19.063	18.926	18.184	17.723	17.79	19.939	19.663	19.04	18.417
Aromatic OH	12.004	11.37	11.581	11.674	12.672	12.418	11.462	11.275	11.505	10.948
Aliphatic OH	15.806	15.649	17.879	16.59	15.499	15.747	16.185	15.883	16.753	16.481
Results (mol H/g lignin)										
Correction Factor (mol/unit area)	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05
Aromatic H	12.28	11.82	11.15	10.82	10.99	10.77	11.92	11.81	11.03	10.37
Ha b-O-4	0.60	0.59	0.40	0.36	0.42	0.40	0.67	0.67	0.52	0.48
OCH3	4.98	4.82	4.77	4.63	4.51	4.45	5.01	4.96	4.79	4.65
Aromatic OH	3.02	2.87	2.92	2.97	3.22	3.11	2.88	2.84	2.90	2.77
Aliphatic OH	3.98	3.96	4.50	4.23	3.94	3.94	4.06	4.00	4.22	4.16
Lignin ID	**E14-eoc**	**E14-eoc**	**C13-eoc'**	**C13-eoc'**	**E14-ai**	**E14-ai**	**E14-eo1**	**E14-eo1**	**C18-ai**	
		(replicate)		(replicate)		(replicate)		(replicate)		
conc. of IS soln (mol/ml)	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	3.36334E-05	
Weight of dry lignin (mg)	22.03	22.02	22.05	22.07	22.01	22.15	22.26	22.31	22.05	
ml of IS soln	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
mol of PFB	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	
Integration Regions										
Internal standard	1	1	1	1	1	1	1	1	1	
Aromatic H	13.633	13.1	14.182	13.931	13.796	13.614	13.796	13.614	14.397	
Ha b-O-4	0.562	0.486	0.507	0.535	1.205	1.169	1.205	1.169	1.319	
OCH3	18.1	17.525	17.679	17.569	16.904	16.689	16.904	16.689	17.675	
Aromatic OH	11.601	11.049	12.372	12.085	9.204	8.962	9.204	8.962	9.2	
Aliphatic OH	16.042	15.608	15.721	15.782	16.759	16.63	16.759	16.63	16.98	
Results (mol H/g lignin)										
Correction Factor (mol/unit area)	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	1.68167E-05	
Aromatic H	10.41	9.94	10.72	10.65	10.53	10.23	10.39	10.29	10.87	
Ha b-O-4	0.43	0.37	0.38	0.41	0.92	0.88	0.91	0.88	1.00	
OCH3	4.61	4.43	4.45	4.48	4.30	4.18	4.24	4.21	4.45	
Aromatic OH	2.95	2.79	3.12	3.08	2.34	2.24	2.31	2.26	2.32	
Aliphatic OH	4.08	3.95	3.96	4.02	4.26	4.16	4.21	4.19	4.27	

Table AIV.3. Quantitative ^{1}H-NMR data for various underivatized unbleached residual lignins.

Lignin ID	**E29 r.l.**	**E18 r.l.**	**E14 r.l.**	**C28 r.l.**	**C18 r.l.**	**C13 r.l.**
Internal standard solution						
conc. of IS soln (mol/ml)	9.59E-05	9.59E-05	9.59E-05	9.59E-05	9.59E-05	9.59E-05
Sample						
Weight of dry lignin (mg)	22.43	22.46	22.48	22.2	22.29	22.47
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.40E-05	2.40E-05	2.40E-05	2.40E-05	2.40E-05	2.40E-05
Integration Regions						
Internal standard	1	1	1	1	1	1
Carboxylic acids	0.341	0.501	0.493	0.507	0.574	0.742
Formyl H	0.521	0.596	0.616	0.605	0.608	0.644
Guaiacyl phenolic hydroxyl	1.576	1.625	1.746	1.65	1.764	1.768
C5 substituted guaiacyl phenolic hydroxyl	0.789	0.84	0.928	0.82	0.894	0.949
Aromatic H	11.909	11.15	11.169	11.586	11.155	10.594
Aliphatic H	9.471	8.937	8.688	9.017	8.342	8.174
Methoxyl H	15.909	14.557	14.068	15.239	14.416	13.189
Results (mol H/g lignin)						
Correction Factor (mol/unit area)	2.40E-05	2.40E-05	2.40E-05	2.40E-05	2.40E-05	2.40E-05
Carboxylic acids	0.36	0.53	0.53	0.55	0.62	0.79
Formyl H	0.56	0.64	0.66	0.65	0.65	0.69
Guaiacyl phenolic hydroxyl	1.69	1.74	1.86	1.78	1.90	1.89
C5 substituted guaiacyl phenolic hydroxyl	0.84	0.90	0.99	0.89	0.96	1.01
Aromatic H	12.73	11.91	11.92	12.52	12.00	11.31
Aliphatic H	10.13	9.54	9.27	9.74	8.98	8.72
Methoxyl H	5.67	5.18	5.00	5.49	5.17	4.69
Total phenolic hydroxyl content	2.53	2.63	2.85	2.67	2.86	2.90

Table AIV.4. Quantitative ^{1}H-NMR data for various underivatized ClO_2 bleached residual lignins.

Lignin ID	**C28 D r.l. (0.05 KF)**	**C28 D r.l. (0.20 KF)**	**C18 D r.l. (0.20 KF)**	**E29 D r.l. (0.20 KF)**	**E18 D r.l. (0.20 KF)**
Internal standard solution					
conc. of IS soln (mol/ml)	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04
Sample					
Weight of dry lignin (mg)	21.96	22.09	22.17	22.35	22.22
ml of IS soln	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions					
Internal standard	1	1	1	1	1
Carboxylic acids	0.431	0.771	0.358	0.768	0.524
Formyl H	0.447	0.334	0.328	0.335	0.328
Guaiacyl phenolic hydroxyl	0.919	0.657	0.585	0.67	0.575
C5 substituted guaiacyl phenolic hydroxyl	0.533	0.499	0.546	0.514	0.506
Aromatic H	7.979	5.745	5.833	6.089	5.674
Aliphatic H	8.072	8.985	9.956	9.436	9.365
Methoxyl H	13.082	11.553	15.695	12.219	11.211
Results (mol H/g lignin)					
Correction Factor (mol/unit area)	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Carboxylic acids	0.51	0.90	0.42	0.89	0.61
Formyl H	0.53	0.39	0.38	0.39	0.38
Guaiacyl phenolic hydroxyl	1.08	0.77	0.68	0.77	0.67
C5 substituted guaiacyl phenolic hydroxyl	0.63	0.58	0.64	0.59	0.59
Aromatic H	9.39	6.72	6.80	7.04	6.60
Aliphatic H	9.50	10.51	11.61	10.91	10.89
Methoxyl H	5.13	4.51	6.10	4.71	4.35
Total phenolic hydroxyl content	1.71	1.35	1.32	1.37	1.26

Table AIV.5. Quantitative ^{1}H-NMR data for various underivatized kraft-treated unbleached residual lignins.

Lignin ID	**C28 r.l.**	**C28 r.l.**	**E14 r.l.**	**C28 r.l.-15**	**E14 r.l.-15**	**C28 r.l.-120**	**E14 r.l.-120**	**C28 r.l.-120'**
Internal standard solution		replicate						
conc. of IS soln (mol/ml)	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04
Sample								
Weight of dry lignin (mg)	22.08	22.08	22.19	22.12	22.26	22.27	22.02	22.09
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions								
Internal standard	1	1	1	1	1	1	1	1
Aromatic H	10.189	10.58	9.31	11.297	10.485	11.116	10.032	11.009
Results (mol H/g lignin)								
Correction Factor (mol/unit area)	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Aromatic H	11.93	12.39	10.84	13.20	12.17	12.90	11.78	12.88

Table AIV.6. Quantitative ^{1}H-NMR data for various underivatized unbleached residual lignins treated with ClO_2.

Lignin ID	**E29 r.l.**	**E29 r.l.-0.05**	**E29 r.l.-0.10**	**E29 r.l.-0.20**	**E18 r.l.**	**E18 r.l.-0.05**	**E18 r.l.-0.10**	**E18 r.l.-0.20**
Internal standard solution								
conc. of IS soln (mol/ml)	9.59E-05	1.03E-04	1.03E-04	1.03E-04	9.59E-05	1.03E-04	1.03E-04	1.03E-04
Sample								
Weight of dry lignin (mg)	22.43	21.83	21.94	21.96	22.46	21.97	22.02	21.85
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.40E-05	2.58E-05	2.58E-05	2.58E-05	2.40E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions								
Internal standard	1	1	1	1	1	1	1	1
Aromatic H	11.909	7.685	5.844	5.294	11.15	7.489	5.584	4.804
Results (mol H/g lignin)								
Correction Factor (mol/unit area)	2.40E-05	2.58E-05	2.58E-05	2.58E-05	2.40E-05	2.58E-05	2.58E-05	2.58E-05
Aromatic H	12.73	9.10	6.88	6.23	11.91	8.81	6.55	5.68
Lignin	**C28 r.l.**	**C28 r.l.-0.05**	**C28 r.l.-0.10**	**C28 r.l.-0.20**	**C18 r.l.**	**C18 r.l.-0.05**	**C18 r.l.-0.10**	**C18 r.l.-0.20**
Internal standard solution								
conc. of IS soln (mol/ml)	9.59E-05	1.03E-04	1.03E-04	1.03E-04	9.59E-05	1.03E-04	1.03E-04	1.03E-04
Sample								
Weight of dry lignin (mg)	22.2	22.01	22.05	21.96	22.29	21.93	21.95	22.05
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.40E-05	2.58E-05	2.58E-05	2.58E-05	2.40E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions								
Internal standard	1	1	1	1	1	1	1	1
Aromatic H	11.586	8.058	5.833	5.253	11.155	8.046	5.624	4.783
Results (mol H/g lignin)								
Correction Factor (mol/unit area)	2.40E-05	2.58E-05	2.58E-05	2.58E-05	2.40E-05	2.58E-05	2.58E-05	2.58E-05
Aromatic H	12.52	9.46	6.84	6.18	12.00	9.48	6.62	5.61

Table AIV.7. Quantitative [1]H-NMR data for various residual lignins from ClO_2-bleached and alkaline-extracted pulps.

Lignin ID	**C28 DE r.l. (0.05)**	**E29 DE r.l. (0.10)**	**E29 D(EO) r.l. (0.10)**	**C28 DE r.l. (0.20)**	**C28 D(EO) r.l. (0.20)**	**E29 D(EO) r.l. (0.20)**	**E18 D(EO) r.l. (0.20)**	**C18 D(EO) r.l. (0.20)**	**E14 D(EO) r.l. (0.20)**
Internal standard solution									
conc. of IS soln (mol/ml)	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04
Sample									
Weight of dry lignin (mg)	22.03	22.16	22.26	21.98	22.26	22.32	22.39	22.32	22.35
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions									
Internal standard	1	1	1	1	1	1	1	1	1
Carboxylic acids	0.607	0.74	0.872	1.31	1.238	1.189	1.297	1.428	0.943
Formyl H	0.419	0.323	0.321	0.256	0.223	0.251	0.223	0.218	0.262
Guaiacyl phenolic hydroxyl	0.815	0.543	0.544	0.353	0.312	0.387	0.341	0.331	0.342
C5 substituted guaiacyl phenolic hydroxyl	0.481	0.388	0.413	0.349	0.356	0.327	0.386	0.374	0.46
Aromatic H	8.587	6.444	6.893	5.758	5.648	6.42	5.5	5.407	5.303
Aliphatic H	8.807	8.722	9.724	9.686	9.718	10.19	9.522	9.043	8.945
Methoxyl H	15.652	13.775	13.036	13.579	13.238	14.014	12.033	11.659	12.672
Results (mol H/g lignin)									
Correction Factor (mol/unit area)	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Carboxylic acids	0.71	0.86	1.01	1.54	1.44	1.38	1.50	1.65	1.09
Formyl H	0.49	0.38	0.37	0.30	0.26	0.29	0.26	0.25	0.30
Guaiacyl phenolic hydroxyl	0.96	0.63	0.63	0.42	0.36	0.45	0.39	0.38	0.40
C5 substituted guaiacyl phenolic hydroxyl	0.56	0.45	0.48	0.41	0.41	0.38	0.45	0.43	0.53
Aromatic H	10.08	7.52	8.00	6.77	6.56	7.43	6.35	6.26	6.13
Aliphatic H	10.33	10.17	11.29	11.39	11.28	11.80	10.99	10.47	10.34
Methoxyl H	6.12	5.36	5.05	5.32	5.12	5.41	4.63	4.50	4.89
Total phenolic hydroxyl	1.52	1.09	1.11	0.83	0.78	0.83	0.84	0.82	0.93

Table AIV.8. Quantitative ^{1}H-NMR data for various dissolved lignins from alkaline extraction effluents.

Lignin ID	**C28 DE d.l. (0.05)**	**E29 D(EO) d.l. (0.10)**	**E29 DE d.l. (0.10)**	**C28 DE d.l. (0.20)**	**C28 D(EO) d.l. (0.20)**	**E29 D(EO) d.l. (0.20)**	**E18 DE d.l. (0.20)**	**C18 D(EO) d.l. (0.20)**
conc. of IS soln (mol/ml)	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04
Sample								
Weight of dry lignin (mg)	22.26	22.25	22.14	22.21	22.2	22.23	22.05	22.17
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions								
Internal standard	1	1	1	1	1	1	1	1
Carboxylic acids	1.073	0.902	0.927	0.98	1.769	1.421	1.528	0.677
Formyl H	0.384	0.243	0.263	0.21	0.211	0.212	0.201	0.536
Guaiacyl phenolic hydroxyl	0.621	0.307	0.357	0.279	0.306	0.276	0.305	0.499
C5 substituted guaiacyl phenolic hydroxyl	0.409	0.339	0.349	0.364	0.333	0.294	0.368	0.578
Aromatic H	7.464	6.576	6.754	5.703	5.963	6.239	6.142	7.005
Aliphatic H	8.483	10.575	10.377	9.783	9.352	10.37	9.636	11.063
Methoxyl H	12.071	13.88	17.355	11.92	11.368	15.255	13.554	14.05
Results (mol H/g lignin)								
Correction Factor (mol/unit area)	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Carboxylic acids	1.25	1.05	1.08	1.14	2.06	1.65	1.79	0.79
Formyl H	0.45	0.28	0.31	0.24	0.25	0.25	0.24	0.62
Guaiacyl phenolic hydroxyl	0.72	0.36	0.42	0.32	0.36	0.32	0.36	0.58
C5 substituted guaiacyl phenolic hydroxyl	0.47	0.39	0.41	0.42	0.39	0.34	0.43	0.67
Aromatic H	8.67	7.64	7.89	6.64	6.94	7.25	7.20	8.17
Aliphatic H	9.85	12.29	12.11	11.39	10.89	12.06	11.30	12.90
Methoxyl H	4.67	5.37	6.75	4.62	4.41	5.91	5.30	5.46
Total phenolic hydroxyl content	1.20	0.75	0.82	0.75	0.74	0.66	0.79	1.26

Table AIV.8. Quantitative ^{1}H-NMR data for various dissolved lignins from alkaline extraction effluents.

Lignin ID	**C28 DE d.l. (0.05)**	**E29 D(EO) d.l. (0.10)**	**E29 DE d.l. (0.10)**	**C28 DE d.l. (0.20)**	**C28 D(EO) d.l. (0.20)**	**E29 D(EO) d.l. (0.20)**	**E18 DE d.l. (0.20)**	**C18 D(EO) d.l. (0.20)**
conc. of IS soln (mol/ml)	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04	1.03E-04
Sample								
Weight of dry lignin (mg)	22.26	22.25	22.14	22.21	22.2	22.23	22.05	22.17
ml of IS soln	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
mol of PFB	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Integration Regions								
Internal standard	1	1	1	1	1	1	1	1
Carboxylic acids	1.073	0.902	0.927	0.98	1.769	1.421	1.528	0.677
Formyl H	0.384	0.243	0.263	0.21	0.211	0.212	0.201	0.536
Guaiacyl phenolic hydroxyl	0.621	0.307	0.357	0.279	0.306	0.276	0.305	0.499
C5 substituted guaiacyl phenolic hydroxyl	0.409	0.339	0.349	0.364	0.333	0.294	0.368	0.578
Aromatic H	7.464	6.576	6.754	5.703	5.963	6.239	6.142	7.005
Aliphatic H	8.483	10.575	10.377	9.783	9.352	10.37	9.636	11.063
Methoxyl H	12.071	13.88	17.355	11.92	11.368	15.255	13.554	14.05
Results (mol H/g lignin)								
Correction Factor (mol/unit area)	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05	2.58E-05
Carboxylic acids	1.25	1.05	1.08	1.14	2.06	1.65	1.79	0.79
Formyl H	0.45	0.28	0.31	0.24	0.25	0.25	0.24	0.62
Guaiacyl phenolic hydroxyl	0.72	0.36	0.42	0.32	0.36	0.32	0.36	0.58
C5 substituted guaiacyl phenolic hydroxyl	0.47	0.39	0.41	0.42	0.39	0.34	0.43	0.67
Aromatic H	8.67	7.64	7.89	6.64	6.94	7.25	7.20	8.17
Aliphatic H	9.85	12.29	12.11	11.39	10.89	12.06	11.30	12.90
Methoxyl H	4.67	5.37	6.75	4.62	4.41	5.91	5.30	5.46
Total phenolic hydroxyl content	1.20	0.75	0.82	0.75	0.74	0.66	0.79	1.26

APPENDIX V

QUANTITATIVE ^{31}P-NMR ANALYSIS

Data from the quantitative ^{31}P-NMR spectra of the various residual lignins analyzed in this dissertation are presented in Tables AV.1-AV.3. The procedures for performing these experiments and calculations can be found in the Materials and Methods section.

Table AV.1. Quantitative ^{31}P-NMR analysis of various unbleached residual lignins.

Lignin ID	**E29 r.l.**	**E29 r.l.'**	**E18 r.l.**	**E14 r.l.**	**C28 r.l.**	**C28 r.l.**	**C28 r.l.**	**C28 r.l.**	**C18 r.l.**	**C13 r.l.**	**A26 r.l.**
Sample						replicate	replicate	replicate			
amount of cyclohexanol (g)	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04
Weight of dry lignin (mg)	24.91	25.07	25.02	25.02	25.14	25.15	25.35	25.09	24.31	25.1	24.21
Integration Regions											
Internal standard	1	1	1	1	1	1	1	1	1	1	1
Aliphatic OH	7.8693	8.2198	7.1452	6.4727	7.3633	7.5808	7.6535	7.5059	6.6025	6.4684	7.6124
Condensed Phenolic OH	3.7791	3.7888	3.9388	4.6606	3.6775	3.7263	3.7181	3.7161	3.9950	4.1413	4.1666
Guaiacyl Phenolic OH	4.8193	4.8494	5.0394	5.8280	5.0243	4.8775	5.0570	4.9839	5.2905	5.3696	4.0791
Carboxylic acid	1.1562	1.0173	1.4758	1.6618	1.2465	1.2394	1.1582	1.1425	1.5107	1.8327	0.8353
Results (mol OH/g lignin)											
Correction Factor (mol/unit area)	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06
Aliphatic OH	1.895	1.967	1.713	1.552	1.757	1.808	1.811	1.795	1.629	1.546	1.886
Condensed Phenolic OH	0.910	0.907	0.944	1.118	0.878	0.889	0.880	0.889	0.986	0.990	1.032
Guaiacyl Phenolic OH	1.161	1.160	1.208	1.397	1.199	1.163	1.197	1.192	1.306	1.283	1.011
Carboxylic acid	0.278	0.243	0.354	0.398	0.297	0.296	0.274	0.273	0.373	0.438	0.207
Total phenolic OH	2.071	2.067	2.153	2.515	2.077	2.052	2.077	2.080	2.292	2.273	2.043

Table AV.2. Quantitative ^{31}P-NMR analysis of kraft-treated residual lignins.

Lignin ID	C28 r.l.	C28 r.l.	E14 r.l.	E14 r.l.	C28 r.l.-15	C28 r.l.-15	E14 r.l.-15	E14 r.l.-15	C28 r.l. -120	C28 r.l. -120	E14 r.l. -120	E14 r.l. -120	C28 r.l. -120'	C28 r.l. -120'
Sample		replicate		replicate		replicate		replicate		replicate		replicate		replicate
amount of cyclohexanol (g)	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04
Weight of dry lignin (mg)	24.99	25.14	25.04	25.19	25.39	25.16	25.32	25.24	25.19	25.29	25.34	25.22	25.44	25.5
Integration Regions														
Internal standard	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Aliphatic OH	7.769	7.8435	6.4989	6.5654	5.006	5.1007	4.6603	4.6821	4.5057	4.6239	4.6062	4.6056	4.4957	4.6672
Condensed Phenolic OH	3.468	3.5179	4.1519	4.1817	4.6642	4.6541	5.4617	5.481	5.2906	5.3315	6.1011	6.0447	5.1096	5.2163
Guaiacyl Phenolic OH	4.8194	4.89	5.1669	5.2264	5.8758	6.0033	6.1498	6.3893	6.1603	6.257	6.8633	6.7756	6.0841	5.9921
Carboxylic acid	1.3383	1.3675	1.9791	1.9873	1.778	1.8083	2.3721	2.4472	1.9235	1.933	2.6819	2.6894	1.9198	1.9034
Results (mol OH/g lignin)														
Correction Factor (mol/unit area)	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06
Aliphatic OH	1.865	1.872	1.557	1.564	1.183	1.216	1.104	1.113	1.073	1.097	1.091	1.096	1.060	1.098
Condensed Phenolic OH	0.833	0.840	0.995	0.996	1.102	1.110	1.294	1.303	1.260	1.265	1.444	1.438	1.205	1.227
Guaiacyl Phenolic OH	1.157	1.167	1.238	1.245	1.388	1.431	1.457	1.519	1.467	1.484	1.625	1.612	1.435	1.410
Carboxylic acid	0.321	0.326	0.474	0.473	0.420	0.431	0.562	0.582	0.458	0.459	0.635	0.640	0.453	0.448
Total phenolic OH	1.990	2.006	2.233	2.241	2.490	2.541	2.751	2.822	2.727	2.749	3.069	3.050	2.640	2.637

Table AV.3. Quantitative ^{31}P-NMR analysis of ClO_2-treated residual lignins.

	E29 r.l.-0.05	E29 r.l.-0.10	E29 r.l.-0.20	E18 r.l.-0.05	E18 r.l.-0.10	E18 r.l.-0.20	E14 r.l.-0.05	E14 r.l.-0.10	E14 r.l.-0.20	A26 r.l.-0.05	A26 r.l.-0.10	A26 r.l.-0.20
Sample												
amount of cyclohexanol (g)	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04
Weight of dry lignin (mg)	24.52	25.25	24.98	25.21	25.05	25.32	24.84	24.78	25.12	24.54	25.1	25.01
Integration Regions												
Internal standard	1	1	1	1	1	1	1	1	1	1	1	1
Aliphatic OH	6.35805	6.2427	6.8929	5.96305	5.86005	5.7749	5.34085	4.8976	5.2041	6.61253333	5.9933	7.1223
Condensed Phenolic OH	2.6462	2.39635	1.72085	2.87915	2.4963	1.4987	3.2703	2.6781	1.93345	2.57626667	2.08965	1.63514
Guaiacyl Phenolic OH	3.4272	2.12245	1.2999	3.5939	2.23035	1.2036	4.10215	2.4161	1.35215	2.6825	1.7001	1.13368
Carboxylic acid	2.0468	3.206	4.1078	2.11205	3.28385	3.7919	2.24595	3.00315	4.80945	1.81583333	2.76805	3.5293
Results (mol OH/g lignin)												
Correction Factor (mol/unit area)	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06
Aliphatic OH	1.556	1.483	1.655	1.419	1.403	1.368	1.290	1.186	1.243	1.617	1.433	1.708
Condensed Phenolic OH	0.647	0.569	0.413	0.685	0.598	0.355	0.790	0.648	0.462	0.630	0.499	0.392
Guaiacyl Phenolic OH	0.839	0.504	0.312	0.855	0.534	0.285	0.991	0.585	0.323	0.656	0.406	0.272
Carboxylic acid	0.501	0.762	0.987	0.503	0.786	0.898	0.542	0.727	1.149	0.444	0.662	0.847
Total phenolic OH	1.486	1.074	0.725	1.540	1.132	0.640	1.781	1.233	0.785	1.286	0.906	0.664

Lignin ID	C28 r.l.-0.05	C28 r.l.-0.10	C28 r.l.-0.20	C18 r.l.-0.05	C18 r.l.-0.10	C18 r.l.-0.20	C13 r.l.-0.05	C13 r.l.-0.10	C13 r.l.-0.20
Sample									
amount of cyclohexanol (g)	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04	6.01E-04
Weight of dry lignin (mg)	25.15	24.92	25.01	24.96	24.88	25.16	25.13	25.04	25.24
Integration Regions									
Internal standard	1	1	1	1	1	1	1	1	1
Aliphatic OH	6.4896	6.1188	6.61605	5.85075	5.4918	5.1528	5.6357	5.3405	6.53005
Condensed Phenolic OH	2.7997	2.2907	1.9152	3.1077	2.5669	1.50665	3.05895	2.69785	2.42045
Guaiacyl Phenolic OH	3.7335	2.16335	1.6177	4.1234	2.37465	1.1213	3.91015	2.3873	1.53175
Carboxylic acid	2.01655	2.8293	3.48855	2.1173	3.0484	3.48425	2.5466	3.37395	4.97485
Results (mol OH/g lignin)									
Correction Factor (mol/unit area)	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06	6.00E-06
Aliphatic OH	1.548	1.473	1.587	1.406	1.324	1.229	1.345	1.280	1.552
Condensed Phenolic OH	0.668	0.551	0.459	0.747	0.619	0.359	0.730	0.646	0.575
Guaiacyl Phenolic OH	0.891	0.521	0.388	0.991	0.573	0.267	0.933	0.572	0.364

APPENDIX VI

PERMANGANATE CONSUMPTION EXPERIMENTS

The consumption of potassium permanganate by a pulp is the basis behind the kappa number test, which is used to estimate the lignin content of a pulp (105). A pulp is treated with a solution of $KMnO_4$, and depending on how much permanganate is consumed by the lignin, a kappa number is calculated. The kappa number is related to the lignin content of the pulp by the following equation: % lignin content = kappa number * 0.15, which is valid for pulps below 70% total yield (105,106). The structure or reactivity of lignin, however, is believed to influence the consumption of permanganate, which would make the equation invalid. For example, bleached pulps contain a lignin that is significantly oxidized and would be expected to consume less permanganate than an unbleached pulp with a similar lignin content. This would result in an underestimation of the true lignin content of the bleached pulp. A similar argument has been made for unbleached pulps with low kappa numbers. Low kappa pulps are believed to have high contents of condensed structures in their residual lignins, which was substantiated in Chapter 1 of the Results and Discussion section, which would be expected to consume more permanganate than a higher kappa pulp with a lower content of such structures in their residual lignins. To determine the relevance of these arguments, various isolated residual and dissolved lignins from unbleached and ClO_2-bleached pulps and alkaline extraction stage effluents were reacted with permanganate and their consumption of permanganate measured. A list of the lignins used was presented in Table 19 on page 89 in the Materials and Methods section. The results have been tabulated in Table AVI.1.

Table AVI.1. Consumption of permanganate by various isolated unbleached and ClO_2-treated lignins.

	Unbleached residual lignins				ClO_2 bleached residual lignins		ClO_2 bleached and alkaline extracted lignins		
Lignin ID	E29 r.l.	C28 r.l.	C18 r.l.	E14 r.l.	C28 D r.l. (0.05)	C28 D r.l. (0.20)	E29 DE r.l. (0.10)	E29 D(EO) r.l. (0.10)	E29 D(EO) d.l. (0.10)
Consumption of MnO4*	0.752	0.736	0.733	0.747	0.671	0.551	0.611	0.596	0.544
Replicate	0.746	0.720	0.750	0.745	0.653	0.535	0.596	0.600	0.531
Average	0.749	0.728	0.742	0.746	0.662	0.543	0.603	0.598	0.538

* ml of 0.1N KMnO4 consumed by 1 mg of lignin

The data show that there is basically no difference in the consumption of permanganate by the isolated unbleached residual lignins. The low kappa residual lignins were expected to consume more permanganate because of their higher content of condensed structures, yet no differences between the low and high kappa residual lignins could be distinguished. An explanation of this may be due to the higher content of carboxylic acid groups in the lower kappa residual lignins compared to higher kappa residual lignins. A higher content of carboxylic acid groups in the lower kappa residual lignins would suggest that these lignins are more oxidized than the higher kappa lignins and would consume less permanganate. The counteracting effects of condensed structures and carboxylic acids groups seem to result in the lignins consuming similar amounts of permanganate. The results from this analysis suggest that the relationship between kappa number and klason lignin still holds regardless of the unbleached kappa number.

After a treatment with ClO_2, the residual lignin becomes severely oxidized, which affects the consumption of permanganate. The residual lignins isolated from the ClO_2-bleached pulps with increasing charges of ClO_2 resulted in a corresponding decrease in the consumption of permanganate. The result is not surprising because the NMR analyses showed that the ClO_2-treated lignin becomes highly oxidized. The data are informative because they suggest that the relationship between kappa number and lignin content (% lignin content = kappa number * 0.15) is no longer valid for a ClO_2-bleached pulp.

A comparison between the residual lignin in a ClO_2-bleached and alkaline-extracted pulp with the dissolved lignin in the corresponding extraction reveals that the dissolved lignin consumes less permanganate. The effect verifies the observations made by the NMR analyses, which found that the dissolved lignins are more oxidized (as evidenced by the higher content of carboxylic acid groups), which would result in the consumption of less permanganate. No differences in the consumption of permanganate were observed between the residual lignins isolated from the DE and D(EO) pulps. Although the NMR analysis suggested that the D(EO) lignin was slightly more oxidized, this technique was not sensitive enough to detect this difference.