

## Effect of lignin content and magnesium-to-manganese ratio on the selectivity of oxygen delignification in softwood kraft pulp\*

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*Abstract:* A series of oxygen delignification experiments were performed on two softwood kraft pulps that had differing starting lignin contents. One had an initial kappa of 40 and the other 25, corresponding to lignin contents of 6% and 3.75% by dry mass, respectively. Several chemical process modifications were examined to determine their influence over the delignification selectivity and final pulp viscosity. A 2k factorial format was used to assess the significance of varying the temperature, time, and Mg/Mn ratio during the oxygen delignification of the pulps. It was found that the lower lignin content pulp displayed greater delignification selectivity than the higher lignin content pulp. Kappa numbers, viscosity values, and ICP metals contents were determined and are the basis of discussion for the results obtained.

Oxygen delignification is one of the principal technical processes used in the pulp and paper industry to reduce the lignin that is resident in the pulp following the kraft pulping (chemical digestion of wood) process [1–3]. Figure 1 shows the most notable chemical features of native softwood *lignin* [4].

Reduction of the residual lignin by use of oxygen delignification will curtail the chemical demand in later bleaching operations for complete removal, ensure environmental compatibility of the effluents, significantly reduce pulp rejects (incompletely digested wood chips), and provide a pulp whose chemical properties may be exploited for particular applications. Although its benefits and implementation have been promoted during the last decade, it suffers from the inability to exceed 50% residual lignin reduction. More importantly, the fundamental principles governing its chemistry are not known [4–6].

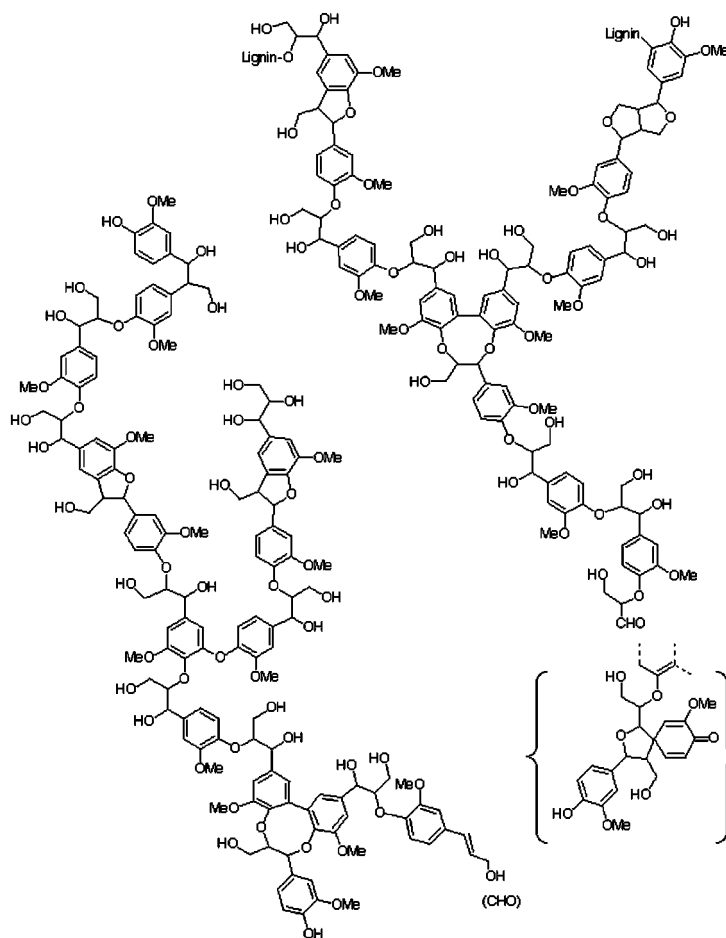
The function of oxygen delignification operations is to target removal of lignin, a ubiquitous plant biopolymer, to the exclusion of pulp carbohydrates. Lignin essentially coalesces the carbohydrate-derived pulp microfibrils into organized arrays and imparts rigidity to the fiber matrix. Fortunately, lignin easily succumbs to base-induced attack during pulping, but its removal must be accomplished without significantly damaging the pulp carbohydrates. Unfortunately, oxygen delignification reactions are not sufficiently selective to preserve the carbohydrate fraction of the pulp that is substantial relative to the residual lignin (on the order of 90–95%). Figure 2 displays the reactions of importance that occur during oxygen delignification.

The guaiacyl unit appended from the “lignin” main branch is the structural motif for softwoods lignin and becomes deprotonated during the base-induced oxygen process, ultimately leading to radicals in the presence of oxygen. The generation of phenoxy radicals from the phenolate electron abstrac-

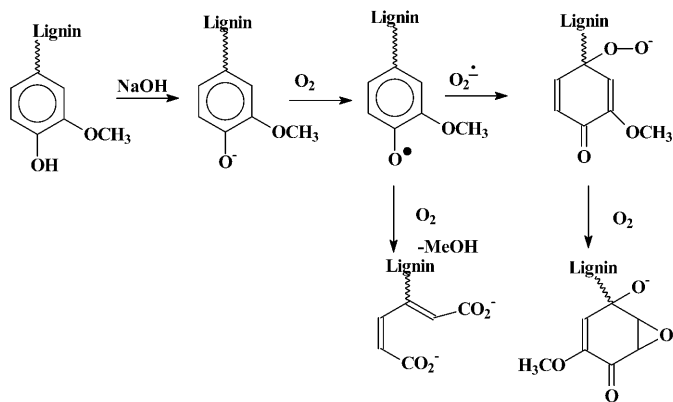
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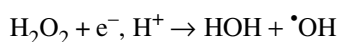
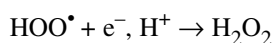
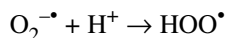


**Fig. 1** The salient chemical structural units associated with lignin in woody tissue.



**Fig. 2** The series of chemical oxidation reactions occurring between molecular oxygen and an idealized guaiacyl lignin unit under heated alkaline conditions.

tion generates superoxide anion that can undergo a multi-electron reduction to water [7 and references therein]. During the process, oxidative cleavage of lignin results first in formation of smaller, partly soluble fragments by a partial depolymerization and in oxidation of resulting aromatic aldehydes, which then produce observed acids that are more soluble and lower in molecular weight. Yet, one of the reactive species during the oxidation sequence is hydrogen peroxide, which is known to disproportionate to hydroxy radicals [8]. The formation of hydrogen peroxide occurs from the protonated superoxide anion. Metals such as iron and manganese have been implicated by numerous research reports to catalyze a Fenton-type reaction for hydrogen peroxide leading to hydroxy radicals that are then able to oxidatively cleave and/or peel cellulose chains [9–12]. The principal reactions of interest in the Fenton-type reaction are displayed below:



The following preliminary work sought to establish how two distinct initial contents of lignin with accompanying metal variation in softwood pulp would impact the oxygen delignification and final viscosity (cellulose integrity) of the pulp. The initial and final physical and chemical states of the pulp were characterized by lignin content or kappa ( $\text{kappa} \times 0.15 = \text{percentage lignin by mass}$ ), viscosity (CED viscosity), and metals content. Table 1 illustrates the differences between the two pulps that were derived from the same tree species by pulping to different final lignin levels.

Obviously, the most pronounced differences shown for the two softwood pulp samples are the original content of lignin, viscosity, and concentrations of magnesium and aluminum. Although the concentration of the main metals of interest are shown above, metals such as copper, cobalt, and other transition metals are generally on the order of 7 mg/kg concentration or less in each of the pulps. The lignin and viscosity are obtained by control of the pulping procedure (time and heating profile of pulping), whereas the metal levels are a function of the binding characteristics of the lignin functional groups [13,14]. The focus of the study was to utilize the above data for evaluating the selectivity response of each pulp under oxygen delignification conditions.

The conditions for the oxygen delignification were as follows: all oxygen delignification was done in a PARR Instruments pressure bomb at 10% solid pulp content, 2.5% w/w dry pulp of NaOH, and an  $\text{O}_2$  pressure of 500 kPa. A 2k factorial design was applied by varying two sets of temperature, two different times, and the Mg/Mn ratio while all runs were repeated at least twice for reproducibility. Thus, 32 experiments were carried out in which the temperature was either 100 or 80 °C, time of reaction varied between 80 or 60 min, and the Mg/Mn ratio was either 33 or 22 mol/mol (adjusted as required by addition of  $\text{Mg}^{+2}$  based on native pulp levels to establish ratio). The 2k factorial analyses (algorithms not reported) indicated that good correlations on the >90% confidence level were available from time, temperature, and Mg/Mn variations in the high- and low-kappa pulps.

The kappas for the two pulps were obtained using the standard TAPPI test method (TM-265b): a predefined mass of pulp was slurried in 250 mL of water, reacted with 25 mL of  $\text{KMnO}_4$  for 10 min,

**Table 1** ICP data obtained for the pulps with relevant metal concentrations.

	Kappa	Viscosity (cP)	Mn*	Mg*	Ca*	Fe*	Al*
High kappa	39.8 ± 0.1	40.20 ± 0.64	41.1	396	1686	36.3	5.9
Low kappa	25.3 ± 0.4	28.41 ± 0.07	33.6	184	1868	37.6	15.1

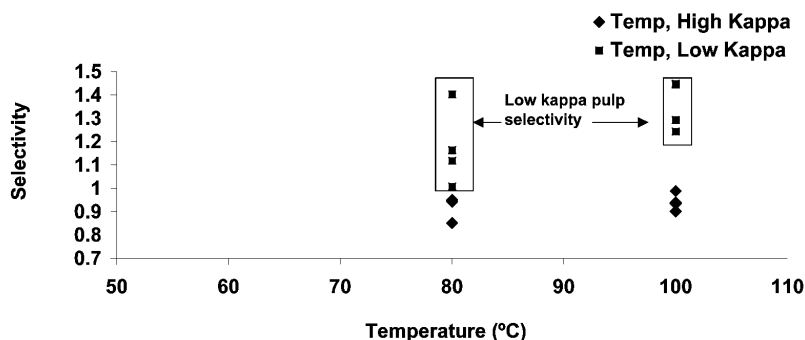
\*All metal concentrations expressed in units of mg/kg.

and the consumption of  $\text{MnO}_4^-$  by the lignin in the pulp (the “kappa number”) was back-calculated by quenching the unreacted  $\text{MnO}_4^-$  with KI and titrating the  $\text{I}_2$  with thiosulfate. The mass, slurry temperature, and volume of thiosulfate were used to calculate the kappa according to the TAPPI test method formula.

### INFLUENCE OF TEMPERATURE ON SELECTIVITY

In this work, *selectivity* of oxygen delignification is defined as the ratio of the delignification level divided by the viscosity changes,  $\Delta\text{kappa}_{(\text{initial-final})}/\Delta\text{viscosity}_{(\text{initial-final})}$ . A noteworthy finding in this general topic of research is the importance of  $\text{Mg}^{+2}$  for the protection of pulp cellulose. Researchers in the last several years have speculated that  $\text{Mg}^{+2}$  coprecipitates with  $\text{Mn}^{+2}$  into a “soluble” aggregate that essentially neutralizes the redox activity of  $\text{Mn}^{+2}$  [9]. The research determined that the minimum Mg/Mn molar ratio required to offset the redox activity of  $\text{Mn}^{+2}$  is approximately 30 (mol/mol). Our initial research focused on determining how the native lignin levels and selected Mg/Mn ratios affect the ultimate selectivity response of the pulps. Figure 3 shows the total of the selectivity responses at the high and low temperature for the 2 pulps with associated time (60 and 80 min) and Mg/Mn ratio changes (22 and 33 mol/mol).

In general, the trend is clear: the lower lignin (kappa = 25) pulp displays a significantly greater selectivity response compared to the high-kappa pulp. The highest selectivity at both temperatures for both pulps was obtained with the high Mg/Mn ratio at the shorter time, whereas the selectivity of the other points decreases at higher temperatures and times. The difference between the high- and low-kappa pulps also held at high and low Mg/Mn ratio and time. The selectivity differences were not as distinct at the lower temperature as at the higher temperature, perhaps as a result of enhancing the kinetics of the selectivity changes (increased delignification at maintained viscosity). Despite the relatively constant delignification changes occurring in the high- and low-kappa pulps (30–40%), the viscosity differences overwhelmingly obtain the selectivity. Interestingly, the lower-kappa pulp underwent losses of 10–30% in viscosity, whereas the high-kappa pulp displayed viscosity losses of 30–50%. Despite the same Mg/Mn ratio in each sample, this result can be partially attributed to the greater oxidized nature of the low-kappa pulp, which demonstrates a preponderance of metal-binding carboxylic acid groups in the lignin [15] by approximately 30% from  $^{31}\text{P}$  NMR data. These acid groups in lignin sequester redox active metals such as iron or copper that are not occluded in the soluble  $\text{Mg}^{+2}$  precipitate, and limit their ability to engage in Fenton chemistry [13]. An additional clue that provides insight into the selectivity difference is the higher proportion of aluminium in the low-kappa pulp by a factor



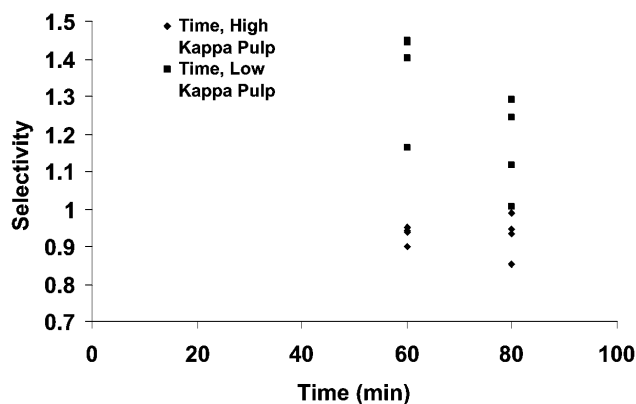
**Fig. 3** The selectivities of the oxygen delignification for both the high- and low-kappa pulps are shown as a function of temperature.

of three. There have been reports that indicate that aluminium salts provide carbohydrate protection in lignocellulosics by helping to complex catalytically active metals, in a way similar to acidic washing of metals [16].

### EFFECT OF TIME ON SELECTIVITY

Time was varied next to observe its impact on the selectivity. Figure 4 shows a graph similar to Fig. 3. Again, not surprisingly, the lower-kappa pulp displayed higher selectivity than the higher-kappa pulp, especially at the shorter time. The trend toward a drop in selectivity for the lower-kappa pulp at longer times is a reflection of the accumulation of “resistant” lignin structures that have been implicated by NMR in this work, as well as by other researchers [17,18]. Resistant lignin structures tend to be condensed biphenolic units connected at the 5,5' position that do not fragment as readily as noncondensed lignin structures. Higher-kappa pulps are less enriched in these structures over the same period of time due to the relative abundance of lignin. In fact, at longer delignification times, the selectivity of the higher-kappa pulps tends to increase slightly as compared to the lower-kappa pulp. The gap at the shorter time between the selectivity of the high- and low-kappa pulps mimics the data shown above (*vide infra*) for the temperature data. This suggests that the highest selectivity for the low-kappa pulps can be achieved at shorter times and higher temperatures, whereas the higher-kappa pulps respond best at longer times, although this result is not appreciably affected at either temperature.

The influence of metal composition on selectivity appears to be much more pronounced for the lower-kappa pulp, which, in all cases, responds best to the 33 mol/mol ratio of Mg/Mn, whereas the higher-kappa pulp does not show a pronounced benefit. The higher-kappa pulp data tends to be more concentrated around a cluster of values. This may indicate the lower carboxylic acid content of the higher-kappa pulps is insufficient to complex the free “harmful” metals that exacerbate the production of radicals. These generated radicals are indiscriminate in their oxidation activity and compromise the integrity of the cellulose of the high-kappa pulps in addition to causing delignification.



**Fig. 4** The selectivities of the oxygen delignification for both the high- and low-kappa pulps are shown as a function of time.

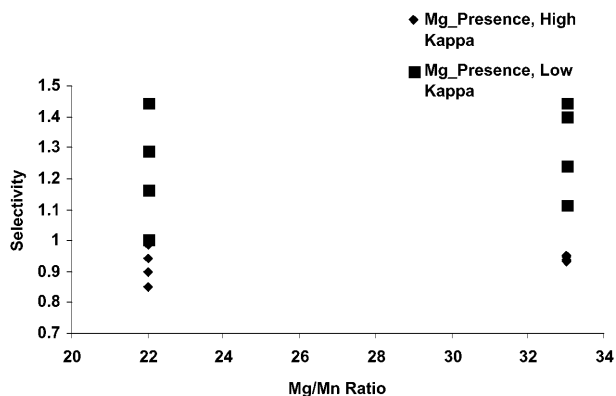
### INFLUENCE OF $Mg^{+2}$ ON SELECTIVITY

The addition of Mg to the pulps to achieve an upper limit of 33 mol/mol was done to examine if it would improve selectivity. Figure 5 clearly demonstrates that a 50% increase in the molar ratio of Mg cluster

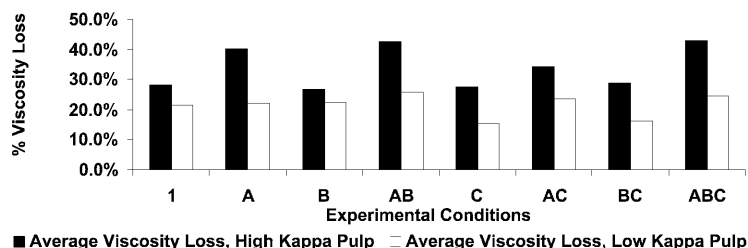
the selectivity data, with a much greater effect for the high-kappa pulps. The higher selectivity is obtained principally through a stabilization of the viscosity values.

This result indicates that the Mg addition acts to mitigate the activity of the Mn ion at all temperatures and times studied, by reducing the fluctuations in the viscosity level. This result is easily demonstrated in the graph displaying the % viscosity loss data for both pulps. In Fig. 6, the low-kappa pulp responds best to the higher Mg/Mn ratio (where 1 = control conditions: lower temperature, lower time, no Mg addition; A = higher temperature; B = longer time; C = 33 mol/mol Mg/Mn).

Yet, the higher protective metal ratio cannot compensate for the damaging effect of higher temperature, which accelerates cellulose damage as observed for the high-kappa pulp.



**Fig. 5** The selectivity of the oxygen delignification for both the high- and low-kappa pulps is shown as a function of Mg/Mn ratio.



**Fig. 6** The % viscosity loss for the high- and low-kappa pulps is shown as a function of experimental conditions used for each experiment (1 = control conditions: lower temperature, lower time, no Mg addition; A = higher temperature; B = longer time; C = 33 mol/mol Mg/Mn).

## SUMMARY

The lower lignin-containing pulp appears to respond most favorably to the conditions employed, and demonstrates clear viscosity preservation under the higher Mg/Mn ratio. The selectivity increase is

apparent for both the high- and low-lignin-content pulps, observed as a clustering of the data around common points. The differences in acid groups between the pulps may play a part in the poorer selectivity of the high-kappa pulp since it may not be able to bind free metals as effectively as the low-kappa pulp. Aluminium may also have an impact on the final viscosity by assisting in neutralizing metals that participate in redox chemistry. These results are encouraging since most industrial operations operate at lower lignin levels and are actively involved in metals management.

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