Extending the Limits of Oxygen Delignification

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EXTENDING THE LIMITS OF OXYGEN DELIGNIFICATION

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ABSTRACT
Oxygen bleachability of a low (kappa 26.6) and high (kappa 56.2) lignin content SW kraft pulp was evaluated under conventional oxygen, extended OO, and (E+O)D30.05(E+O) conditions. The bleachability of the high kappa pulp was found to be superior to that of the low kappa pulp. At a constant charge of caustic, the relative percent delignification was found to be \( \text{OO} \rightarrow \text{O} \rightarrow (E+O)D30.05 (E+O) \) for the low and high kappa pulps. The mild conditions of the latter sequence yielded pulps with higher viscosity values. Hexenuronic acids contributed 22% to the kappa number of the low lignin content brownstock and negligibly to the high lignin content brownstock. Changes in pulp bleachability of the high and low kappa SW kraft pulps were further investigated by isolating and characterizing the residual lignin of the pulps and the bleaching effluents. \(^{13}\)C NMR analysis of the brownstock residual lignins indicated that the high kappa pulp had a greater amount of \( \beta \)-O-aryl ethers and methoxyl groups in comparison to the low kappa pulp. The high kappa pulp had less condensed aromatic units and diphenyl methane functional groups in the lignin. These results support the hypothesis that condensed phenolics influence pulp bleachability for O delignification. Analysis of the effluent lignins provided supporting evidence for the differences in pulp bleachability under varying reaction conditions. Differences in pulp bleachability were attributed to differences in the structure of lignin and hexenuronic acids present in the high and low kappa brownstocks.

INTRODUCTION
The benefits of oxygen delignification for the production of bleached kraft pulps have been recognized for well over four decades. Research studies over this period have examined many applied and fundamental components of oxygen delignification [1,2,3,4,5]. Initial studies examined the basic chemistry of oxygen delignification and process engineering parameters. As the incorporation of an O stage into pulp bleaching operations became common practice, research studies were generally directed at improving the selectivity of oxygen delignification and/or improving the overall environmental performance of kraft bleaching operations via oxygen delignification. As environmental issues have now been addressed, research has once again returned to extending the performance of this proven technology.

Among the future opportunities for oxygen delignification is the possibility of using an O stage to improve overall pulp yields. Several researchers have noted that it is possible to improve pulp yields by halting the kraft cook prior to the residual phase and to remove the additional lignin via oxygen delignification. In general, for SW kraft pulps, this requires employing an O stage on a brownstock pulp having a kappa number > 40. The overall wood savings following this approach has been reported to be in the range of 2 – 6% for a modern pulp mill [6]. Coupling this approach with modified kraft cooking conditions such as the use of polysulfide, AQ, or surfactant-based chip penetrates has been reported to increase pulp yields by 4-6%. Magnotta et al. have reported improved selectivity with an extended oxygen OO system on high kappa kraft pulps [7]. Employing kraft pulps with a kappa number of 40 or greater, it was demonstrated that an OO system can increase pulp yields \( \approx 4\% \) prior to ECF bleaching. Bokstrom et al. have reported that commercial OO systems can achieve greater than 70% delignification with a kappa 30 SW kraft pulp [8]. Interestingly, lab and mill studies suggest that an OO stage can attain greater delignification and selectivity in comparison to a one-stage oxygen system.

At the other end of the oxygen delignification technology spectrum lies the use of a "mini-O". This system typically removes lesser amounts of lignin but requires less capital investment. Histed has reported that the use of a 0.05-kappa-factor D pretreatment stage followed by a higher than normal temperature in the \((E+O)\) stage can achieve approximately 50% delignification of an SW kraft pulp [9]. McKenzie reported that the commercial use of a mini-oxygen delignification system prior to a conventional O stage provided an additional 25% delignification of an SW kraft pulp [10].
Despite the diversity of oxygen delignification technologies, it has been generally assumed that the delignification chemistry involved in this process is primarily due to the oxidative destruction of phenolics. The preeminent model compound studies by Gierer, Gratzl, Ljunggren, Gellerstedt, and others into the chemistry of oxygen delignification have certainly detailed how phenolic lignin-like structures can be oxidized under an O stage [11, 12, 13]. Typically, oxidative reactions involve the loss of an electron from the phenolate anion to oxygen and subsequent attack of the phenolate radical by oxygen (see Figure 1).

Fig. 1. Fundamental O-delignification chemistry

The initial electron transfer process is known to generate superoxide and this leads to the generation of several other oxidative species, including hydrogen peroxide anion and hydroxy radicals [14]. The presence of several types of oxidative chemical agents in an O-stage dramatically increases the complexity of the delignification chemistry occurring in an O stage.

Structural analysis of residual lignin after an O-stage has further defined the delignification chemistry involved in this process. Studies by Gellerstedt et al. [15], Moe and Ragauskas [16], and Asgari and Argyropoulos [17] have all noted that the structure of lignin after a conventional O stage is not dramatically altered. In general, non-condensed phenolics are diminished after an O stage and the residual lignin is enriched in condensed structures and acid groups. Increases in carbonyl groups for oxygen delignified pulps have been reported by Zawadzki and Ragauskas [18], Lachenal et al. [19], and Gellerstedt et al. [15]. Although these results are consistent with model compound studies, it appears that, overall, residual lignin is less reactive to an oxygen stage than model compounds would suggest. These differences between model compounds and residual lignin studies have been attributed to possible mass transfer effects.

This paper examines the reactivity of a high and low kappa SW kraft pulp to conventional, extended, and mini-O oxygen delignification technologies. Pulp bleachability was assessed by characterizing the pulps in regard to physical pulp properties and fundamental lignin structures. The results of varying these operational parameters serve to highlight the structures in lignin that are involved in oxygen delignification chemistry and to provide a basis from which improved extended oxygen delignification systems can be designed.

METHODS AND MATERIALS

An industrial SW kraft pulp with a kappa # of 26.6 and a laboratory prepared SW kraft with a kappa # of 56.2 were employed for all studies in this paper. The mill pulp had a viscosity value of 29.6 cP and the lab pulp had a viscosity value of 42.0 cP. Prior to the oxygen delignification studies, the pulps were extensively washed until the wash water was pH neutral and colorless.

Metals Analysis of Kraft SW Brownstocks

Nonprocess elements of the two kraft brownstocks were determined using standard ICP methods [20]. Table 1 summarizes the results of ICP analysis.

<table>
<thead>
<tr>
<th>TABLE I. METAL ANALYSIS OF KRAFT BROWNSTOCKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Ni</td>
</tr>
</tbody>
</table>

Hexenuronic Acid Analysis of Kraft SW Brownstocks

The high and low kappa SW kraft pulps were analyzed for hexenuronic acid content by refluxing in pH 3 solution, following literature methods [21]. Hexenuronic acids contributed approximately 22.5 and 1.0% to the kappa number of the low and high SW kraft pulps, respectively.
**Oxygen Delignification**

The kraft pulps were oxygen delignified in a stirred Parr Reactor. Table II summarizes the delignification conditions.

**TABLE II. BLEACHING CONDITIONS**

<table>
<thead>
<tr>
<th>Stage</th>
<th>O₂ Pres. /psi</th>
<th>NaOH° L - H</th>
<th>Temp. /°C</th>
<th>Time/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>80</td>
<td>1.5 - 2.5</td>
<td>105</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>i) 130</td>
<td>2.5 - 4.1</td>
<td>i) 80</td>
<td>i) 20</td>
</tr>
<tr>
<td>ii) 60</td>
<td></td>
<td>3.5 - 5.8</td>
<td>ii) 105</td>
<td>ii) 60</td>
</tr>
<tr>
<td>(E+O)D</td>
<td>80</td>
<td>1.5 - 2.5</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

°MgSO₄ charge: 0.30%; Consistency: 12%; °L represents the NaOH charges for the 26.6 kappa SW pulp and H designates the NaOH charges employed for the 56.2 kappa SW pulp; °caustic charge was split between two (E+O) stages, the (E+O) pulp was washed and then treated to a D stage employing a 0.05 k.f. charge of ClO₂, at 10% csc and 70°C, for 30 min, with a terminal pH: 2.2. The (E+O)D pulp was washed prior to the second (E+O) stage.

Delignified pulps were analyzed for kappa number following TAPPI method om-246 [22]. Typical experimental standard deviations for this procedure were determined to be ±2.0% for the low kappa pulps (<30) and ±0.6% for the high kappa pulps (>30). Pulp viscosity values were determined in accordance with TAPPI Standard T-230 om-89 [19] and standard deviations were ±0.4 for the low kappa pulps and ±1.5 for the high kappa pulps.

**Lignin Isolation**

Oxidized lignin from the oxygen delignification effluents was isolated by concentrating the bleach effluents to a fourth of their initial volume and acidifying to a pH of 1.5 using 1.00 N H₂SO₄. The precipitated lignin was removed by ultra-centrifuge, washed twice with pH 2.00 sulfuric acid solution, and then freeze dried. The isolated material was then further dried under high vacuum at 45°C prior to NMR analysis.

Isolation of residual lignin from the brownstocks, O, OO, and (E+O)D(E+O) pulps was accomplished employing standard literature methods [23]. In brief, air-dried pulp (30 – 50 g oven dry weight) was added to an aqueous 1.00 N HCl (100 ml), p-dioxane (900 ml) solution. The pulp slurry was refluxed for 2 hr under an argon atmosphere and then cooled, filtered, and concentrated. The precipitated lignin was isolated by ultra-centrifuge, washed with acidic water (pH 2), and then dried. This procedure afforded, on average, 40–55% yield of residual lignin, based on mass recovery of lignin and starting pulp kappa number.

**13C NMR Analysis of Residual Lignin**

Quantitative 13C NMR spectra were recorded with an inverse gated 90° pulse sequence, a 14s delay, a TD of 32k, and a sweep width of 330 ppm [24]. The NMR experiments were performed at 50°C on samples containing 150-300 mg lignin/ml of DMSO-d₆. The Fourier transformed spectra were integrated in accordance with reported chemical shifts for lignin functional groups. The integrals were normalized to the aromatic signals, which were assumed to have 6 carbons.

**31P NMR Analysis of Residual Lignin**

Lignin samples were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane following the literature method [17] and analyzed by 31P NMR.

**RESULTS**

**Oxygen Bleachability of Kraft Pulps**

Previous studies reported by Moe and Ragauskas [16] have shown that O bleachability of high kappa SW kraft pulps (i.e., ITC, conventional, and PS/AQ) can be readily correlated to the initial kappa number of the pulp. This study further explores the bleachability of SW kraft pulps under oxygen delignification conditions employing conventional O, extended oxygen OO, and the mini-O sequence (E+O)D(E+O) with a 0.05 kappa factor in the D-stage. The experimental conditions were selected from previous literature reports [3,8,9]. To minimize the number of experimental variables, the consistency of all O stages was maintained at 12% and a constant charge of MgSO₄ was employed. The oxygen pressure was maintained at 80 psi for all studies except for the OO experiments. This later sequence required an initial O₂ pressure of 130 psi for 20 minutes at 80°C and was then lowered to 60 psi for 60 minutes at 105°C. All oxygen delignification studies were stirred at a constant
rate throughout the experiment. The low kappa pulps were O-delignified using 1.50, 2.50, and 3.50% charge of caustic. Oxygen delignification of the high kappa pulps was accomplished with caustic charges of 2.50, 4.10, and 5.80%. In the OO experiments, the reactor was charged with all the caustic at the beginning of the first stage, whereas the (E+O)D(E+O) sequence had the charge split between the two (E+O) stages. Hexenuronic acid analysis of the high kappa brownstock suggested a negligible presence of this sugar in the pulp. In contrast, the kappa number analysis of the low lignin content brownstock suggested that hexenuronic acids contributed 22% to the starting kappa number.

The delignification response for the low kappa SW kraft pulp under varying oxygen conditions is summarized in Figure 3. It is interesting to observe that the different operating conditions for the O and OO stages allowed the latter system to slightly improve the overall extent of delignification. The mild conditions of an (E+O) stage yielded 13% delignification using a 1.50% charge of caustic and 25% delignification with a 3.50% charge of NaOH. The use of a low charge of ClO₂ (kf:0.05) and splitting the caustic charge between the two (E+O) stages significantly improved the response of the pulp towards delignification in the second (E+O) stage. This effect is presumably due to the ability of chlorine dioxide to degrade hexenuronic acids and lignin fragments prior to the second (E+O) stage.

Fig. 3. Changes in kappa number for low lignin content SW kraft pulp before and after O, OO, (E+O), and (E+O)D(E+O). An examination of the extent of delignification for the high kraft pulps (Fig. 4) under alkaline oxygen indicates that the OO stage outperformed the O stage at all three caustic application levels. Clearly, the temperature/oxygen profiling in the OO stage improves delignification for the high kappa pulp. The delignification efficiency of the mini-O sequence was comparable effective for the high kappa and low kappa kraft pulps.

![Fig. 4. Changes in kappa number for high lignin content SW kraft pulp before and after O, OO, and (E+O)D(E+O).](image)

Changes in delignification in terms of pulp bleachability (i.e., Δ kappa/charge of caustic) for the low and high kappa SW kraft pulps are summarized in Figure 5.

![Fig. 5. Pulp bleachability of 26.6 (LK) and 56.2 (HK) kappa SW kraft pulps for O, (E+O), and OO.](image)

These results clearly demonstrate that the high kappa pulp responds more favorably to the alkaline oxygen conditions than the low kappa pulp. The low bleachability response of the (E+O) stage emphasizes the need for a low charge of ClO₂.
The changes in pulp viscosity for the high and low kappa pulps for O, 00, and (E+O)D(E+O) are summarized in Figure 6.

![Fig. 6. Pulp viscosities (cP) for brownstocks BS), O, 00, and (E+O)D(E+O) high (H) and low (L) kappa kraft pulps.](image)

Although the O and 00 sequences yielded relatively comparable amounts of delignification for the low kappa pulp, the 00 exhibited improved viscosities. Interestingly, the sequence (E+O)D(E+O) using 3.5% NaOH provided the same amount of delignification that the O stage yielded with 1.5% caustic but had an improved viscosity value. For the high kappa pulp the 00 stage is clearly superior with respect to delignification and viscosity retention. Comparison of the viscosity changes for the low and high kappa pulps cannot be solely attributed to lignin and pulp carbohydrates given the differences in metal content for the two pulps (see Table I).

**Lignin Analysis**

In general, the high kappa brownstock exhibited improved pulp bleachability over the low kappa brownstock. The role of residual lignin structure in determining pulp bleachability was assessed by isolating lignin from each brownstock employing an acidic dioxane extraction procedure. The residual lignin samples were then analyzed by quantitative $^{13}$C NMR spectroscopy. Figure 7 presents the spectral data acquired from the residual lignin isolated from the high kappa kraft pulp.

The results of this analysis provide a facile means of characterizing a variety of functional groups present in the residual lignin samples and these results are summarized in Table III.

![Fig. 7. Quantitative $^{13}$C NMR analysis of residual lignin from high kappa kraft brownstock.](image)

**TABLE III. RESIDUAL LIGNIN FUNCTIONAL GROUP ANALYSIS VIA $^{13}$C NMR**

<table>
<thead>
<tr>
<th>Brownstock</th>
<th>High Kappa</th>
<th>Low Kappa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$-Ph</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>MeO-Ph</td>
<td>0.89</td>
<td>0.81</td>
</tr>
<tr>
<td>C$_5$ in $\beta\beta$ and C$_5$ in $\beta$-5</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>C$_7$ in $\beta$-O-4</td>
<td>0.32</td>
<td>0.27</td>
</tr>
<tr>
<td>Aromatic C$_5$-R</td>
<td>1.96:1.00</td>
<td>2.05:1.00</td>
</tr>
<tr>
<td>Aromatic C$_7$-H</td>
<td>1.96:1.00</td>
<td>2.05:1.00</td>
</tr>
<tr>
<td>Acid</td>
<td>0.17</td>
<td>0.31</td>
</tr>
</tbody>
</table>

*the signal intensity of functional groups was made relative to the signal intensity of the aromatic carbons, which was given a value of 6.*

The differences in residual lignin structure for the two pulps are consistent with past investigations into the structure of residual lignin from kraft pulps with varying kappa numbers [25]. The increased content of diphenyl methane units and the changes in Aromatic C$_5$-R : Aromatic C$_7$-H both suggest an increase in amounts of condensed phenolics for the low kappa kraft brownstock. $^{31}$P NMR analysis of the phosphitylated lignins supported the $^{13}$C NMR analysis as the ratio of C$_5$-noncondensed phenolics:C$_5$-condensed phenolics was 1.00:0.87 for the high kappa pulp lignin and 1.00:0.93 for the low kappa pulp. These results support the hypothesis that the low-kappa pulp has greater amounts of condensed phenolic structures.

With regards to oxygen bleachability, the increased presence of condensed lignin structures in the low kappa pulp appears to be a key contributor to reducing pulp bleachability. This result is consistent with past studies from our group and others [15-18].
Another approach to evaluating the fundamental oxidative chemistry involved in O, OO, and (E+O)D(E+O) sequences studied in this report is to examine the nature of the oxidized lignin fragments in the effluents. This was accomplished by acid precipitating the oxygen effluents and $^{31}$P NMR analyzing the phosphitylated residues. Table IV summarizes the bleach effluents that were selected for analysis.

**TABLE IV. BLEACH EFFLUENTS ISOLATED, PHOSPHITYLATED, AND ANALYZED BY $^{31}$P NMR.**

<table>
<thead>
<tr>
<th>Low Kappa Pulp</th>
<th>1.5% NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional O</td>
<td>3.5% NaOH</td>
</tr>
<tr>
<td>(E+O)D(E+O)</td>
<td>3.5% NaOH</td>
</tr>
<tr>
<td>OO</td>
<td>3.5% NaOH</td>
</tr>
<tr>
<td>High Kappa Pulp</td>
<td>5.8% NaOH</td>
</tr>
<tr>
<td>Conventional O</td>
<td>5.8% NaOH</td>
</tr>
<tr>
<td>(E+O)D(E+O)</td>
<td>5.8% NaOH</td>
</tr>
<tr>
<td>OO</td>
<td>5.8% NaOH</td>
</tr>
</tbody>
</table>

For the samples analyzed, the acid group content of the effluents was increased by 200–340% with respect to the acid group content of the residual lignins in the brownstock. This result is a simple reflection of the oxidative chemistry involved in the oxygen stages studied. In addition, the aliphatic hydroxyl group content of the effluent lignins increased between 10 – 50%. An increase in aliphatic hydroxyl groups (i.e., hydroxyl groups attached to the linking propane-chain of lignin) suggests that the oxygen bleaching chemistry involved in an O, OO, or (E+O)D(O+O) is primarily directed at the aromatic hydroxyl groups and not oxidative chemistry on the side-chain. Of greater interest, are the oxidative chemistries involving phenolic groups. The $^{31}$P NMR method employed allows a facile measurement of C5 condensed and noncondensed phenolics. Changes in phenoxy content of the O-delignified effluents with respect to the phenoxy content of the brownstock residual lignins are summarized in Figures 7 and 8.

The $^{31}$P NMR effluent data indicates that for the O and OO-treatments of the low and high kappa pulps, the C5 noncondensed phenolics are more readily depleted than the C5 condensed phenolics with respect to the brownstock residual lignins. This result implies that condensed phenolics are resistant to oxygen delignification conditions.

![Fig. 7. Changes in phenoxy content of recovered effluent lignins after treatment of low kappa SW kraft pulp with O, OO, and (EO)D(EO). Brownstock pulp had a C5 noncondensed, C5 condensed phenoxy content of 0.88 and 0.82 nmol/g of lignin, respectively.](image)

Increased oxidative removal of condensed phenolics requires increasing amounts of caustic. The loss of phenolics in the (E+O)D+(E+O) stage was less severe and this is probably due to the milder conditions of this procedure.

![Fig. 8. Changes in phenoxy content of recovered effluent lignins after treatment of high kappa SW kraft pulp with O, OO, and (EO)D(EO). Brownstock pulp had a C5 noncondensed, C5 condensed phenoxy content of 0.84 and 0.73 nmol/g of lignin, respectively.](image)

The $^{31}$P NMR spectra of the phosphitylated bleach effluents and kraft brownstock residual lignins also suggested that hydroxy-phenolic structures were resistant to oxygen delignification conditions. Although only low amounts of these structures are present in the
brownstock lignin (≥ 0.07 mmol/gr) they were enriched in the bleach effluents by approximately 10%. The stability of p-hydroxyphenyl units to oxygen conditions was further explored by adding phenol to a conventional oxygen stage and recovering this chemical after the cook. GC analysis of the recovered phenol indicated recovery yields of +98%. This result further supports the above NMR evidence that p-hydroxyphenyl lignin units are resistant to oxygen delignification conditions.

SUMMARY
The oxygen delignification studies confirmed the proposed benefits for an OO stage delignification system for both low kappa and high kappa pulps. The use of a mini-O system to remove lignin from kraft pulps having a kappa #< 30 continues to be a promising technology. Analysis of the residual lignin structure of kraft brownstocks and bleach effluents emphasize the important role condensed phenolics play in controlling oxygen delignification technology. In addition, p-hydroxyphenyl units may also hinder O-delignification. Although the use of vigorous oxygen delignification conditions can extend lignin removal, future advancements in O-delignification will need to develop alternative technologies that selectively remove lignin resistant functional groups such as condensed phenolics.

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REFERENCES


21. VUORINEN, T., FAGERSTROM, P.,