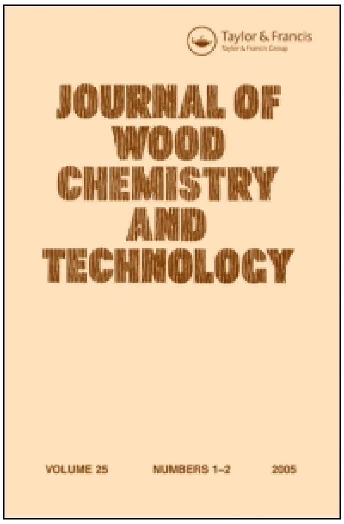

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Oxygen Delignification Chemistry and Its Impact on Pulp Fibers

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ABSTRACT

Two southern pine kraft pulps with kappa numbers of 30.0 (SW1-0) and 48.0 (SW2-0) were oxygen delignified by 30–60% by varying the reaction temperature (78–110°C) and charge of sodium hydroxide (1.6–4.4%). O-bleachability was found to be correlated to the incoming kappa number and charge of sodium hydroxide employed. In general, a lower charge of caustic and a higher brownstock kappa number improved pulp bleachability. The residual lignin in the brownstocks and O-delignified kraft pulp samples was isolated and characterized by ^{13}C and ^{31}P NMR. ^{13}C NMR analysis of the residual lignin samples indicated that the post-oxygen delignified pulps were

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enriched with α-carbonyl groups and carboxylic acid groups. The content of β-*O*-aryl structures was increased by 23–36% depending on the extent of oxygen delignification. The post-oxygen delignified pulps were also shown to have increased substituted aryl carbons. ^{31}P NMR indicated that the relative content of condensed phenolic units increased by 9–20% after the oxygen delignification, depending on the severity of the O-stage. This observation was probably due to the accumulation or formation of 5,5-biphenyl structures in the process. The physical strength properties of brownstock and post-oxygen delignified pulps were assessed in terms of zero-span strength, tensile strength, tear strength, and burst strength. Oxygen delignification led to a slight increase in the curls and kinks of the pulp fibers. The O-stage was shown to cause a 4.8–15.6% decrease in zero-span strength. In contrast, oxygen delignification increased tensile strength. This result could be explained as the improvement of fiber bonding after the oxygen bleaching.

Key Words: Lignin; Oxygen delignification; NMR; Phenolics; Strength.

INTRODUCTION

Over the past two decades single and two-stage oxygen delignification has become a frequently employed technology in modern pulp bleaching operations.[1–3] To a large extent, this technology has been rapidly introduced into modern pulp bleaching operations primarily as a means of addressing environmental concerns. Typically, an O- or OO-stage can remove from 35 to 55% of the residual lignin in a kraft pulp before the selectivity of the process significantly decreases and detrimentally impacts physical pulp properties. Obviously, an increase in O-selectivity is a very attractive research goal that has recently attracted the attention of several research groups.[4–9] Key to improving the oxygen delignification process is the need to refine our understanding of the process chemistry involved in degradation of lignin during an oxygen stage.

The fundamental chemistry of oxygen delignification has been extensively studied with lignin model compounds. As reviewed by Gierer,[10] the degradation of lignin in an alkaline–oxygen medium arises from the integral actions of hydroxide and oxygen with the phenoxy hydroxyl group, as shown in Fig. 1.

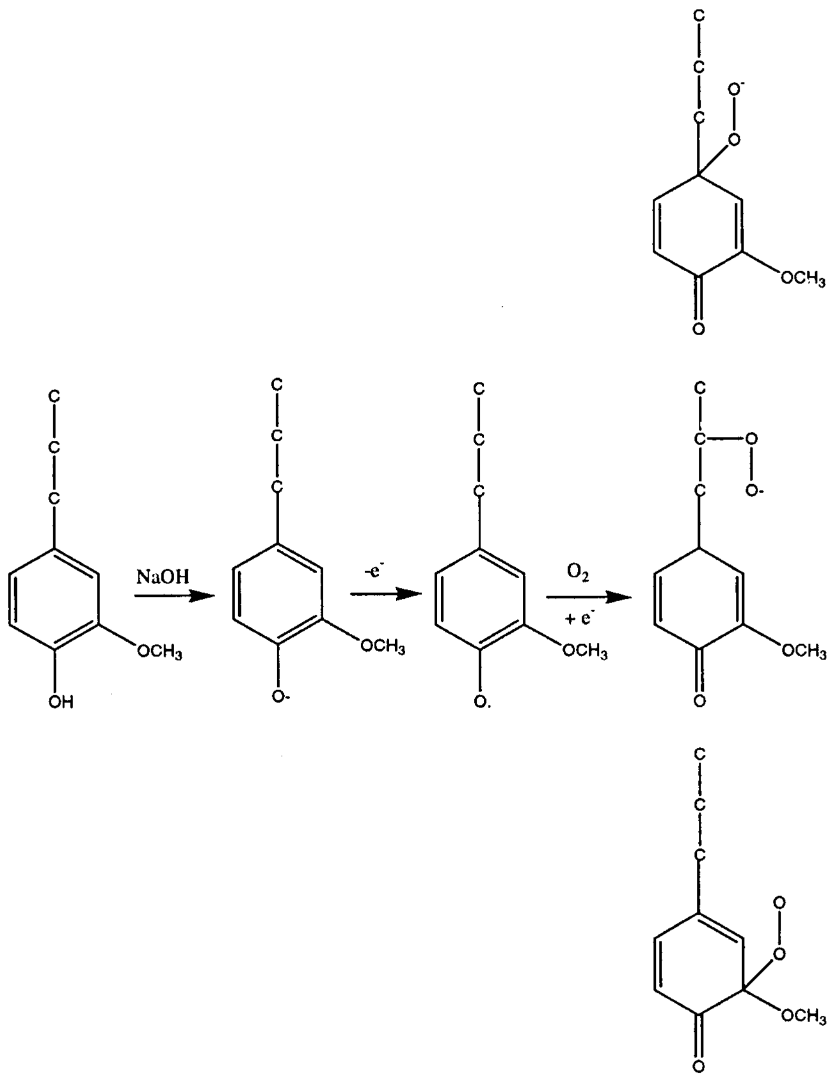


Figure 1. Initial chemical reactions involved in oxygen delignification.

The hydroperoxides have been proposed to form dioxetanes that subsequently induce the fragmentation of the aromatic ring of lignin and side chain scission. These types of reactions have been shown to ultimately lead to the degradation and introduction of carboxylic acid into lignin. At the same time, some of these oxidative fragments are believed to undergo polymerization to form dimeric species that may contribute to the delignification barrier observed in oxygen bleaching.[11,12]

Although the chemistry of oxygen delignification has been primarily attributed to phenolic units in lignin, nonphenolic structures have also been proposed to be involved in the process.[10,13] The degradation of etherified phenolic units has been suggested to begin with the benzylic oxidation of lignin resulting in the formation of α-carbonyl groups. The presence of an α-carbonyl group in the side chain of lignin has been shown to significantly increase the reactivity of nonphenolic units under oxygen delignification conditions by inducing side chain cleavage reactions.[14]

Studies on residual lignin after an O-stage have begun to provide further information on the overall oxygen delignification process. Studies by Gellerstedt et al.,[15] Moe and Ragauskas,[16] and Asgari and Argyropoulos[17] have all indicated that the oxygen delignification process does not dramatically alter the structure of residual lignin. The most significant changes in residual lignin structure were due to a loss of noncondensed phenolics, typically occurring in a range of 50–60%, whereas C-5 condensed phenolics were found to be approximately 50% less reactive to oxygen delignification than noncondensed phenolics. Recently, Chakar et al.,[18] Akim et al.,[19] and Tamminen et al.[20] have reported that *p*-hydroxylphenyl groups are unreactive under oxygen delignification stages. It has been hypothesized that this functional group could act as a blocking group to further degradation of the lignin macromolecule. The lack of reactivity of *p*-hydroxylphenyl groups under O-delignification conditions is unexpected based upon prior oxygen bleaching kinetic studies using lignin model compounds.[21] This study had reported that the ratio of the half-lifes of apocynol and propylphenol in an alkaline/oxygen rich were 1.00:1.36. The differences observed in pulp clearly illustrate that differences exist between model compound studies performed in a homogenous phase and the complex heterogeneous matrix in a pulp fiber.

The oxidation of lignin phenolics is believed to generate several functional groups including muconic acids and quinoidal structures. Zawadzki and Ragauskas[22] have reported a slight enrichment of quinoidal units in lignin after an oxygen stage, but the increase was several orders of magnitude less than what has been detected after a D_0-stage. Presumably, the known instability of quinones to alkali prevents this functional group to increase in concentration during an O-stage.[23]

At the same time that lignin is removed from the fiber during oxygen delignification the pulp carbohydrates are also degraded. According to McDonough[2] the C-2 sites of cellulose are prone to oxidize to the corresponding carbonyl group under oxygen delignification conditions. Under alkaline conditions, the glycosidic carbonyl groups can induce β-elimination reactions resulting in cleavage of the glycosidic bond which detrimentally impacts physical strength properties of pulp fibers.

To further define the limiting chemistry involved in the oxygen delignification, we examined the oxygen bleachability of two SW kraft pulps under mild and vigorous oxygen delignification conditions. Changes in lignin structure due to O-delignification were established by characterizing the residual lignin before and after the O-stage via NMR. In addition, pulp properties were accessed by determining fiber properties.

EXPERIMENTAL

Materials

All reagents and solvents were commercially purchased and used as received except for *p*-dioxane which was freshly distilled over $NaBH_4$ prior to usage. Two commercial SW kraft pulps, kappa 30.0 (SW1-0) and 48.0 (SW2-0), were employed for all studies in this report. Prior to usage, the kraft brownstock pulps were extensively washed until the filtrate was pH neutral and colorless.

Oxygen Delignification

All O-stages were conducted in a 1000 mL rotary autoclave. In a typical experiment, the reactor was charged with SW kraft pulp (100 g o.d.) and the consistency was adjusted to 10% using deionized water. The reactor was then charged with 0.05% $MgSO_4$ and varying amounts of NaOH (1.6–4.4%). After sealing the reactor, the vessel was pressurized with O_2 (276 kPa) and rapidly heated to the desired temperature (76–105°C). The reaction was terminated after 1 h; the reactor was cooled and the O_2 pressure was released. The pulp was then washed, dried, and analyzed for pulp properties.

Lignin Isolation

Residual lignin was isolated from the pulps by employing a mild acid hydrolysis procedure that has been described in the literature.[24] In brief, the pulp (50 g o.d.) was adjusted to 4% consistency with 0.10 N HCl solution containing 90% *p*-dioxane and 10% water (v/v). After refluxing for two hours under an argon atmosphere the pulp slurry was cooled and filtered; the filtrate was pH adjusted to 6 using a saturated $NaHCO_3$ aqueous solution. The solution was then concentrated to 10% of its initial volume under reduced pressure. The concentrated lignin solution was then acidified to a pH of ≈ 2.5, frozen, and subsequently thawed. The lignin suspension was centrifuged and the supernatant was decanted. The isolated lignin was washed (3×200 mL) and centrifuged with an aqueous 0.10 N HCl (400 mL) solution prior to freeze drying. Lignin isolation yields varied from 50.2–43.8% (NB: yields were calculated by determining (mass of lignin recovered)/(theoretical mass lignin content in pulp)).

Lignin Characterization

Residual lignin samples, isolated from the brownstocks and post-oxygen delignified pulps, were analyzed using a 400 MHz Bruker DMX spectrometer. Quantitative ^{13}C NMR spectra were acquired and analyzed in accordance with established literature methods.[25] In brief, lignin (100–130 mg) was dissolved in 500 μL of DMSO-d_6 before being transferred into a 5-mm NMR tube. ^{13}C NMR spectra were recorded with an inverse gated decoupling sequence, 90° pulse angle, 14-s pulse delay, 23,000-Hz sweep, 11–40,000 transients, at 50.0°C. The Fourier transformed spectra were integrated according to reported chemical shifts for lignin functional groups.[25] The integrals were normalized to the aromatic signals, which were assumed to have a value of 6 carbons, this yielded integration results that typically varied less than ±8% between replicates.

Lignin samples were also derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and analyzed by ^{31}P NMR following literature methods.[26,27] ^{31}P NMR spectra were recorded using an inverse gated decoupling sequence, 90° pulse angle, 25-s pulse delay, 13,000-Hz sweep, and 150 transients, at room temperature. This procedure yielded integration results that typically varied less than ±5% between replicates.

Fiber Quality Analysis

Fiber properties including % fines, mean fiber length, and mean curl and kink values were determined using an Optest Fiber Quality Analyzer, Model LDA96.

Physical Strength Measurement

TAPPI standard methods[28] were used to determine CSF, zero-span, fold endurance, tear, tensile, and burst index values for the two brownstocks and corresponding oxygen delignified kraft pulps.

RESULTS AND DISCUSSION

The relationship between O-bleachability and reaction conditions was examined by varying the charge of caustic and O-stage reactor temperature. Table 1 summarizes the O-delignification conditions employed and the changes in pulp property as a result of the O-stage. As previously reported, O-bleachability was found to be influenced by the kappa number of the incoming pulp, with the higher lignin content pulp being more responsive to O-delignification conditions.[18] These results also serve to demonstrate that reactivity of the lignin in the pulp towards O-delignification decreases as the extent of delignification is increased. O-bleachability is increased as the reactor temperature is increased, but the overall selectivity decreases.

To further explore the relationship between O-bleachability and reaction conditions, the chemical nature of the residual lignin in the kraft brownstock and O-delignified pulps was explored. Residual lignin samples were acquired using a mild acid hydrolysis procedure and subsequently

Table 1. Oxygen delignification conditions and results.

Pulp sample	NaOH (%)	Temperature (°C)	Kappa number	Viscosity (cP)	Bleachability[a]	Selectivity[b]
SW1-0	Brownstock		30.0	29.6		
SW1-1	1.6	78	17.1	23.7	8.06	2.19
SW1-2	4.4	78	16.4	20.7	3.09	1.53
SW1-3	1.6	104	14.3	20.6	9.80	1.74
SW1-4	4.4	104	12.4	15.6	4.00	1.26
SW2-0	Brownstock		48.0	32.8		
SW2-1	2.0	110	25.2	20.3	11.40	1.82
SW2-2	3.3	94	27.2	21.2	6.30	1.79
SW2-3	4.4	88	24.7	22.2	5.30	2.20

[a]Δ kappa/NaOH charge; [b]Δ kappa/Δ viscosity.

Table 2. ^{31}P NMR analysis of kraft brownstock and post-oxygen delignified residual lignin samples.[a]

Lignin sample	Aliphatic	Condensed C5 phenolic (cPhOH)	Noncondensed C5 phenolic (ncPhOH)	cPhOH: ncPhOH	*p*-Hydroxyphenyl units	Acids
SW1-0	1.71	1.04	1.04	1.00	0.16	0.39
SW1-1	2.13	1.15	1.02	1.13	0.18	0.68
SW1-2	1.93	1.00	0.88	1.14	0.17	0.74
SW1-3	2.15	1.10	0.93	1.18	0.18	0.75
SW1-4	1.89	0.94	0.84	1.12	0.18	0.86
SW2-0	1.85	1.02	1.01	1.01	0.14	0.31
SW2-1	2.27	0.99	0.82	1.21	0.14	0.67
SW2-2	2.31	1.02	0.87	1.18	0.14	0.72
SW2-3	2.28	0.99	0.90	1.10	0.14	0.65

[a] Functional lignin units measured as mmol/g lignin.

analyzed using advanced NMR techniques. Table 2 summarizes the results of ^{31}P NMR analysis of phosphitylated residual lignin samples. It is evident from this analysis that the acid group content of the residual lignin samples increased by 74–120% after oxygen delignification and that the magnitude of the increase parallels the severity of the O-delignification conditions.

The formation of carboxylic acid groups appears to originate primarily from the oxidation of C-5 noncondensed guiacol phenolic units in lignin. The relative content of condensed phenolic units, as indicated by the ratio of condensed/noncondensed phenolic units, increased by 9% to 20% depending on the pulp sample and the oxygen delignification conditions. The data thus clearly suggest that the C-5 condensed guiacol units are resistant to oxidative degradation under the oxygen delignification conditions employed. This result implies that the post-oxygen delignified pulps contain more condensed lignin structures. Although 5,5-biphenyl moieties in lignin have been shown to be resistant toward oxygen degradation,[11] it was not clear if our observations are due to a simple enrichment process or due to phenyl coupling induced by radicals during oxygen bleaching.[10]

The presence of *p*-hydroxyphenyl groups was also quantified, and this analysis indicates that the content of these structures in post-oxygen delignified pulps was slightly enriched for the SW1-0 pulps, whereas for the SW2-0 pulps the presence of this functional group remained relatively constant. This functional group is present in native lignin of softwood species[29] and as discussed by Chakar et al.[18] *p*-hydroxyphenyl has been shown to be resistant toward oxygen delignification conditions. The effect of this group towards retarding the overall efficiency of O-delignification remains uncertain, although the fact that these functional groups must be located at the terminal ends of the lignin macromolecule suggests that it could have a dramatic effect on the overall degradation of the lignin during an O-stage.

Although ^{31}P NMR analysis of phosphitylated lignin has many advantages, it can only reveal the structure of lignin hydroxyl groups. Since etherified phenolic structures are a major component of residual kraft lignin, further exploration of lignin by ^{13}C NMR was necessary. The ^{13}C NMR spectra for the residual lignin samples isolated from SW1-0 and SW1-2 are presented in Fig. 2. Data clearly indicated that the content of acidic groups in residual lignin increased after oxygen delignification. This result is in agreement with ^{31}P NMR data listed in Table 2.

Interestingly, the spectral data in Fig. 2 indicate that a peak at δ 191 ppm intensified after the oxygen delignification. According to model compound studies,[30,31] this signal can be assigned to the α-carbonyl group on the side chain of lignin. Integration of the signal at δ 191 indicated that the intensity of this peak increased by 53% for the SW1-2 residual lignin with respect to SW1-0.

As discussed by Gierer,[10] lignin units with a benzylic alcohol group can be oxidized to a carbonyl group by hydroxyl radical, as illustrated in Fig. 3.

The spectral data presented in Fig. 2 provides some of the first direct evidence for the formation of carbonyl groups in residual lignin

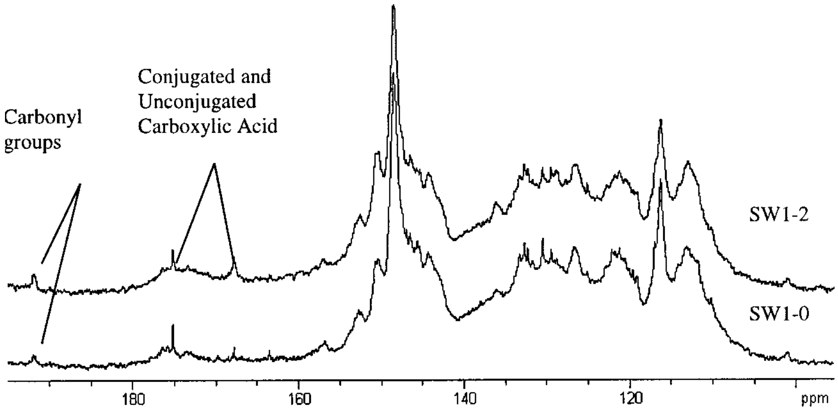


Figure 2. ^{13}C NMR spectra (40,000 Scans) of isolated lignin from brownstock SW1-0 and oxygen delignified kraft SW1-2.

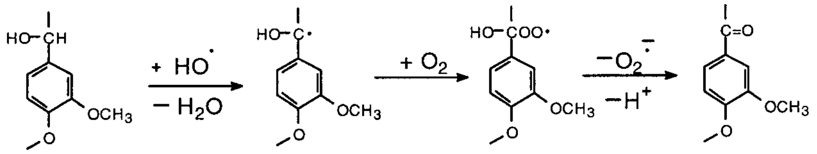


Figure 3. The formation of α-carbonyl group in lignin during the oxygen delignification.[10]

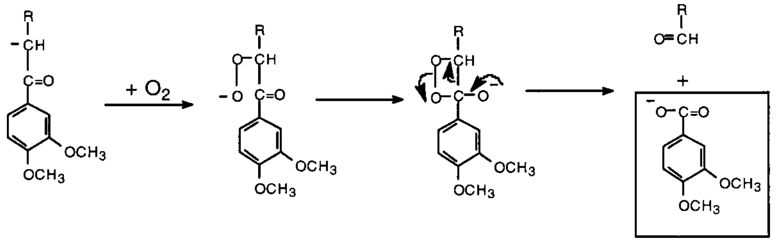
Table 3. Quantitative ^{13}C NMR analysis[a] of residual lignin for pulps SW1-O–SW1-4.

Carbon	SW1-0	SW1-1	SW1-2	SW1-3	SW1-4	SW2-1	SW2-3
–OMe	0.85	0.87	0.86	0.89	0.86	0.86	0.86
C_γ in β-*O*-4	0.22	0.27	0.30	0.30	0.28	0.40	0.46
C_α in β-*O*-4, Aliphatic C-O	0.37	0.53	0.65	0.60	0.57	0.61	0.62
C_β in β-*O*-4 + C_α in β,β	0.31	0.46	0.56	0.52	0.51	0.41	0.50
Ar-C (unsub.)	2.29	2.12	1.96	1.90	1.89	2.19	2.01
Ar-C (sub.)	3.71	3.88	4.04	4.10	4.11	3.81	3.99
5,5′-Diphenyl	0.49	0.49	0.46	0.49	0.48	0.58	0.55
Carboxyl-conjugated	0.01	0.09	0.19	0.16	0.18	0.07	0.08
Carboxyl-nonconjugated	0.12	0.29	0.41	0.43	0.51	0.21	0.29

[a] All function groups ratio to the aromatic carbon signals in the ^{13}C NMR. See experimental section for further details.

after O-delignification. Zawadzki and Ragauskas[22] and Lachenal et al.[32] have reported that the carbonyl group content increased in oxygen delignified pulp lignin employing indirect techniques. Aoyagi et al.[14] and Yang et al.[13] also demonstrated that carbonyl group could be generated in etherified lignin units through a benzylic oxidation during oxygen bleaching.

The analysis of the remaining ^{13}C NMR spectral data of the residual lignin samples was accomplished following standard literature methods and the results are summarized in Table 3. In good agreement with the published results,[16] the ^{13}C NMR data indicate that the residual lignin from the post-oxygen delignified pulps has an increase in carboxyl acids paralleling the results observed with the ^{31}P NMR analysis.



Conjugated Carboxyl acid

Figure 4. Formation of conjugated carboxyl acid through side chain cleavage.[33]

The ^{13}C NMR procedure conveniently permits analysis of conjugated and nonconjugated carboxylic acids, and it is clear that the latter acids are the dominant species present in post-oxygen delignified residual lignin. This result suggests that most of the muconic acids formed in residual lignin during an O-stage are further oxidatively fragmented.

The formation of conjugated acids can come about by cleavage of the C_α–C_β bond of etherified structures containing α-carbonyl group and formation of benzylic-type carboxyl acids. As discussed by Gierer,[33] the carbonyl moieties are readily attacked by oxygen. The oxidative structure formed a four-membered oxirane intermediate that can undergo a ring opening and yield conjugated aromatic acids, as depicted in Fig. 4. Another reaction leading to the formation of conjugated carboxyl involves the oxidative attack of oxygen toward phenolic moieties in lignin eventually causing aromatic ring opening and the generation of muconic acids under alkaline conditions.

Although several articles have suggested that demethylation occurs during oxygen bleaching,[10,17,34] data shown in Table 3 indicate little change in methoxyl group content of the post-oxygen delignified pulps.

^{13}C NMR analysis of the residual lignins from the kraft brownstock and oxygen delignified pulps provides strong evidence that the amounts of substituted aromatic units increase as the extent of oxygen delignification is increased. Likewise, the proportion of unsubstituted aromatic carbons decreased for the post-oxygen delignified kraft pulps. These results thus further confirm the conclusion that residual lignin from post-oxygen delignified pulps becomes more condensed after an O-stage. The condensed nature of the residual lignin after an oxygen stage undoubtedly contributes to its reduced reactivity to extended oxygen delignification conditions.

Table 4. Fiber properties as analyzed by fiber quality analyzer.

Sample	Percentage fine (%)	Mean fiber length (mm)	Mean curl (arithmetic)	Mean kink (mm)
SW1-0	4.65	2.87	0.079 ± 0.003	0.96
SW1-1	9.2	2.69	0.118 ± 0.005	1.27
SW1-2	7.4	2.73	0.114 ± 0.005	1.30
SW1-3	6.9	2.70	0.108 ± 0.005	1.24
SW2-0	6.56	2.80	0.082 ± 0.004	0.97
SW2-1	6.6	2.74	0.120 ± 0.005	1.26
SW2-2	5.7	2.72	0.102 ± 0.004	1.17
SW2-3	5.8	2.81	0.111 ± 0.005	1.21

Pulp Strength Properties

The influence of oxygen bleaching on pulp fibers was evaluated by fiber quality analysis and physical strength measurements on the kraft brownstock and oxygen delignified kraft pulps, as summarized in Table 4. The post-oxygen delignified pulps from the low-kappa SW were found to contain an additional 40–98% fines, whereas the oxygen delignified high-kappa pulp did not lead to an increase in fines. The SW1-0 pulp did exhibit a general decrease in mean fiber length after oxygen delignification; this reduction in fiber length was not as significant for the SW2-0 post-oxygen delignified pulps. For both the SW1-0 and SW2-0 pulps, the curls and kinks were increased after oxygen bleaching, and these fiber deformations seemed to correlate well with bleaching temperature (i.e., the higher the temperature, the more the curls and kinks). Sjöholm et al.[35] had reported similar results that high-temperature alkaline treatment of HW kraft pulp created more fiber deformations than that at low temperature, especially for a prolonged treatment. They believed that the deformation of the fiber due to chemical degradation could result in low zero-span strength.

Table 5 lists the physical strength properties of the kraft brownstocks and O-delignified pulps. Because pulp beating could eliminate the effect of curls on pulp physical strength, all the pulp samples were tested without beating as indicated by the high value of CSF. Burst, tear, and folding strength were low and did not show too much difference between the samples. However, zero-span strength decreased steadily with an increased delignification as higher temperature and alkaline charges were employed. As indicated, SW1-0 pulp suffered a 4.8 to 9.6% decrease in zero-span strength, whereas SW2-0 pulp showed a similar decrease

Table 5. Physical strength of brownstock and oxygen delignified pulps.[a]

Sample	SW1-0	SW1-1	SW1-2	SW1-3	SW2-0	SW2-1	SW2-2	SW2-3
Kappa	30	17.1	16.4	14.5	48	25.2	27.2	24.7
CSF	710	700	709	705	715	700	700	700
Density (g/cm^3)	0.40	0.46	0.47	0.47	0.42	0.47	0.46	0.47
Tear index (mN.m^2/g)	22.4	23.1	23.0	23.0	22.2	22.9	21.9	22.3
Burst index (kPa.m^2/g)	2.1	1.9	1.9	2.1	1.9	1.9	1.9	1.9
Tensile index (N.m/g)	32.6	32.2	34.1	35.3	33.2	35.0	34.4	35.2
Zero span (N.m/g)	165.9	158.0	156.8	149.9	169.5	153.9	158.8	143.1

[a]See Table 1 for oxygen delignification conditions.

that ranged from 6.3 to 15.6%. On the contrary, tensile strength of the pulp samples increased with lignin removal.

This trend, however, was well accommodated with the bonding effect of fibers. As residual lignin was removed, the fibers became more flexible. This facilitated a more intimate contact between the fibers and thus increased the bonding area. On the other hand, the increase in delignification was generally accompanied with additional damage to cellulose.[36]

CONCLUSIONS

The studies described in this report clearly demonstrate a relationship between pulp bleachability and the structure of the residual lignin in the pulps. The high-kappa pulp was found to have lesser amounts of condensed phenolics and *p*-hydroxyphenols. Upon exposure to oxygen delignification reaction conditions, these functional units of lignin are enriched in the residual lignin of the O-delignified pulp, suggesting that they are resistant to further degradation and most likely contribute to reduced O-bleachability. The residual in post-oxygen delignified pulps was shown to be enriched with acid groups and this correlated well with the extent of delignification. It is our hypothesis that the increased acid group content of residual lignin can be best attributed to the presence of lignin carbohydrate bonds that retard the release of oxidized lignin into the bleaching liquors. If this situation is one of the dominant issues retarding further delignification of lignin during an O-stage, then the key to developing extended, selective oxygen delignification conditions will be the development of lignin side chain cleavage reactions which can further fragment the macromolecule.

The oxygen delignification caused fiber deformation and led to the increase in curls and kinks in pulp fibers and decreased zero-span strength values for the oxygen delignified pulps. Under the conditions explored, the tensile strength of oxygen delignified pulp increased slightly with lignin removal which was probably due to the improvement of bonding between fibers after the oxygen delignification.

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