The worldwide installed capacity of oxygen delignified kraft pulp in 2010 was estimated at about 300000 metric tons/day, representing most of the world’s bleachable grade pulp. Oxygen delignification removes about 40%-60% of the lignin remaining in pulp after cooking for softwood (about 30%-45% for hardwood). The advantages of oxygen delignification are lower emissions and operating costs. The disadvantages are lower delignification-cellulose degradation selectivity and yield preservation compared to chlorine dioxide treatment and its high capital cost. The mechanism of oxygen delignification is considered to be the attack of oxygen on dissociated phenolate anions to form oxygen-based radicals (HO, HOO, $O_2$ organic peroxides, etc.), which further oxidize and degrade lignin to organic acids (of the muconic-type in particular), carbon dioxide, and other small molecular weight organic products via ring opening, cleavage of aliphatic side chains, and demethoxylation reaction. In addition to this major phenolic delignification route, another smaller delignification pathway called peeling delignification was proposed by Backa et al. Where lignin is removed together with hemicelluloses due to alkaline peeling of the latter, to which lignin fragments are covalently bound (as lignin carbohydrate complexes [LCCs]). Ji [5] has shown that the impact of peeling delignification is relatively small and limited to the initial delignification phase. Both primary and secondary peeling reactions are responsible for decreasing the carbohydrate yield during oxygen delignification. Hexenuronic acids are not removed during conventional oxygen delignification. To increase delignification of softwood pulp beyond about 60%, oxygen system design should be changed so that alkali concentration and charge are decoupled, as is similarly done in modern cooking systems.

**Application:** It is possible to delignify kraft softwood pulp above 60%, without excessive cellulose degradation, by keeping the hydroxide concentration low and uniform over time through replenishment of the alkali while it is being consumed.
oxygen delignification is extended for a long enough period of time. The kinetics also showed that the NaOH concentration order of delignification is first-order at low alkali concentrations and zero-order at very high alkali concentration. Ji [3] also showed that cellulose degradation is caused by two contributions: one due to radicals produced by phenolic delignification and the other due to direct alkaline hydrolysis of the cellulose chains. Thus, the increase in the number of moles of cellulose per gram of pulp, \( m_n \), can be described as:

\[
\frac{dm_n}{dt} = -k_c \frac{dK}{dt} + k_i [OH^-]
\]

where \( K \) is kappa number; \( k_c \) is the radical yield constant; \( k_i \) is the alkaline hydrolysis rate constant; and [OH] is the alkali concentration in g/L. This behavior implies that the delignification selectivity improves (high \( -dK/dm_n \)) at lower [OH] and decreases over time as the relative importance of alkaline hydrolysis (the 2\(^{nd}\) term on the right hand side \( \text{rhs} \)) of Eq. [1] increases.

In the present paper, based on the thesis of Ji [9], the properties of the oxygen delignified Southern Pine pulps produced in a Berty throughflow reactor at different alkali concentrations, temperatures, oxygen pressures, and times are presented and compared to those generated in a conventional batch reactor. The objective of the paper is to identify conditions that achieve the highest degree of delignification while maintaining pulp quality and yield.

### EXPERIMENTAL

#### Berty throughflow reactor

A commercial Berty reactor (Autoclave Engineers; Erie, PA USA) with a stationary basket that holds a pulp pad was used. The 280 ml reactor contains a 100 ml basket with a rotor underneath that induces flow through the pulp bed inside the basket. The entire reactor is filled with an oxygen saturated caustic solution that is fed to the reactor at a constant flow rate. The reactor temperature and outflow rate were carefully controlled. The UV-VIS absorption at 280 nm of the outflow stream is monitored every 15 s. The UV-VIS data is converted into dissolved lignin concentration using a calibration curve prepared with Indulin AT lignin obtained from MeadWestvaco. For further operational details of the entire system, one is referred to Ji [9].

#### Pulp and analytical procedures

Unbleached Southern Pine kraft pulp with an initial kappa number of 24.4 was determined with TAPPI Standard T 236 cm-85 “Kappa number of pulp” at one-tenth of the amount in the standard method. Intrinsic viscosity of 1189 cm\(^3\)/g was determined with ASTM Designation D 1795-62 “Standard test method for intrinsic viscosity of cellulose” (re-approved in 1985). The yield of the oxygen-delignified pulps was determined by evaporation to dryness at 105°C. The hexenuronic acid (HexA) content of pulp was determined by the HUT method described by Tenkanen et al. [10]. The method was scaled down to a pulp sample size of 200 mg. Since the kappa number includes HexA as a carbohydrate-based, oxidizable structure, the residual lignin content reported in this paper is corrected by subtraction of the HexA content (in mmol.g\(^{-1}\) pulp), using 10 mmol.g\(^{-1}\) as equivalent to 1 kappa unit [11]. The lignin (Klason and UV) and carbohydrate composition of the pulps was determined after a standard two-stage acid hydrolysis (primary hydrolysis with 72% H\(_2\)SO\(_4\) at 30°C and secondary hydrolysis with 4% H\(_2\)SO\(_4\) at 121°C) based on the work of Kaar et al [12,13]. The monomeric sugar content in the final hydrolysate was measured using a Dionex HPAEC (Thermo Fisher Scientific; Sunnyvale, CA, USA). The content of the sugar-reducing ends in the pulps was measured using the method described by Miller [14].

### RESULTS AND DISCUSSION

#### Comparison of Berty throughflow reactor performance with that of a batch reactor

The oxygen delignification performance of the Berty throughflow reactor was compared with that of a batch reactor operating at similar conditions: batch reactor at 90°C, 75 psig, 10% consistency, 3% NaOH on 20 g o.d. pulp; and 90°C, 75 psig with a flow of 3.3 g/l NaOH fed continuously to 4 g o.d. pulp in the Berty throughflow reactor. The concentration of 3.3 g/l NaOH was chosen for the Berty throughflow reactor to obtain the same initial NaOH concentration as in the batch reactor, i.e., 0.03×20/(0.9×0.2)×1000=3.3 g/l. Thus, the main difference between these two systems is the caustic concentration, which decreases rapidly in the batch reactor while remaining 3.3 g/l in the Berty throughflow reactor. This is reflected in the pH of the spent liquors from both reactors shown in Table I. The Berty throughflow reactor spent liquors all have the same pH, while the pH decreases continuously in the batch reactor. After 20 min, the pH in the batch reactor is 1 unit lower than that of the Berty throughflow reactor (12.3 versus 13.3), indicating that the alkalinity is only 10% of that in the Berty throughflow reactor.

The kappa number, intrinsic viscosity, and yield of the oxygen-delignified pulps obtained in the two reactor systems are listed in Table II. It can be seen that kappa numbers of

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Batch</th>
<th>Berty Throughflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>13.3</td>
</tr>
<tr>
<td>10</td>
<td>12.4</td>
<td>13.3</td>
</tr>
<tr>
<td>20</td>
<td>12.3</td>
<td>13.3</td>
</tr>
<tr>
<td>40</td>
<td>12.2</td>
<td>13.3</td>
</tr>
<tr>
<td>60</td>
<td>12.1</td>
<td>13.3</td>
</tr>
<tr>
<td>180</td>
<td>10.7</td>
<td>13.3</td>
</tr>
</tbody>
</table>

I. pH of oxygen delignification spent liquors produced in batch and Berty throughflow reactors.
the Berty throughflow and batch reactor samples are almost the same during the first 20 min. However, at longer times, the kappa numbers obtained with the Berty throughflow reactor are lower than that of the batch reactor and at 180 min, the Berty throughflow sample has a 3 point lower kappa number. Similar to the kappa number results, the intrinsic viscosities of the Berty throughflow and batch reactor samples are almost the same during the first 20 min. However, at longer times, the viscosity drops further for the Berty throughflow samples, leading to a 237 ml/g lower intrinsic viscosity after 180 min.

Because both kappa number and intrinsic viscosity drop faster in the Berty throughflow reactor than the batch reactor at longer times, it is of interest to compare the delignification-cellulose degradation selectivity of the two systems. Figure 1 shows the kappa number change plotted versus cellulose cleavages per glucose unit calculated as $1/\text{DP}_t - 1/\text{DP}_0$, where DP is the degree of polymerization. The delignification-cellulose degradation selectivity for these experiments is calculated as $K_0 - K_1$.

The DP of cellulose is now calculated using $\text{DP} = (1.65 \times [\eta])^{1.111}$ because the hemicellulose and cellulose mass fractions were not determined for all samples. However, considering the relatively small changes in the cellulose mass fractions (Table III) and the small contribution of the hemicellulose mass fraction to the DP (Eq. [2]), the selectivity calculated in this way may still be used for relative comparison of the different operating conditions.

It can be seen that a linear relationship is obtained for the batch reactor data, while the change in kappa number decreases with increasing number of cellulose cleavages for the pulps in the Berty throughflow reactor. This indicates that the delignification-cellulose selectivity remains constant in the batch reactor while it decreases in the Berty throughflow reactor. The explanation for this behavior is that the cellulose...
degradation in the batch reactor is caused almost exclusively by radical species. On the other hand, in the Berty reactor, the relative importance of alkaline hydrolysis (i.e., the second term on the rhs of Eq. [1]) increases as phenolic delignification slows down.

### Reducing ends content of pulps

Theoretically, reducing ends may be present in hemicelluloses as well as in cellulose. However, since the DP of cellulose is much higher than that of hemicelluloses, we assumed that the reducing ends are only associated with hemicellulose. Therefore, the content of reducing ends in the pulps is normalized with respect to their hemicellulose content in Fig. 2. It shows no difference between the Berty throughflow and batch reactors during the first 40 min of reaction. The normalized reducing end content initially decreases and then increases with reaction time.

The initial decrease in reducing end content may be explained by “peeling” and/or oxidation of the hemicelluloses. The subsequent increase may be interpreted as radical attack on hemicelluloses that leads to new reducing ends.

### Cellulose DP and hemicellulose DP of pulps

The DP of cellulose in Table III was calculated using Eq. (2), according to the method presented earlier by Da Silva Perez [15]:

$$\text{DP of Cellulose} = \left( \frac{1.65[n]}{G} - 116H \right)^{1.111}$$  \hspace{1cm} (2)

where $[n]$ is intrinsic viscosity (cm$^3$/g), and $G$ and $H$ are the mass fractions of cellulose and hemicellulose in the pulp (Table III).

The DP of hemicelluloses was estimated by Eq. (3):

$$\text{DP of Hemicellulose} = \frac{1}{C_{\text{Reducing ends}} \times H \times 162}$$  \hspace{1cm} (3)

where $H$ is mass fraction of hemicellulose in pulp and $C_{\text{Reducing ends}}$ is the reducing end content of the pulps in mol/g pulp.

Table III shows that the DP of hemicelluloses increases in the first 10 min and decreases after 20 min. The DP values are comparable to those reported in literature for softwood hemicelluloses [16]. The initial increase in hemicellulose DP might be interpreted as removal of low DP hemicellulose during “peeling” delignification. Subsequently, the DP of the residual hemicellulose decreases are due to radical attack and alkaline hydrolysis.

It is important to note that the mass closure of Table III is low. This is because the HPAEC (High Performance Anion Exchange Chromatography) sugar analysis gave a recovery of about 85%-90% of the sugars. We did not normalize the data to correct for the approximately 10% sugar loss (caused by degradation during hydrolysis, etc.). If the sugar data was normalized to 100% recovery, the DP values of cellulose in Table III would decrease by about 5%-10%.

### Effect of operating conditions in the Berty throughflow reactor on oxygen delignification-cellulose degradation selectivity

Oxygen delignification experiments were performed in the Berty throughflow reactor at different oxygen pressures, temper-
temperatures, and caustic concentrations. In all cases, only one variable was changed while all other variables were kept at the standard conditions of 90°C, 3.3g/l NaOH, 75 psig oxygen pressure, and 60 min. Table IV shows that temperature and caustic concentration have a larger effect on the degree of delignification than oxygen pressure. High NaOH concentration and/or temperature lead to low intrinsic viscosities.

In Figs. 3, 4, and 5, the delignification-cellulose degradation selectivity for these experiments is calculated as

\[ \frac{K_0 - K_r}{DP_0 - DP} \]

The DP of cellulose is now calculated using \( DP = (1.65 \times [\eta])^{1.111} \) because the hemicellulose and cellulose mass fractions were not determined for all samples. However, considering the relatively small changes in the cellulose mass fractions (Table III) and the small contribution of the hemicellulose mass fraction to the DP (Eq. [2]), the selectivity calculated in this way may still be used for relative comparison of the different operating conditions.

Figure 3 shows the selectivity of the final pulp samples obtained at different oxygen pressures. It can be seen that the selectivity does not change significantly with oxygen pressure. The effect of temperature on the delignification-cellulose degradation selectivity is shown in Figure 4. It can be seen that the selectivity does not change much from 80°C to 100°C. However, it decreases 30% to 40% when the temperature is raised to 110°C-115°C. The latter lower selectivity and the higher capital cost (due to higher pressures) explain why the industry generally does not operate above 100°C. This behavior may be interpreted such that, up to about 100°C, the selectivity is dominated by phenolic delignification at essentially constant radical yield (i.e., constant value of \( k_c \) in Eq. [1]), while alkaline hydrolysis becomes significant above 100°C.

The effect of caustic concentration on the selectivity of the final pulp samples is displayed in Fig. 5. This figure shows that the selectivity decreases dramatically with increasing caustic concentration. The selectivity decreases by almost a factor 2 over the NaOH concentration range of 1 to 7 g/l, i.e., the region of interest for industrial oxygen delignification. The steep decrease in selectivity with increasing alkali concentration may be interpreted as the radical yield increasing during phenolic delignification with increasing alkali concentration (increasing \( k_c \) with increasing [OH-] in Eq. [1]), and/or that the relative importance of alkaline hydrolysis (i.e., the 2nd term on the rhs of Eq. [1]) increases with increasing alkali concentration.

Effect of operating conditions in the Berty throughflow reactor on oxygen delignified pulp yield

Table V shows the yield of the different final pulp samples. The yield drops with higher oxygen pressure, reaction temperatures, caustic concentrations, and reaction time. At an extremely high NaOH concentration of 50 g/l, the yield drops to 86.1%.

The yield loss, \( \Delta \text{Yield} \), is plotted versus \( \Delta \text{Kappa} \) in Fig. 6. It can be seen that the yield loss for all data, except those obtained at 110°C and 115°C and at 20 g/l and 50 g/l NaOH and at 360 min, increase proportionally with the kappa number reduction. Thus, at conventional oxygen delignification con-
Delignification conditions, which lead to a decrease in kappa number of up to about 60%, the yield loss may be described by:

\[ \text{Yield loss (\%)} = 0.40 \times \Delta \text{Kappa} \quad (4) \]

The yield loss in addition to that caused by the removal of lignin (Lignin Loss = 0.15 \times \Delta \text{Kappa}) represents carbohydrate loss during oxygen delignification as:

\[ \text{Carbohydrate loss (\%)} = 0.25 \times \Delta \text{Kappa} \quad (5) \]

Equations (4) and (5) show that the contribution of the carbohydrate loss to the total yield loss, 0.25 \times \Delta \text{Kappa}, is larger due to lignin removal, 0.15 \times \Delta \text{Kappa}. It should be noted that in the latter relationship, the constant of 0.15 is chosen because the present experiments were performed on a brownstock pulp. However, this ratio changes during bleaching depending on how the lignin end units are oxidized when the pulp is treated with an oxidant [17-20]. At high temperature (110°C and 115°C), high caustic concentration (20 g/l and 50 g/l) and very long time (360 min) tests, the linear relationship between carbohydrate loss and \( \Delta \text{Kappa} \) breaks down. This shows that delignification at those conditions (beyond a kappa number decrease of 60%) should be avoided because it leads to excessive carbohydrate loss.

McDonough [21] found that the temperature must be kept below 120°C to avoid excessive pulp yield loss.

**Figure 7** shows the carbohydrate yield loss (i.e., \( \Delta \text{Yield-0.15} \times \Delta \text{Kappa} \)) versus (1/DP<sub>t</sub>-1/DP<sub>0</sub>) of final pulp samples. A linear relationship is obtained independent of operating variables, i.e., including very high temperature, alkaline concentration, and long reaction time conditions. The authors’ hypothesis is that the carbohydrate loss (mostly hemicellulose) may be monitored by the cleavage of cellulose, which is caused by radicals generated from oxygen delignification. Since these radicals are non-selective, the hemicelluloses are equally attacked. Dissolution of hemicelluloses occurs by peeling when their DP is small enough that they become soluble.

**HexA content**

Table VI shows the HexA content of the oxygen delignified pulps. It can be seen that the HexA content does not change significantly during oxygen delignification regardless of the reaction conditions, except for the very high temperature, caustic concentration, and long reaction time experiments which show a small decrease. This confirms that HexA is not reactive at conventional oxygen delignification conditions.
However, at severe operating conditions, the pulp experiences an excessive yield loss so that part of the HexA groups may be removed together with hemicellulose chains, which are now small enough to dissolve.

In Fig. 8, the HexA content is plotted versus (ΔYield-0.15ΔKappa). The HexA content is constant when the yield loss due to the carbohydrate degradation is not excessive. However, the HexA amount decreases when the carbohydrate yield loss is higher than 5%. The results confirm that the HexA content remains essentially unchanged during normal oxygen delignification. HexA is only removed at severe operating conditions when the DP of xylan is low enough that direct dissolution is possible.

**Klason lignin and acid soluble lignin content**

Table VII lists the klason and acid soluble lignin of the pulps obtained at different operating conditions. It can be seen that klason lignin content decreases with increased delignification as expected, while acid soluble lignin content remains constant at about 0.4% based on oven-dried weight. The latter

<table>
<thead>
<tr>
<th>Pressure (psig)</th>
<th>HexA (µmol/g)</th>
<th>Temperature Varying</th>
<th>HexA (µmol/g)</th>
<th>NaOH Varying</th>
<th>Acid Soluble (%)</th>
<th>Time Varying</th>
<th>HexA (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>24.0±1</td>
<td>80</td>
<td>23.9±1</td>
<td>1.1</td>
<td>25.7±1</td>
<td>0</td>
<td>25.1±1</td>
</tr>
<tr>
<td>55</td>
<td>24.1±1</td>
<td>90</td>
<td>24.6±1</td>
<td>3.3</td>
<td>24.6±1</td>
<td>10</td>
<td>25.6±1</td>
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<td>75</td>
<td>24.6±1</td>
<td>100</td>
<td>23.5±1</td>
<td>5.5</td>
<td>24.7±1</td>
<td>20</td>
<td>25.1±1</td>
</tr>
<tr>
<td>95</td>
<td>24.0±1</td>
<td>110</td>
<td>22.7±1</td>
<td>7.7</td>
<td>24.5±1</td>
<td>40</td>
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<tr>
<td>115</td>
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<td></td>
<td>21.9±1</td>
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<td>50</td>
<td>17.6±1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>360</td>
<td>20.2±1</td>
</tr>
</tbody>
</table>

**VI. HexA content of different pulp samples. Other conditions, if not specified: 90°C, 3.3 g/l NaOH, 75 psig O₂ (except 360 min experiment was performed at 100°C, 90 psig and 7.7 g/l NaOH).**

<table>
<thead>
<tr>
<th>Pressure (psig)</th>
<th>Klason Lignin (%)</th>
<th>Acid Soluble (%)</th>
<th>Temp (°C)</th>
<th>Klason Lignin (%)</th>
<th>Acid Soluble (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>2.13</td>
<td>0.42</td>
<td>80</td>
<td>2.40</td>
<td>0.42</td>
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<tr>
<td>55</td>
<td>2.01</td>
<td>0.43</td>
<td>90</td>
<td>1.97</td>
<td>0.36</td>
</tr>
<tr>
<td>75</td>
<td>1.97</td>
<td>0.36</td>
<td>100</td>
<td>1.44</td>
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<tr>
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<td></td>
<td></td>
<td>115</td>
<td>0.71</td>
<td>0.44</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>NaOH (g/l)</th>
<th>Klason Lignin (%)</th>
<th>Acid Soluble (%)</th>
<th>Time (min)</th>
<th>Klason Lignin (%)</th>
<th>Acid Soluble (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2.68</td>
<td>0.42</td>
<td>0</td>
<td>3.89</td>
<td>0.36</td>
</tr>
<tr>
<td>3.3</td>
<td>1.97</td>
<td>0.36</td>
<td>10</td>
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</tr>
<tr>
<td>5.5</td>
<td>1.68</td>
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<td>2.92</td>
<td>0.38</td>
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<tr>
<td>7.7</td>
<td>1.32</td>
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<td>2.78</td>
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<tr>
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<tr>
<td>50</td>
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<td>1.19</td>
<td>0.42</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>360</td>
<td>0.31</td>
<td>0.34</td>
</tr>
</tbody>
</table>

**VII. Klason and acid-soluble lignin content of different pulps. Other conditions, if not specified: 90°C, 3.3 g/l NaOH, 75 psig O₂ (except 360 min experiment was performed with 100°C, 90 psig, and 7.7 g/l NaOH).**
**DELIGNIFICATION**

In Fig. 9, (Kappa-HexA/10)x1.5 is plotted versus (Klason Lignin)x10, with both expressed in mg lignin/g pulp. It shows that klason lignin is directly proportional to lignin content calculated from the kappa number corrected for HexA content. The slope of the correlation indicates that klason lignin represents 78% of the lignin calculated from kappa number corrected for HexA content. This pure lignin was also determined by Li [22] as the kappa number after HgAc2-NaBH4 treatment of pulp and was called Ox-Dem kappa. They also found that these actual lignin structures represent about 80% of the conventional kappa number for softwood kraft pulps. The remaining 20% are identified by Li [22] as non-lignin and non-HexA based oxidizable structures. However, the NaBH4 treatment is performed at strong alkaline conditions, and thus may lead to extraction of Klason lignin. Data from Costa and Colodette [23] indicated that the Ox-Dem treatment of eucalyptus kraft pulps removes roughly 25% of the Klason lignin content. This may call into question the estimate of Li [22] of the “non-HexA and non-lignin” substances contributing to the kappa number difference. However, the data in Fig. 9 appears to confirm that Klason lignin represents about 80% of real lignin and the rest is non-lignin and non-HexA structures.

Ji [5] found that when oxygen delignification was performed in 50% ethylene glycol, a strong radical scavenger, the pulps had significantly higher viscosities and kappa numbers than corresponding regular oxygen delignified pulps. The higher viscosity and kappa in ethylene glycol-water is expected due to scavenging of radicals by ethylene glycol. Ji [5] also indicated that approximately 15% of the total lignin cannot be removed by oxygen delignification in 50% ethylene glycol-water, even at excessive reaction time. This suggests that radicals may be required for removal of non-lignin based oxidizable structures (excluding HexA). Thus, besides the negative effect of radicals on pulp viscosity and yield, radicals may also be needed for removal of non-lignin and non-HexA oxidizable structures, which contribute to kappa number. This means that for very high degree of oxygen delignification, measured in terms of HexA corrected kappa number, the generation of radicals may be essential.

**IMPLICATIONS**

High delignification-cellulose degradation selectivity is needed to produce a highly delignified pulp of good viscosity. High selectivity will simultaneously minimize pulp yield loss because of the relationship between cellulose degradation and carbohydrate yield loss (Fig. 7). The present results show that the temperature should not be increased above about 100°C (Fig. 4), the NaOH concentration should be kept as low as possible (Fig. 5), and that the oxygen pressure has little effect on the selectivity (Fig. 3). However, low temperatures and low alkali concentrations lead to slow delignification rate and thus long reaction time. Also, the consumption of alkali is related to the degree of delignification, and thus the minimum initial alkali concentration in a conventional medium consistency oxygen delignification system is set by the desired reduction in kappa number. As a result, in conventional oxygen delignification systems, the initial temperature is relatively low when the major amount of alkali is charged, while a higher temperature is used in the later stage when most alkali is consumed. Therefore, further improvement beyond 60% delignification from standard softwood brownstock pulp is not likely when using conventional two-stage oxygen systems to produce good quality pulp at an acceptable yield loss. To increase delignification beyond 60% for softwood pulp, the oxygen system design should be changed so that alkali concentration and charge are decoupled, as is similarly done in modern cooking systems. This means that a similar approach as that of modern cooking systems should be adopted, i.e., multiple alkali addition points combined with careful temperature control.

A crossflow operation such as in a diffusion washer with multiple washing zones would be a possible configuration for such a system. The alkali concentration should be maintained at a low level throughout the crossflow reactor with multiple alkali addition points to compensate for the alkali consumption. The reintroduction of the spent liquor streams should be arranged such that pulp and liquor are in countercurrent contact. The entering brownstock temperature is lower than that at the reactor exit, while the average alkali concentration at the brownstock entrance is higher than that at the reactor exit. These conditions lead to a more uniform delignification rate throughout the reactor, and therefore higher overall delignification-cellulose degradation selectivity and pulp yield. Temperatures higher than about 100°C should be avoided.
CONCLUSIONS
The highest oxygen delignification while maintaining pulp quality and yield is obtained when the overall delignification-cellulose degradation selectivity is maximized. This is achieved at low alkali concentrations and temperatures of about 100°C or less. Oxygen pressure has little effect on the selectivity. If the DP of cellulose is optimal, then the pulp yield loss is also minimized because the reduction in cellulose DP is mainly caused by radicals generated by phenolic delignification, and to a much smaller extent by random alkaline hydrolysis. Since the newly generated reducing ends in both cellulose and hemicelluloses undergo peeling reaction, the carbohydrate yield loss is linearly correlated with cellulose degradation. Hexenuronic acids are not removed during optimal oxygen delignification, and must be removed in a subsequent bleaching stage. Although radicals have a negative effect on pulp viscosity and yield, they are also needed for removal of non-lignin and non-HexA oxidizable structures, which contribute to kappa number. This means that for a very high degree of oxygen delignification, the generation of radicals may be essential. In order to increase delignification beyond about 60% for softwood pulp, the oxygen system design should be changed so that alkali concentration and charge are decoupled, as is similarly done in modern cooking systems, to create a more uniform delignification rate throughout the reactor. TJ

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LITERATURE CITED

ABOUT THE AUTHORS
Oxygen delignification is an environmentally friendly technology, with benefits that could increase the degree of delignification beyond present limits. This work presents more explicitly the implications for industrial implementation. Pretreatment is the most important step in biomass conversion. The selection of conversion technology and associated pretreatment technologies were the most difficult aspect of this research. This paper provides a review of pretreatment methods with commercial application potential.

Developing the Berty reactor, traditionally used for catalyst testing of petrochemical reactions in the pulp-caustic system, has proven that it is possible to delignify kraft softwood pulp more than 60% without excessive cellulose degradation, if the hydroxide concentration is kept low and uniform over time by replenishing the alkali during consumption. If the DP of cellulose is optimal, the pulp yield loss is minimized due to the reduction in cellulose. DP is mainly caused by radicals generated by phenolic delignification. In order to decrease delignification in softwood pulp, the oxygen system must be changed so that alkali concentration and charge are decoupled to create a more uniform delignification rate throughout the reactor. Mills can use this as the pretreatment method for a potential biorefinery application.

We will continue research on hot-water extraction of woody biomass and biomass conversion technologies to further commercialize the process. The concept is being developed by integration with high kappa kraft pulping.

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DELIGNIFICATION


IBBC 2012
International Bioenergy & Bioproducts Conference
October 17-19, 2012
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TAPPI’s International Bioenergy and Bioproducts Conference will focus on technical advancements and commercialization of bioconversion technologies that leverage the forest products manufacturing infrastructure.

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• Bioelectricity using combined heat and power (CHP)
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